Levels of brominated flame retardants in human samples from Norway through three decades

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Introduction

Brominated chemicals are used as flame retardants (BFRs) to protect a wide variety of products from catching fire. BFRs have been shown to be potential persistent organic pollutants (POPs) and are found widespread in the environment, in wildlife and in humans[1,2].

The objective of this study was to complete and extend a previous study on time trends of PBDEs in Norwegian pooled serum samples[3]. We further compare these levels with levels in other human samples from Norway in order to put together an overview of the PBDE body burden in the general population from 1977 to 2004.

Materials and Methods

Chemicals

The PBDE standards (BDE-18, 28, 37, 47, 51, 77, 85, 99, 100, 103, 119, 138, 153, 154, 181, 183, and 209) as well as tetrabromobisphenol-A (TBBP-A) were obtained from Wellington Laboratories (Guelph, Ontario, Canada), CIL (Andover, MA) or AccuStandard (New Haven, CT). Chlorotribromobisphenol-A (CtriBBP-A) was a gift from the Wallenberg Laboratory (University of Stockholm, Sweden). All solvents used were of pesticide grade from sds (Peypin, France).

Serum samples

The study was conducted on serum samples archived by the National Institute of Public Health in Norway. The serum had been sampled from patients at five different county hospitals and stored at –20 °C. Pools consisting of serum from about 20 persons were made for different age and gender groups. The lipid content of the pooled serum samples was determined at The National Hospital of Norway (Oslo, Norway) according to a method described by Grimvallet al.[4].

Sample preparation and quantitative determination

The serum samples were extracted using solid phase extraction (Oasis®HLB, 540 mg/ 3 mL, custom made from Waters Corporation (Milford, MA)). Our previously presented SPE method[5] was modified and adapted to an automated solid phase extractor (ASPEC XL4, Gilson, Middleton, WI). TBBP-A was derivatised using diazomethane, and the extracts were analysed both before and after the derivatisation. Separation and quantitative determination of the BFRs were performed by capillary gas chromatography coupled to a mass spectrometer operated in the electron capture mode with methane as buffer gas. The brominated compounds were monitored at *m/z* 79 and 81. BDE-209 was detected at *m/z* 484.6 and 486.6 (native) and *m/z* 494.6 and 496.6 (^{13}C-labelled). Identification was based on retention time and isotope abundance ratio. The total uncertainty of the analytical method was found to be about 20 %. Both the sample preparation and quantitative method are described in detail elsewhere[6].

Results and Discussion

Temporal trends and age distribution of PBDEs

The temporal trend of the sum of 7 PBDEs (28, 47, 99, 100, 153, 154 and 183) in the pooled serum from the present

study are in close agreement with the levels found in the previous study[3], except for the pools from 1991 and 2002 (Figure 1), which were found to be considerably higher than expected from results of preceding and following years. This was surprising as the pools contained at least 20 individual samples (men aged 40-50 years). In Figure 2A, the PBDE serum levels in different age groups are presented for samples obtained in 1998 and 2002. In the samples from 2002, the mean of sum 7 PBDEs is 3.8 ng/g lipids (serum from the youngest group excluded) and 3.5 ng/g lipids in men of age 25-59 years. It is thus reasonable to suggest that the pool in the trend study contains serum from one or several persons with high PBDE level and that this pool not is representative for the serum level in 2002. So far, no duplicate of the pool from 1991 has been analysed.

Also presented in Figure 1 is the Sum 7 PBDE level in three breast milk pools[7] and the median of 151 individual breast milk samples[8]. In general, for similar time periods the levels in breast milk seem to be somewhat lower than in the serum, but the same overall trend is observed. This confirms that the PBDE body burdens have risen rapidly from 1977 to about 1997, but now seems to have stabilized or even to have decreased. This is in accordance with the trends observed in Swedish breast milk[9].

