BODY BURDENS AND FOOD EXPOSURE IN CANADA FOR POLYBROMINATED DIPHENYL ETHERS (BDES)

John Jake Ryan and Benoit Patry

Health Products and Food Branch, Health Canada, Ottawa K1A 0L2, Canada

Introduction

Brominated diphenyl ethers (BDEs)[1,2] are useful industrial chemicals that are now known to occur in the environment. However at present it is uncertain whether this presence impacts on human health. In order to assess human risk from these environmental chemicals, data on human exposure is essential. Levels of BDEs in human milk give information on total uptake for a selected segment of the population and data on commercial foods evaluate for the general population the role of food consumption as a pathway for such exposure. To date, it has been shown that the predominant route of exposure of humans to virtually all persistent organic pollutants (POPs) is through food consumption. Some information has been reported on BDEs in human milks from North America[3] but, apart from fish and wildlife, little is known about the presence of these compounds in common commercial foods[4]. Human uptake of BDEs was estimated by sampling human milk from earlier surveys of organochlorines. Human intake was evaluated by sampling commercial foods from an ongoing total diet market basket study. The intake of BDEs from the same foods was compared to similar data for dioxins, furans, and PCBs.

Methods

Sampling

Human milks were obtained from previous surveys of more than 500 individual mothers collected countrywide according to population in 1992. Pooled composite samples of large numbers of individual milks were available from similar programs in 1982 and 1986 and from a small pool of 17 donors taken in 1997 in upstate New York. Composites of commercial foods as part of the total diet market basket program were available from Whitehorse, Yukon in early 1998. These foods for estimation of organohalogen content were all taken from commercial outlets, were prepared as for normal human consumption, and consisted of mainly fatty foods of animal origin.

