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TEMPORAL AND SPATIAL CHANGES OF BROMINATED DIPHENYL ETHERS (BDEs) AND OTHER POPs IN HUMAN MILK FROM NUNAVIK (ARCTIC) AND SOUTHERN QUEBEC

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Introduction

The pioneering work of Norén and Meironyté [1] in Swedish human milk showed that the concentrations of most persistent organic pollutants (POPs) such as PCBs, dioxins/furans, DDTs, and chlordanes decreased by at least a factor of two from the early 1970s to 1997. A notable exception to this trend was the brominated diphenyl ethers (BDEs) used as flame retardants. These increased steadily and reached levels of 3-4 ug/kg (ppb) on a milk lipid basis. It is now known that BDEs are ubiquitous environmental contaminants being found in environmental samples, biota, and man[2-4]. The levels of BDEs in human milk from Europe appear to have stabilized but that cannot be said for North America. We reported previously[5-6] on the BDE content of more than 150 individual human milks collected across Canada and found median levels for total BDEs had changed from 1992 to 2002 by about an order of magnitude (2.9 to 22 ppb milk lipid). Recent reports on the BDE content of human samples from the United States[7,8] indicate even higher general exposure in that country. BDEs are now known to be present in remote northern regions having been found in the Arctic by Ikonomou et al.[9] in ringed seals, a common traditional food of Inuits. In the latter study the BDEs increased by about a factor of ten from 1981 to 2000. This finding was significant since it provided strong evidence that BDEs were transported to remote areas thus satisfying one of the four important criteria for classification as a POP.

For some time we have been studying the exposure and health effects of Inuit peoples living in northern Quebec (Nunavik). This work has resulted in collection of human milk samples in the early 1990s[10] and more recently in the late 1990s[11]. We have used these samples to investigate the BDE content of the peoples from this remote region. This work has been carried out both on a time basis and spatially using data from the more populated and industrious southern Quebec. In addition we compare the BDE exposure with that for two of the most common POPs, chlorinated dibenzodioxins/furans and PCBs. We report here on the BDE, dioxin/furan/PCB content of human milks from both the Nunavik and southern Quebec regions in the years 1990 to 2002.

Material and Methods

Sample Collection

All Nunavik participants in both the 1990s and 2000 study groups resided on the East Coast of Hudson Bay (figure 1). Milk samples originated from the villages of Puvirnituk and Inukjuak, with a

small proportion from Kuujjuaraapik. Sampling days post-partum in the earlier years was generally in the first month after birth and that in the late 1990s was usually greater than 25 days.

Human milks from southern Quebec were obtained in 2002 from community centres in Montreal and Quebec. Those in the earlier years of 1992 and 1989 were archived samples from previous exposure and health studies[10,12]. In most cases information on age and smoking status was available and, less frequently, on parity, weight and height of the donor. Concentrations are expressed on a lipid basis using medians and ranges, and toxic equivalents (TEQ) are calculated using WHO toxic equivalent factors (TEFs).

Analysis

Individual milks (2 to 20 mL) were analysed for a wide range of POPs consisting of: 1) BDE congeners with three to seven bromines, 2) the major PCB congeners (including all eight mono ortho with TEFs), and 3) dioxins/furans/non ortho PCBs (all seven, ten and four with TEFs). All analyses were completed on the same initial milk sample extract[5,6]. In summary, the method involved the addition of mixtures of isotopically labelled BDEs, PCDDs, PCDFs, and non ortho PCBs, and seventeen PCBs including all those with TEFs for isotope dilution MS. Milks were extracted with a mixture of acetone-hexane and lipid removed with strong acid. Further purification was accomplished on columns of acid silica and activated Florisil. The major PCBs eluted from Florisil with the first non polar hexane fraction and the BDEs eluted in the second fraction along with dioxins/furans and noPCBs. The BDEs were separated from the latter by a carbon column specific for planar compounds. Identification and determination of all three groups was accomplished by gas chromatography with high resolution (8-10K) mass spectrometry in the electron impact mode. Quantification was by the isotope dilution method using an eight point calibration curve. Sample batches included a laboratory blank to estimate contribution from that source (which is significant for BDEs; the total in the blank is subtracted from the total in the sample) and a reference or repeat control sample for accuracy and precision. The laboratory has participated successfully in both international interlaboratory studies for BDEs sponsored by the flame retardant industry (BSEF)[13] as well as the Norway interlaboratory food[14] study for dioxin-like compounds in the last three years.

Results and Discussion

The BDE, PCDD, PCDF and PCB content of human milks collected in 1989-91 and 1996-2000 from Nunavik (Arctic Quebec) are shown as their median values on a milk lipid basis in table 1. Listings for the BDEs consist of the most prominent congener 47 as well as the sum of the seven

major BDE congeners. For the PCBs, congener 153 and totals of 16 congeners are given. The dioxins, furans, non- and mono-PCBs are reported as their TCDD toxic equivalents (TEQ).

Although the number of samples is limited, the Nunavik results show for the first time the presence of BDEs in milk samples from this region. The concentrations show an increase during the study period of about 10 years despite the fact that the results may be somewhat confounded by the long span of years of sample collection. In contrast both PCBs and dioxins decrease markedly in these samples over the same time frame by factors ranging from 3 and 9 times. The levels of the same analytes for human milks taken in the same years from southern Quebec and their comparison to Nunavik are shown in figures 1 and 2. BDEs increase and PCBs and TEQ decrease in southern Quebec although the BDE increase is more substantial and the TEQ reduction possibly less than in Nunavik. These first results showing the presence and increase of BDEs in human samples in remote regions suggest exposure is acquired through consumption of traditional marine mammal foods containing these compounds. The decreasing concentrations for dioxin-like compounds and PCBs is in agreement with recent reviews on this subject in human milk[15,16] and may be related to decreasing concentrations of these compounds in the environment, to changes in diet and life-style, or a combination of these factors.

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Table 1. BDEs, PCDDs/PCDFs, and PCBs in human milks collected in Nunavik (Arctic Quebec)
Median values on milk lipid basis

Year	1989-91	1990	1996-2000
Number of samples	10	pool of 5	10
BDEs µg/kg (ppb)			
Congener 47	0.88	-----	3.4
ΣBDE (n=7)	2.2	-----	6.2
PCBs µg/kg (ppb)			
Congener 153	228	717	108
ΣPCB (n=16)	850	1723	393
TEQ ng/kg (ppt)			
PCDD (n=7)	17.7	19.2	2.3
PCDF (n=10)	3.6	6.0	0.9
Non ortho PCB (n=4)	20.9	13.3	2.1
Mono ortho PCB (n=8)	13.8	14.6	6.6
ΣTEQ (n=29)	56	53.1	11.9