A TIME RELATED STUDY ON BROMINATED FLAME RETARDANTS IN SERUM SAMPLES FROM THE GENERAL POPULATION IN NORWAY

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Introduction

A large number of chemicals are used as flame retardants to protect different products from catching fire. Brominated flame retardants (BFRs) represent about 39 % of the world-wide production and the use has increased considerably during the last decades.[1,2] The most important BFRs are tetrabromobisphenol A (TBBP-A) and polybrominated diphenyl ethers (PBDEs). TBBP-A is mainly used as a reactive flame retardant in printed circuit boards, while PBDEs are used as additives in plastics, textile coatings and electrical components found in many common goods such as television sets and computers.[2] Due to their lipophilic and persistent character, the BFRs might accumulate in the food web and finally in humans, and are thus a potential environmental health problem.

Several PBDEs have been reported in various environmental samples, human adipose tissue, plasma and mother's milk.[3] Retrospective time trend studies are a valuable tool for judging the development of a pollution situation. In Sweden, the levels of PBDEs have been found to increase in sediments,[4] guillemot eggs[5] and human milk[6] since the 1960s. Recently, increasing PBDE concentrations in environmental and human samples have also been observed in other countries.[7]

The aim of the present study was to determine the concentrations and the time trends of PBDEs and TBBP-A in serum samples from the general Norwegian population, sampled during the period 1977 to 1999. In addition, the current concentration of BFRs in serum from different age groups was investigated.

Materials and Methods

Chemicals

TBBP-A and chlorotribromobisphenol-A (CtriBBP-A) were a gift from the Wallenberg Laboratory (University of Stockholm, Sweden) and Wellington Laboratories (Guelph, Ontario, Canada) kindly supplied the PBDEs. 2,4,6-Tribromophenol (TriBP) were purchased from Aldrich (Milwaukee, WI, USA) and 3,3',4,4'-tetrabromobiphenyl (BB-77) from AccuStandard Inc. (New Haven, CT, USA). All solvents were pesticide grade from Labscan (Dublin, Ireland).

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, regardless of disease and the reason for hospitalization, during the same five weeks of autumn, and stored at

–20 °C. In the investigation for a time trend, the study was restricted to men in the age range of 40-50 years, to avoid variation of body burden with age. The serum samples were pooled and stored at –20 °C. Each pool consisted of serum from about 20 persons. The current concentration of BFRs in different age groups was also sought, and serum sampled in 1998 was chosen for this purpose. The serum samples had originally been divided into eight age groups (see Figure 2), and samples from between 10 and 14 individuals was pooled. The lipid content of the pooled serum samples was determined at The National Hospital of Norway (Oslo, Norway) according to a method described by Grimvall et al..[8]

Sample preparation and quantitative determination
The serum samples were extracted using solid phase extraction (Isolute ENV+, (200 mg) from International Sorbent Technology, Mid Glamorgan, UK) according to a previously described method.[9] 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;81 and confirmed by controlling the isotope abundance ratio and the retention time. The uncertainty of the analysis was found to be about 20 %.

Results and Discussion
The congeners BDE-47, BDE-99 and BDE-153 were found in all samples, while BDE-28, BDE-100 and BDE-154 and TBBP-A were found in the most recent samples (Figures 1 and 2). BDE-183 was not identified in any of the samples. The estimated detection limits were in the range 0.4-1.6 pg/g serum. As can be seen from Figure 1, the serum concentrations of all the investigated BFRs increase during the entire period, with the greatest changes between 1986 and 1995. The sum of the six PBDEs increased from 0.44 ng/g lipids in 1977 to 3.3 ng/g lipids in 1999. To get a more mathematical depiction on the development of body burden of PBDEs during these decades, the six points were subjected to different trend lines. The best curve fit was obtained with an exponential trend line, which resulted in an R-value of 0.968.

The concentrations of the BFRs in the serum samples from different age groups in 1998 are shown in Figure 2. The PBDE concentrations in serum from the individuals of age 0-4 years differ clearly from the other serum concentrations, which on the other hand seem to be relatively similar. These results are contradictory to studies of other persistent organic pollutants (POPs), where an increase in body burden with age often is observed. Also, for the individuals of age above 25 years the women seem to have lower serum concentrations of BFRs compared to the corresponding group of men. Further studies are needed in order to explain these findings.

TriBP was also determined in the serum samples, but no temporal or age related trends were observed (results not shown).

BDE-47 was by far the most abundant congener in all the serum samples and contributed to between 30 and 65 % of the total concentration of PBDEs (mean 47 %). This is in accordance with the congener patterns reported in human whole blood,[10] plasma[11] and milk.[6] When excluding the age group of 0-4 years, the current concentration of BDE-47 in serum from the general population in Norway was in the range of 1.2-3.4 ng/g lipids. BDE-47 has previously been reported in

concentrations of 1.6 ng/g lipids (median, n=19, 1997, Sweden),[11] 0.63 ng/g lipids (median, n=12, 1988, USA)[12] and 3.0 ng/g lipids (median, n=20, 1999, Germany)[10] in general populations.

