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CONGENER SPECIFIC MEASUREMENT OF POLYBROMINATED DIPHENYL ETHERS IN 47 INDIVIDUAL MILK SAMPLES FROM NURSING MOTHERS IN THE U.S.A.

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Introduction

Polybrominated diphenyl ethers (PBDEs), synthetic brominated flame retardants, have recently been measured in human tissues in a number of countries [1-5]. To date, congener specific analyses of PBDEs in individual human milk in the USA have not been reported. This paper reports findings of up to 13 PBDE congeners in milk from 47 nursing mothers' milk from Austin and Dallas, Texas.

Based on a relatively small but growing amount of toxicology data, these synthetic compounds are believed to be persistent, bioaccumulate, may cause alterations in function of the nervous system, cause endocrine disruption, and may be carcinogenic [6]. Few if any epidemiology studies could be found in the literature at this time.

Methods and Materials

Clinical Methods

The milk was obtained in 2002 from a milk bank in Austin, Texas, and clinics sponsored by the University of Texas Southwestern Medical Center in Dallas, Texas. Milk was frozen and shipped frozen to the laboratories in Hamburg, Germany and in Ottawa, Canada.

Analytic Methods, Germany

All analyses were performed following the isotope dilution method. Twelve native standards were obtained from Cambridge Isotope Laboratories. One native standard was from Wellington. Laboratories, Guelph, Canada. Out of 7 internal ^{13}C labeled standards 6 were delivered by Wellington. One, PBDE No 209 was from Cambridge. Before extraction the mixture of 7 internal PBDE standards were added to the sample. Five ml of human milk was extracted three times with pentane. The extract was washed with water and dried over sodium sulfate. After solvent evaporation gravimetric lipid determination was performed. Measurements were performed using high-resolution gas chromatography/high resolution mass spectrometry. Two most abundant masses were used for measurement (M+ for Tri- and Tetra-BDE, and M – 2BR + for Penta-to Deca-BDE). Identification of BDEs was based on retention time and correct isotope ratio.

Quantification was performed using internal and external standards. Quantification was only done if sample data was at least twice the blank data. Lipids in each sample were determined.

Analytic Methods, Canada
Carbon ^{13}C labeled BDEs were purchased as two mixtures from Wellington Laboratories. Most of the carbon ^{12}C BDE congeners were obtained from Cambridge Isotope Laboratories. A mixture of 500 pg each of six ^{13}C labeled BDEs (congeners 28, 47, 99,153, 154, 183) was added to 10 to 20 g of human milk. Samples were homogenized and extracted with acetone-hexane with concentrated sulphuric acid, adsorbed on separated on activated magnesium. Chromatography on Florisil was adjusted to less polar PCBs were separated from the bulk of the BDEs. A 30 M methyl silicone gas chromatographic column effected separation of the mono-hepta-homologues. Detection was performed with mass spectrometry in the electron impact mode, quantification was carried out with isotope dilution. Identification and quantification including the isotope dilution method is similar in principle to previous techniques in which organochlorines were determined. Eight to ten unknown samples contained a laboratory reagent blank and a control human milk repeat sample. The former was used to measure the contribution of the laboratory to the total signal, which was then subtracted from samples prior to quantification milk samples was used as an measure of laboratory precision.

Results and Discussion
The results are summarized in three Figures. Figure 1 presents the sum of the congeners listed by ascending levels of PBDEs. It shows the high levels of PBDEs and the skewed distribution. Figure 2 presents the sums of the congeners as percentile in ascending order with the median of 34 part per billion (ppb). Total levels of these compounds range from 6 to 419 ppb lipid which is 10 to 100 times higher than levels in human milk or other tissues reported in European samples. Figure 3 compares median levels in milk of PBDE 47, 99, and 153 from Canada, Germany, Sweden and Finland [1-5]. In each case US levels are higher. Increasing levels over time between 1992 and 2002 are noted in Canada. Congener 47 was found at highest levels in these samples. Congener 99 was usually the next highest. The distribution of congeners in milk was not identical to the distribution found in commercial mixtures. The lower brominated PBDEs are found in higher levels than are the higher brominated PBDEs in these milk samples. Unlike dioxins and dibenzofurans which are found in parts per trillion, the PBDE congeners are found at parts per billion levels [7].

Very high levels of PBDE congeners were found in this first study of milk from 47 individual nursing mothers from the United States in comparison to levels currently reported in Europe. Up to 13 PBDE congeners were measured. These levels may well be representative of levels in other nursing women throughout the United States. They are similar, on a lipid basis, to levels measured in adipose tissue and blood samples obtained in California and Indiana and previously reported [8-9]. These findings are consistent with expectations that PBDE levels from the USA where PCDEs are not banned would be much higher than levels expected and found in Europe, where these chemicals are either not used or are being phased out in many countries. Increasing human levels of PBDEs in Canada and the US suggest the elevated levels seen in North American women may be of recent origin.

