Polybrominated Diphenyl Ethers (PBDEs) in serum from Swedish men 1988-2002. A longitudinal study

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Introduction

Polybrominateddiphenyl ethers (PBDEs) have been extensively used as additive flame retardants since the 1970s. Their concentrations have been reported to increase with time both in humans and in wildlife from all environmental compartments [1-3]. Retrospective time-trend studies conducted using environmental samples originating from the Swedish environment showed a peak in environmental levels in the mid-1980's, after which environmental concentrations decreased or remained unchanged [4]. In Swedish human breast milk, the concentrations of low-medium brominated diphenyl ethers redoubled every 5 years until the late 1990s; thereafter a decrease has been indicated, at least for BDE-47[5]. However, there is yet no information on human time trends for hepta-, octa-, nona- and deca-BDEs, neither in Sweden or elsewhere. Further, no longitudinal studies on individual basis have yet been reported.
In 1991 men with a high dietary intake of fish from the Baltic Sea, 12–20 meals/month, had considerably higher BDE-47 levels than men with negligible consumption of fish[6]. These men were resampled in 2001. Time trends for PCB and DDE have been reported elsewhere [7]. Here, we report data on time trends for PBDEs in these men.

Material and methods

Study groups
We had remaining serum (>5 ml) for PBDE-analysis from 37 out of totally 39 men sampled in 1991 and 2001. In 1991 they were between 23 and 69 (median 42) years old. No one was occupationally exposed to PBDEs to our knowledge. Eighteen of these men were stable non-consumers of fish at both sampling occasions. The remaining nineteen men, who were moderate or high consumers of fatty fish from the Baltic Sea in 1991 (Table 1) had reduced their fatty fish consumption in 2001 compared to ten years earlier; from median 8 (range 4-20) to 3 (1-9) meals per month. For ten of the 37 men serum samples from 1988 and 2002 were also available.

Chemical analysis: The chemicals used, extraction of serum, lipid determination, partitioning with an alkaline solution, procedure and analysis have been described in detail elsewhere [8]. Lipids were removed from the extracts by treatment with concentrated sulfuric acid. Fractions containing both the neutral and phenol type substances were subjected to cleanup on two additional steps. First, remaining lipids and endogenous organic material were reduced by running the samples through columns packed with silica mixed with concentrated sulfuric acid (1 g). The analytes were eluted with dichloromethane (10 ml). The last refining cleanup step was performed on a column packed with activated (300ºC, 12 h) silica gel (1 g). The silica columns were first prewashed with n-hexane (6 ml) before the samples were applied. A first fraction was collected in n-hexane (3 ml) and a second in dichloromethane (6 ml). The solvent in fraction two was reduced under a gentle stream of nitrogenand replaced with n-hexane prior to gas chromatography-mass spectrometry (GC-MS. Reference compounds, synthesised in house, were used as standards. All solvents were of the highest available commercial grade.
Identification and quantification were performed using a GC-MS Finnigan TSQ 700 (Thermoquest, Bremen, Germany) operating in electron capture chemical ionization (ECNI) mode, tracing the bromide ions (*m/z* 79 and 81). A DB-5HT column (15 m × 0.2 mm i.d. and 0.1 µm film thickness) from Supelco (Bellefonte, USA) was used with temperature program of 80ºC (1 min) – 15ºC/min – 300ºC – 2 ºC/min – 320ºC (2 min). On-column injections were performed using a septum equipped programmable injector fitted with a high performance insert. The injector temperature was 60ºC and increased with 150ºC per minute up to 300ºC for each injection. Helium was used as carrier gas. The transfer line temperature was 290ºC and the temperature in the ion-source was 200ºC.

