# Determination of PBDE levels in a sub-arctic aboriginal population

Eric N Liberda[1], Leonard Tsuji[2], Evert Nieboer[3], John J Ryan[4], Bruce Wainman[1]

[1]Dept. of Obstetrics & Gynecology, McMaster University
[2]Dept. of Environmental Studies, University of Waterloo
[3]Dept. of Biochemistry, McMaster University
[4]Bureau Chemical Safety, Health Canada

## Introduction

Polybrominated diphenyl ethers (PBDEs) are a concern because they are lipophilic, resist catabolism, and may be endocrine disruptors, much like other persistent organic pollutants (POPs) such as DDT, PCBs, polychlorinated dibenzo-p-dioxins (PCDDs) and furans (PCDFs)[1,2]

Levels of POPs in human plasma have, in general, decreased dramatically. However, this is not the case for PBDEs. The concentration of PBDEs in plasma and other biological fluids has steadily increased since their inception. Current PBDE production has been estimated at 35 million kilograms per year[3], thus environmental loadings of PBDEs will continue to rise. The increase in PBDE use is primarily because brominated flame retardants (BFRs) are one of the least expensive flame retardant commercially available[4].

First Nations peoples in Canada carry larger loads of many POPs compared to the general Canadian population. The increase in load arises primarily from a traditional diet, which relies heavily on fish and other foods high in POPs. It is not clear if the general increase in POPs is reflected in an increase in PBDEs.

The potential of PBDEs to impact the health of First Nation people is a growing concern. In the James Bay area, much of the diet comes from top predators such as: northern pike (brochet, *Esox lucius*), walleye (pickerel, doré, *Sander vitreus*), brook trout (*Salvelinus fontinalis*), and lake trout (*Salvelinus namaycush*)[5]which are typically high in POPs. To address concerns about PBDEs and their relationship to other POPs the current study investigates the PBDE levels in plasma of the Oujé-Bougoumou community, a sub-arctic First Nation population.

An additional goal of the study is to compare the performance of the relatively expensive high resolution gas chromatography-mass spectroscopy (HRGC-MS) analysis to lower cost low resolution gas chromatography-mass spectroscopy (LRGC-MS) results. This work is necessary because the measurement of PBDE levels in the Cree and other people is inhibited by the cost incurred.

## Materials and Methods

### Sample Collection

Women between the ages of 18 to 40 who have not been lactating, using an intrauterine device, hormonal contraception, or other hormone replacement therapy in the three months prior to the study commencement date were eligible candidates for this study. Females who have been pregnant in the last 6 months, have a chronic disease, endocrine disorder, or other reproductive endocrine disorders were excluded.

### Analysis

Extraction and analysis was followed under Health Canada's methodology[6]. Human plasma samples (6-10g wet weight) were spiked with a 500pg mixture of $^{13}$C-BDEs containing 9 congeners. The nine carbon-13 labelled BDEs (congeners 28, 47, 66, 99, 100, 153, 154, 160, and 180) were obtained from Wellington Laboratories and Cambridge Isotope Laboratories. The samples were homogenized and extracted with acetone-hexane, defatted with concentrated sulphuric acid, and separated in a series of packed florisil, carbon, and silicate columns.

Samples were prepared and injected on both high resolution and low resolution GC-MS. LRGC-MS analysis was conducted on an Agilent 6890 GC-MS using Chemstation software. A DB-5 MS bonded phase capillary column of 15m length, 0.25mm inner diameter, and 0.25µm thickness with a retention gap was used for the analysis. The MS was a micromass auto spec ultimat operating in electron impact (EI) mode at 40 eV ionization energy, source temperature of 250$^{o}$C, interface temperature of 270$^{o}$C and a mass resolution of 10K (10% Valley). One µl was injected on column at 80$^{o}$C with a fast ramp to 300$^{o}$C in a total run time of approximately 15 min. Identification of each analyte was governed by its GC retention time, correct amu ion ratio, and a signal to noise ratio of at least 3:1. The M+ and M-2Br ions were monitored for the analysis. The compounds were quantitated in Chemstation with known amounts of target compounds, internal standards, and recovery standards. Due to blank quality control measures, BDE-99 was not reported.