Figure 1. PBDEs in US human milk, 2002 (ng/g or ppb of lipid)

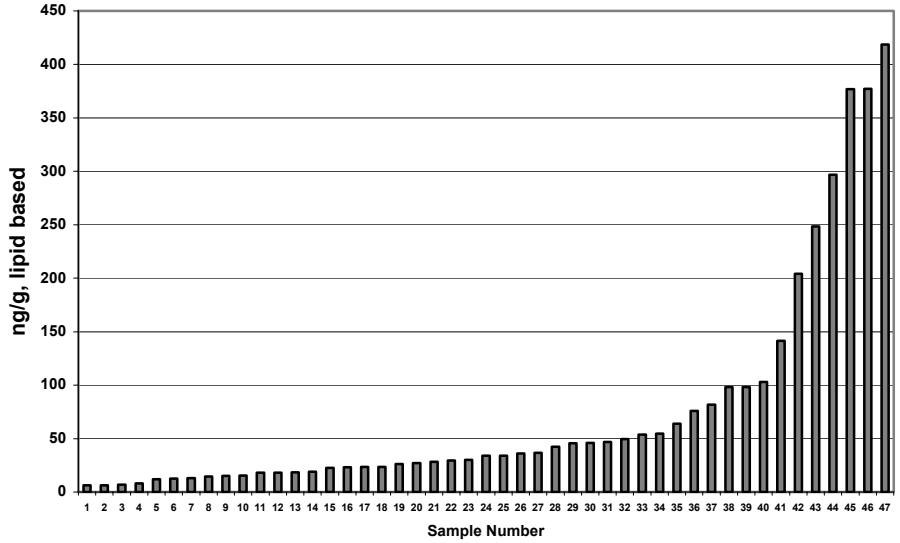


Figure 2. PBDEs in US human milk, 2002, n=47 (ng/g or ppb of lipid).

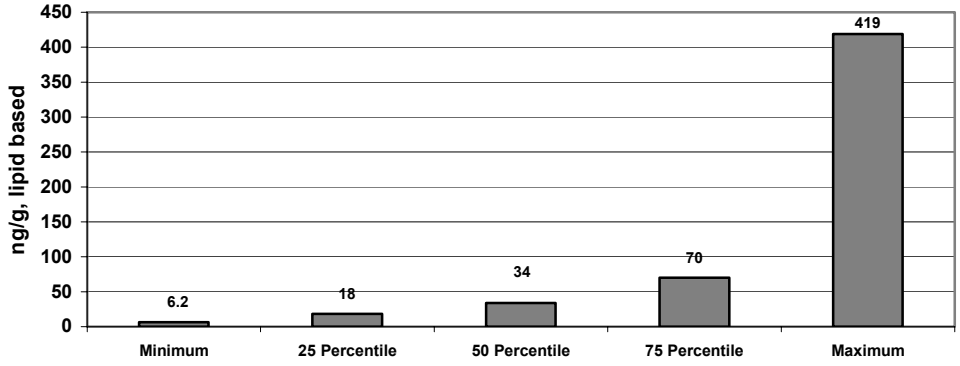
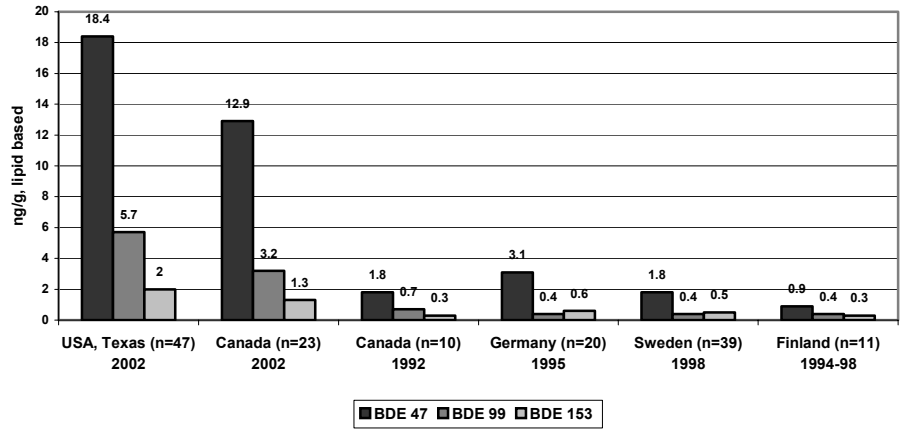


Figure 3. Median levels PBDE congeners 47, 99, and 153 in different countries (ng/g or ppb lipid)



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