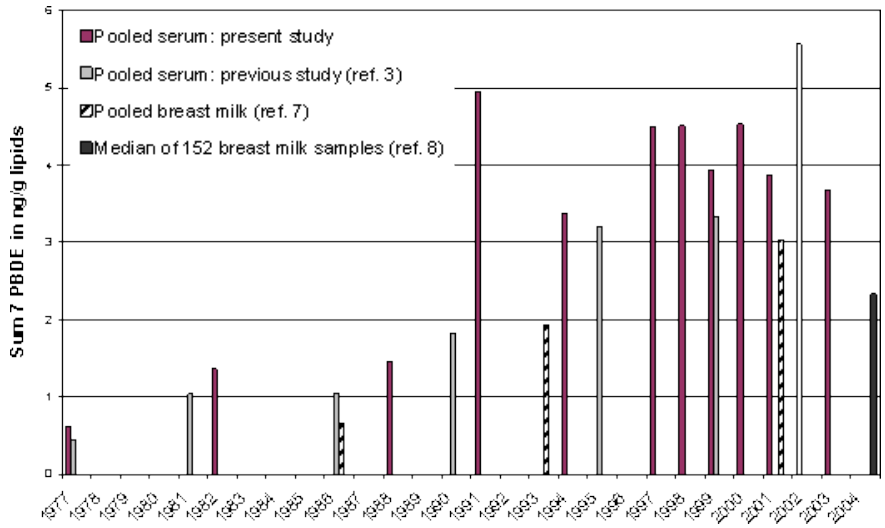
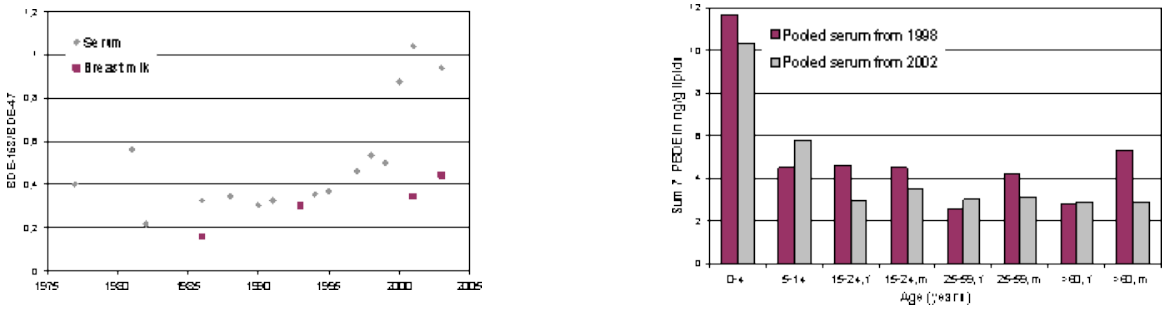


Figure 1.The sum of 7 PBDEs in ng/g lipids in human samples from Norway from 1977 to 2004.

Of the 7 PBDEs, BDE-47 was found in the highest concentration in all but one of the samples. The amount of BDE-153 versus BDE-47 is presented in Figure 2B, which shows that the relative amount of BDE-153 has increased during the last decade. The relative amount of BDE-153 is lower in breast milk than in serum, but seems to be increasing as well. A recent increase in the level of BDE-153 compared to the level of BDE-47 has also been observed in breast milk from the Faroe Islands[10].

The PBDE level was previously found to be about twice as high in a serum pool from infants up to four years of age compared to serum pools from elder persons[3]. This finding was confirmed in the present study (Figure 2A). However, it seems that in 2002 also children of age 5-14 years show higher levels of PBDEs than the average adult.