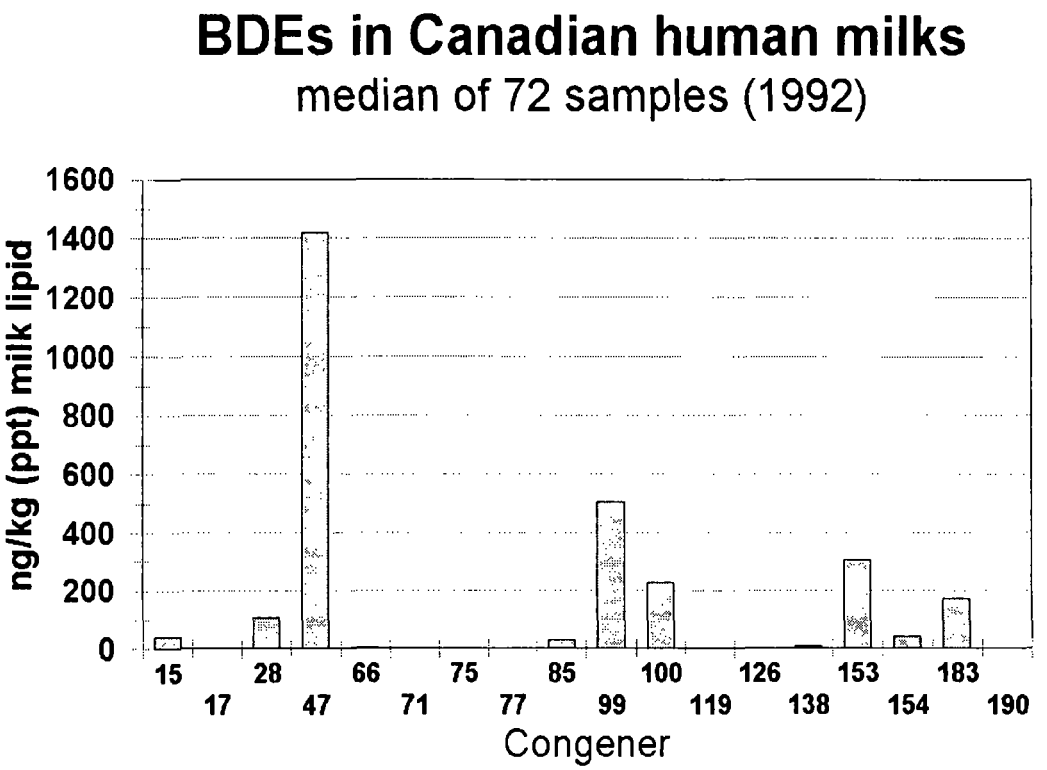
Analysis

The presence of all ten homologues of the BDEs (more than 40 specific congeners were available) in both human milk and common commercial foods was assayed using established analytical techniques[3] except for BDE-209 for which a new carbon-13 standard and short GC column were used. Extraction was carried out with acetone-hexane, and enrichment by defatting with strong acid or gel permeation, followed by separation on activated Florisil. The majority of BDEs elute with the dioxins in the second semi-polar fraction from Florisil. BDE-209 (deca) eluted with the PCBs in the first non-polar fraction along with a few other higher brominated congeners. Measurement was by gas chromatography-high resolution mass spectrometry (GC-MS) in the electron impact (EI) mode with monitoring of either M^+

or M-2Br$^+$. Quantification was effected by the isotope dilution internal standard method using seven carbon-13 congeners including BDE-209 and a calibration curve. Data on the dioxin, furan, and PCB content of the same samples were available using similar methodology[5].

Results and Discussion

Analysis The methodology is capable of quantifying most of the congeners of the BDEs in biota except for the octa and nona homologues for which standards are not available. The use of high resolution GC-MS in the EI mode combined with carbon-13 surrogates ensures low detectablility and a high degree of both specificity and accuracy. Measurement of BDE 209 is still a problem even though a carbon-13 standard is available to correct for analyte losses. The presence of significant amounts of several BDEs (47, 99, 100, 183 and especially 209) in laboratory blanks makes quantification of these congeners uncertain in those samples already containing low levels. Specifically, the low levels of BDE-209 that probably occur in biota are difficult to distinguish from that in the sample preparation in the laboratory.



Human uptake The BDEs in 72 human milk samples collected in 1992 from all provinces of Canada according to relative population are shown in the figure in histogram form. As has been reported previously[2,3], a typical pattern is seen for human samples with BDE-47

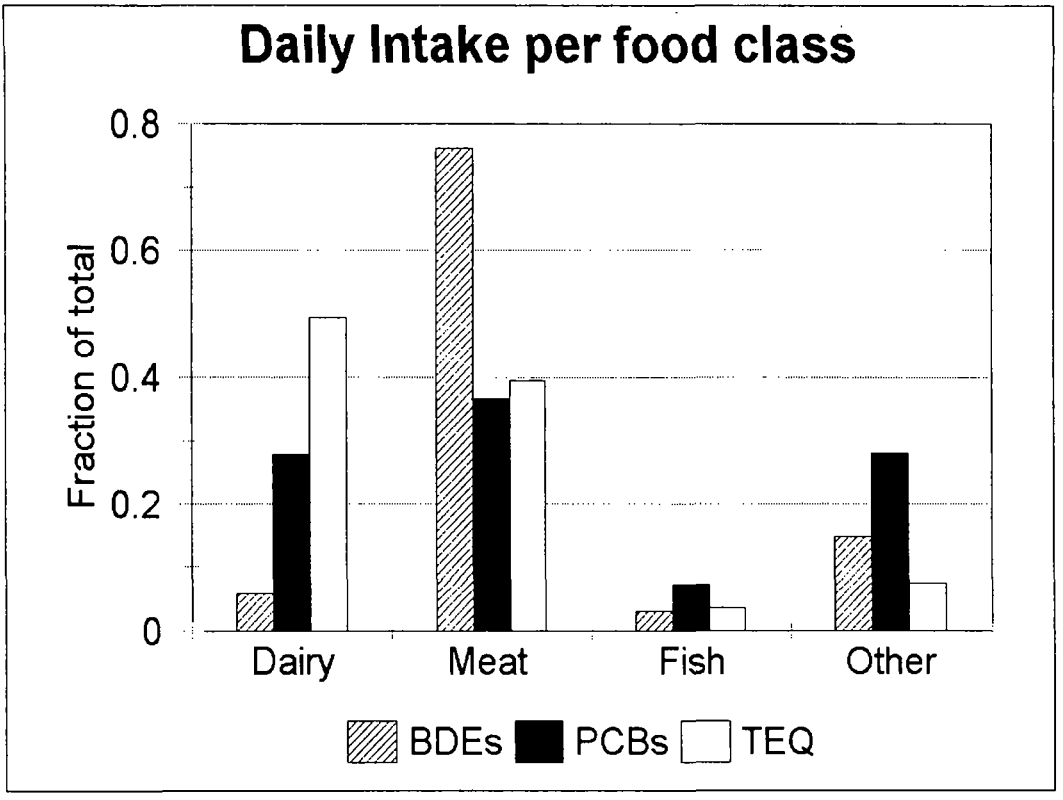
dominating in amounts following by 99 and 100. Little or no BDE 209 could be detected in these biota. The variation of BDE values in these individual samples was considerable with two samples having levels near mg/kg on a milk lipid basis. Median levels of BDE 47 were about 25x less than PCB 153 and total BDE congeners were about 75x less than total PCB congeners. There is a high correlation among BDE congeners but not between BDEs and PCBs; the latter are also highly correlated among themselves.