In conclusion, there seems to be an ongoing increase in the human exposure to BFRs, and the current body burden seems to be independent of age, except for infants of age 0-4 years, where higher concentrations were observed.

Acknowledgements
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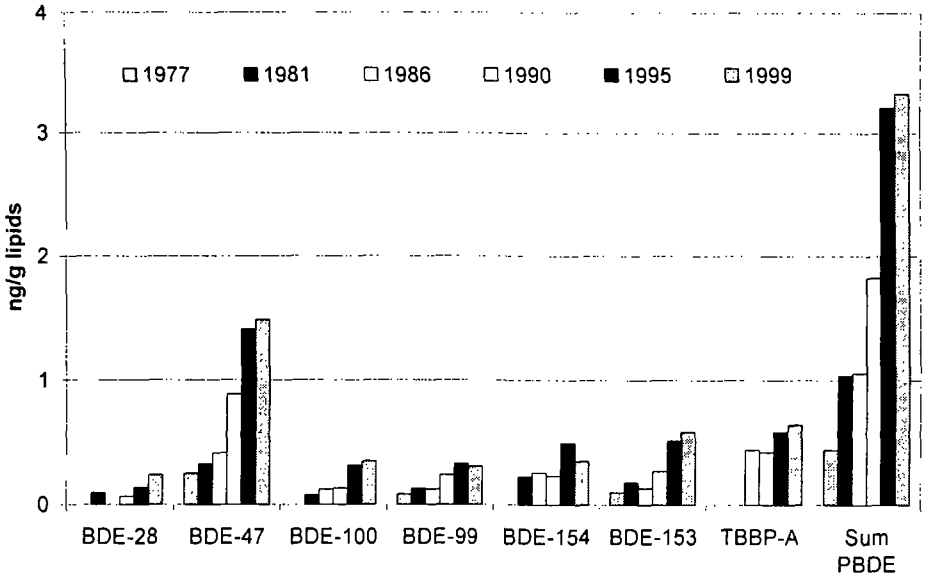

Figure 1. Concentration of the individual PBDE congeners, TBBP-A and sum PBDE (ng/g lipids) in pooled serum samples from Norwegian men of age 40-50 years, sampled in 1977, 1981, 1986, 1990, 1995 and 1999.

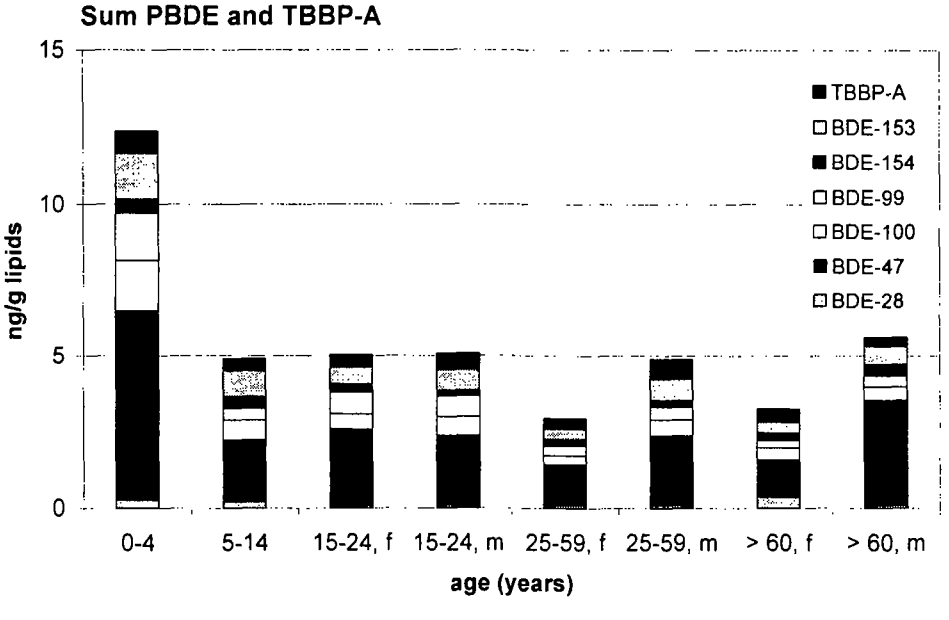

Figure 2. Concentration of the PBDE congeners and TBBP-A (ng/g lipids) in pooled serum from different age groups of Norwegian male (m) and/or female (f) subjects sampled in 1998.