Results and Discussion

Fifteen PBDE congeners listed in elution order from the unpolar GC column ; BDE-28, -47, -100, -99, -154, -153, -128, -183, -197, -203, -196, -208, -207, -206 and -209 were detected and quantified. In the subset of ten men sampled four times between 1988 and 2002, the time trends for selected PBDE congeners are illustrated in Figure 1. Four of these men never ate fish. Between 1988 and 1991 there was a significant increase of BDE-47 (p=0.05; Wilcoxon signed rank test), followed by a decrease (p=0.12; Friedman test). In contrast, BDE-153 clearly increased between 1991 and 2001, but not there after. There was also a tendency of increasing levels of BDE-207 (p=0.11; Friedman test) in these ten men while no tendency is confirmed for BDE-209.

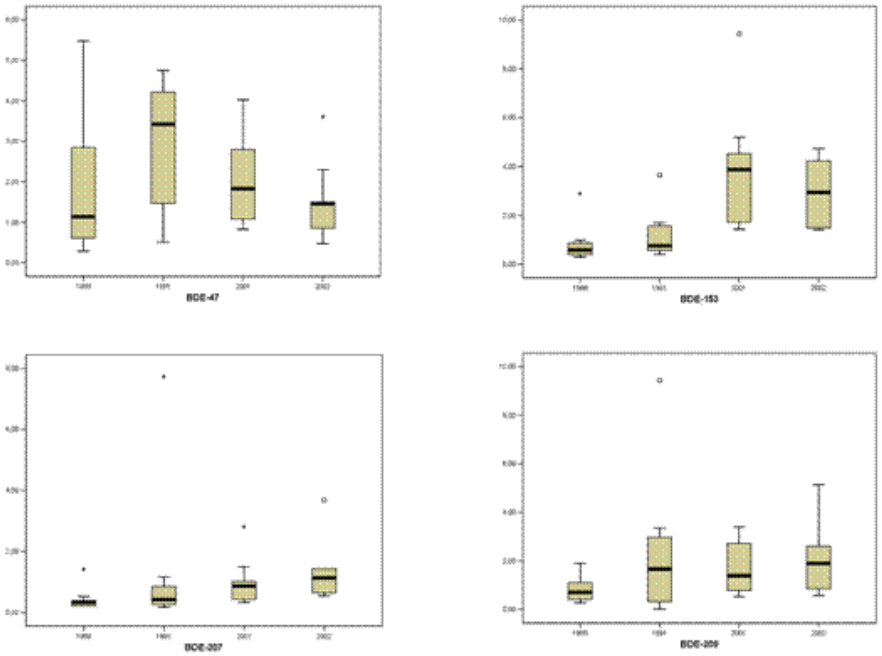

Figure 1. Serum concentrations of BDE-47 (upper left), BDE-153 (upper right), BDE-207 (lower left), and BDE-209 (lower right) (pmol/g lipid weight) in ten men, sampled in 1988, 1991, 2001, and 2002 are presented. Median, 25, 75 percentiles, range and outliers if present are denoted.

Among the 18 stable non-consumers of fish, the sum of PBDEs increased markedly between 1991 and 2001 (Table 1). The level of BDE-47 did not decrease. There was a three-fold increase of BDE-153 between 1991 and 2001 in the stable non-consumers as well as among the 19 consumers of fatty fish from the Baltic Sea. For hepta- to deca-BDEs the levels were stable over time, regardless of fish consumption pattern.

Table 1. Concentrations of selected PBDEs (pmol/g lipids, median and range) and sum of PBDEs in serum sampled 1991 and 2001 from a group of Swedish men with varying consumption of fatty fish from the Baltic Sea.