Human intake In order to obtain data on intake and source, the BDE content of about 40 commercial foods mostly of animal origin and high lipid content has been measured. The results for dairy products show relatively low parts per trillion (10^{-12}) levels for fluid milk and somewhat higher concentrations for more processed foods such as cream, cheese and butter whether expressed on a whole or lipid basis. Concentrations in animal meat products such as beef, pork, and poultry are higher than dairy products. Fresh water fish, in agreement with literature information, contains higher concentrations of BDEs than either marine or shellfish. The congener pattern in all food samples is remarkably constant. As in the human milk samples, BDEs 47 and 99 are the two main congeners. However the ratio of 47 to 99 in animal foods is between 0.5 and 1.0. This ratio is different from the ratio found in human milk reported above (between 2 and 3). The ratio of 47 to 99 in the commercial flame retardant is about 0.5. Huwe et al. (4) reported previously on this same BDE congener pattern in animal tissues. This difference in the relative amounts of congeners 47 and 99 between human and other animal species may be related to the distinction in half-lives for clearance between these congeners.

The data on the BDE content of these 40 common commercial foods were combined with food consumption data. This resulted in a daily intake of total BDEs of about 44 ng. At present there is little information on levels of BDEs in air and water in order to estimate the daily intake from those pathways. However, half-lives of less than one year for the most prominent BDEs, congeners 47 and 99, combined with simple pharmacokinetics, indicate that most of the exposure to BDEs is probably through food consumption -a pathway inference in line with most other POPs. Similar daily intake values from analyses of the same 40 food samples for total PCBs and PCDD/PCDF TEQ gave values of 285 ng and 45 pg, respectively. The daily intake information has been summarized by dividing the food classes among dairy (milk, butter etc), meats (beef, pork, poultry), fish, and other foods as shown in the second chart. This shows that the contribution by each class of foods to the daily intake of each of the three groups of POPs, BDEs, PCBs, and TEQ, appear to possess similarities as well as differences. However the generality and robustness of these estimations remain to be verified.

Acknowledgements

The Toxic Substances Research Initiative (TSRI) of Health Canada provided funding for this work. Nicole Beaudoin, Pat Mills and Brian Shields are all thanked for their efforts in standard and sample preparation. Josee Doucet of Health Canada kindly provided the PCB data.



References

1. de Boer, J., de Boer, K. and Boon J. P. (2000) Handbook Environmental Chemistry (Passivirta, J., ed.), Springer-Verlag, ch 4; 61-95.
2. Noren, K. and Meironyte, D. (2000) Chemosphere 40, 1111-1123.
3. Ryan, J. J. and Patry, B. (2000) Organohalogen Compounds 47, 57-60.
4. Huwe, J. K., Lorentzsen, M., Thuresson, K. and Bergman, A. (2000) Organohalogen Compounds 47, 429-432.
5. Ryan, J. J., Beaudoin, N., Mills, P. and Patry, B. (1997) Organohalogen Compounds 32, 229-232.