A) **B)**

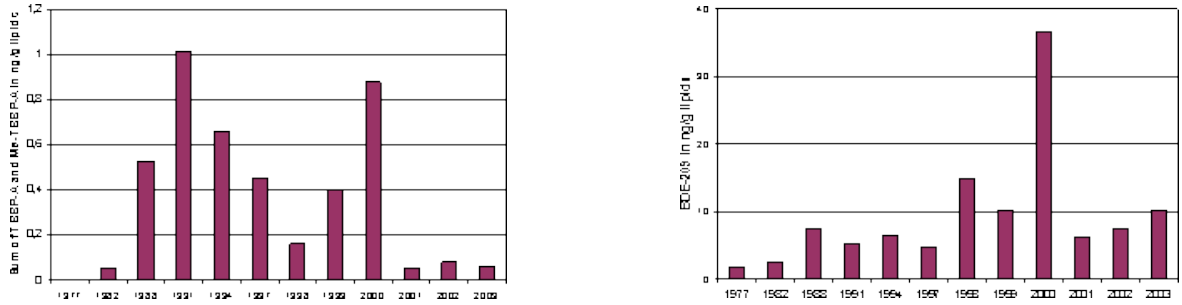


Figures 2A/B. A) The sum of 7 PBDEs in ng/g lipids in serum pools from persons with different age and gender sampled in 1998 and 2002 (f: female, m: male). B) The amount of BDE-153 relative to BDE-47 in serum and breast milk samples.

BDE-209 and TBBP-A

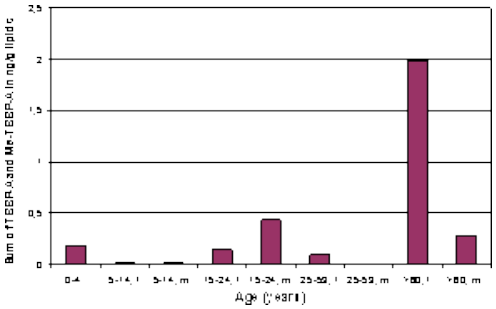
The decabrominatedBDE (BDE-209) and TBBP-A derivatised to methylatedTBBP-A was also determined in the present study (Figures 3 and 4). Traces of naturally methylatedTBBP-A were observed in all the samples and the concentrations presented in Figure 3B and 4B are the sum of TBBP-A and methylatedTBBP-A. No increase with time was observed for these compounds. In the serum pools from persons of different age, the median BDE-209 and TBBP-A were 8.7 and 0.15 ng/g lipids, respectively, compared to 1.3 ng/g lipids for BDE-47. As is also seen from Figure 3A, the level of BDE-209 is remarkably high in the sample from 2000. Some high levels of BDE-209 have also been reported in an investigation of serum from the general population in the UK[11], however, contamination of this sample can not be totally excluded.

A) **B)**

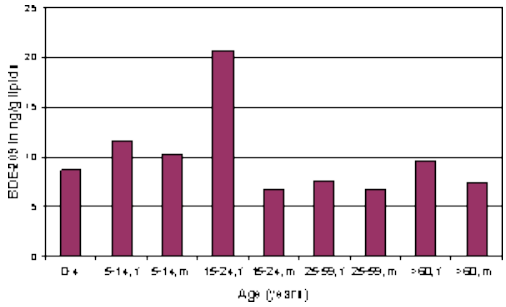


Figures 3A/B. The concentration in ng/g lipids of A) BDE-209 and B) the sum of TBBP-A and methylatedTBBP-A in pooled serum samples sampled between 1977 and 2003.

A)



B)



Figures 4A/B. The concentration in ng/g lipids of A) BDE-209 and B) the sum of TBBP-A and methylatedTBBP-A in pooled serum samples from persons with different age and gender sampled in 2002 (f: female, m: male).

To summarise briefly, the previously observed rapid increase in tri- to hexabrominatedPBDE levels in human samples from Norway during two decades from 1977 has been confirmed. The levels now seem stabilized or to be decreasing since the late 1990s. In serum from different age groups, the highest sum 7 PBDE levels are observed in the serum from the youngest individuals. Similar trends were neither observed for BDE-209 nor TBBP-A, although these two BFRs were detected in almost all of the samples.

Acknowledgement

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