GROUP		BDE-47	BDE-99	BDE-154	BDE-153	BDE-183	BDE-197	BDE-207	BDE-209	sumBDE[2]
All subjects,	1991	2.1	0.40	1.3	0.93	0.41	0.45	0.61	1.3	11
(n=37)		0.35-17	0.16-7.4	0.15-5.6	0.34-3.7	0.11-5.4	0.05-14	0.07-7.7	0.01-21	3.3-59
	2001	1.6	0.64	1.1	3.0	0.46	0.58	0.70	1.4	14
		0.36-13	0.13-6.3	0.30-3.2	0.66-34	0.17-1.9	0.18-8.3	0.31-2.8	0.47-5.2	4.2-57
p-value[1]		p=0.09	p=0.04	-	p<0.001	-	p=0.19	-	-	-
Fish consumption[3]										
None	1991	1.2	0.31	1.3	0.78	0.39	0.54	0.42	0.39	6.0
(n=18)		0.35-8.1	0.16-2.5	0.31-2.4	0.40-3.7	0.11-3.8	0.05-14	0.07-7.7	0.01-9.4	3.3-47
	2001	1.5	0.73	1.1	2.5	0.52	0.61	0.69	1.5	13
		0.54-5.3	0.30-2.5	0.40-2.9	1.2-8.6	0.27-1.9	0.34-8.3	0.31-2.8	0.47-3.4	6.2-26
p-value[1]		-	p=0.003	-	p<0.001	-	-	-	-	p=0.03
Moderate	1991	4.7	0.88	1.3	1.6	0.46	0.65	1.2	2.7	17
(n=10)		0.77-17	0.17-7.4	0.53-3.1	0.60-2.8	0.14-5.4	0.16-1.3	0.09-2.1	0.01-21	8.6-59
	2001			1.4			0.60			14
		2.6	0.91	0.30-3.2	3.9	0.40	0.24-	0.76	1.1	4.2-27
		0.36-13	0.13-3.0		0.66-9.4	0.25-1.6	0.87	0.35-1.0	0.75-2.5	
p-value[1]		p=0.08	-	-	p=0.007	-	-	p=0.04	p=0.17	-
	1991			1.4			0.29			12
High		3.4	0.51	0.15-5.8	1.0	0.42	0.15-	0.44	0.50	5.9-22
(n=9)		1.2-7.2	0.32-1.2		0.34-1.7	0.14-3.5	0.68	0.17-1.2	0.01-3.2	
	2001			1.3		0.33	0.47			15
		1.4	0.49	0.74-3.0	3.1	0.17-	0.18-	0.82	1.3	7.5-57
		0.99-7.6	0.37-6.3		1.7-34	0.58	0.88	0.35-2.3	0.63-5.2	
p-value[1]		p=0.11	-	-	p=0.008	-	p=0.09	-	-	-

[1]Wilcoxon paired test. p-levels >0.2 are not given in the table

[2] sum of BDE-28,-47, -100, -99, -154, -153, -128,-183, -197, -203, -196, -208, -207, -206, -209

[3]Consumption of fatty fish from the Baltic sea as classified in 1991.
Moderate: 4-8 meals/month. High: 12-20 meals/month.

The serum levels of BDE-28, BDE-47, BDE-100, and BDE-154 showed moderate positive correlations (correlation coefficients around 0.3; $p<0.1$) with fish consumption (measured as meals of fatty fish from the Baltic Sea or total fish meals per month) in1991. In 2001 no correlations with PBDE congener levels were evident, neither for fish consumption data in 1991 nor in 2001. Neither BDE-153 nor any of the hepta- to decaBDEs showed any correlations with fish consumption at any point of time.

The men included in our study are not representative of the general Swedish population. They were originally selected in order to represent a wide range of consumption pattern of fatty fish from the Baltic Sea, for studies of the change over time of levels of various persistantorganochlorine compounds (POCs). In Sweden, fatty fish from the Baltic Sea has been an important dietary source of these compounds [9]. For PBDEs, our data indicate that the relative contribution from fatty fish, compared to other sources, may differ between the PBDE congeners, and also over time. Not only diet, but also other sources like air-borne exposure in the home environment are believed to be important[10].

In these men, the average decline of POCs like CB-153, p,p'-DDE and hexachlorobenzene between 1991 and 2001 was 30-50% [7]. In contrast, we observed no over-all decline of the sum of all PBDEs, but marked changes in congener patterns between the two early sampling points and the latter two. This is in accordance with data we have obtained also in some other recent studies [11]. It is notable that BDE-153 clearly was the dominating PBDE congener in early 2000s. Also, it may be pointed out that the concentration of BDE-209 is similar to BDE-47 in the samples from the present decade.

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