**Results and Discussion**

The mean lipid corrected concentration of PBDEs for the Oujé-Bougoumou Cree (n=10) was 28.99ppb (SD=19.63) for HRGC-MS (Table 1) and 26.96ppb (SD=21.15) for the LRGC-MS (Table 2) of the BDE congeners compared (28, 47, 66, 100, 153, and 154). These 6 congeners constitute approximately 96% of the total sum of the 8 BDE congeners measured. The PBDE levels in the Oujé-Bougoumou Cree are substantially higher than the reported 1996-2000 Nunavut (located in the Canadian Arctic) levels who had median values of 6.8ppb for BDE congeners 28, 47, 85, 99, 100, 153, 154, 183[6]. However, the southern Canadian PBDE lipid values are much higher when compared to the Oujé-Bougoumou Cree values. Ryan and Van Oostdam[6] and Ryan *et al.*[7] found mean values of 60ppb and 49ppb in southern Canadian human milk, respectively. In Summary, the Oujé-Bougoumou Cree have more of the traditional POPs and less of the PBDEs compared to southern Canadians who have higher levels of PBDEs and lower levels of other POPs. This suggests that other routes of exposure aside from the normal dietary route, such as dermal absorption of dust, may contribute a significant portion of the total PBDE levels.

**Table 1. High-Resolution GC-MS Results (lipid weight in ppt)**

| | Congener | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Sample ID** | **BDE-28** | **BDE-47** | **BDE-66** | **BDE-100** | **BDE-153** | **BDE-154** | **BDE-160** | **BDE-183** |
| EL1-2 | 4186 | 35093 | 139 | 1536 | 1784 | (ND) | 443 | (ND) |
| EL1-3 | 3244 | 38853 | 178 | 4997 | 12575 | 603 | 469 | (ND) |
| EL1-4 | 1284 | 6673 | 5 | 175 | 709 | (ND) | 177 | (ND) |
| EL1-5 | 2607 | 17057 | (ND) | 3381 | 6570 | 54 | 343 | (ND) |
| EL1-6 | 4863 | 25363 | 66 | 5576 | 9487 | (ND) | 445 | (ND) |
| EL1-7 | 1129 | 11594 | (ND) | 1197 | 3474 | (ND) | 245 | (ND) |
| EL1-8 | 1390 | 8828 | (ND) | 1946 | 4484 | (ND) | 333 | (ND) |
| EL1-9 | 679 | 3455 | (ND) | (ND) | 1730 | (ND) | (ND) | (ND) |
| EL1-10 | 2161 | 24510 | (ND) | 3906 | 6879 | 30 | (ND) | (ND) |
| EL1-11 | 2409 | 12680 | 49 | (ND) | 638 | (ND) | (ND) | (ND) |
| EL1-12 | 1497 | 25961 | 74 | 2394 | 2341 | 16 | (ND) | (ND) |
| | | | (ND): Not Detectable | | | | | |

**Table 2. Low-Resolution GC-MS Results (lipid weight in ppt)**

| | Congener | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Sample ID** | **BDE-28** | **BDE-47** | **BDE-66** | **BDE-100** | **BDE-153** | **BDE-154** | **BDE-160** | **BDE-183** |
| EL1-2 | 5257.7 | 34051.5 | (BC) | 3907.2 | 1907.2 | (ND) | (ND) | 556.7 |
| EL1-3 | 2156.3 | 34262.5 | 12.5 | 4925.0 | 12887.5 | 825.0 | 0.0 | (BC) |
| EL1-4 | 1210.9 | 5732.4 | (ND) | 390.0 | 1047.6 | (ND) | (ND) | (BC) |
| EL1-5 | 921.9 | 6126.4 | (ND) | 297.4 | 1223.0 | (ND) | 356.9 | (BC) |
| EL1-6 | 2876.3 | 23793.8 | (ND) | 5422.7 | 9366.0 | (ND) | 278.4 | (BC) |
| EL1-7 | (ND) | 10815.7 | (ND) | 543.8 | 21625.4 | (ND) | 12954.7 | 13353.5 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| EL1-8 | 1198.9 | 8698.9 | (ND) | 1505.4 | 3241.9 | 2924.7 | 43.0 | (BC) |
| EL1-9 | 505.7 | 4170.5 | (ND) | 108.0 | 2375.0 | 306.8 | 125.0 | (BC) |
| EL1-10 | 1295.3 | 19899.3 | 389.3 | 4745.0 | 6691.3 | 463.1 | 5396.0 | 13966.4 |
| EL1-11 | 1390.6 | 12161.5 | (ND) | 130.2 | 458.3 | (ND) | 239.6 | (BC) |
| EL1-12 | 833.7 | 23770.0 | (ND) | 2299.8 | 2689.9 | (ND) | 6349.1 | 9310.1 |
| (ND): Not Detectable (BC): below calibration | | | | | | | | |

Results of HRGC-MS and LRGC-MS analysis are comparable (Figure 1). While there are many advantages in using a HRGC-MS such as increased detection limits, the ability to detect higher brominated congeners, and increased sensitivity, the cost of such a machine is often too great for smaller laboratories. A more affordable LRGC-MS produces results that are similar to HRGC-MSs at a fraction of the price.

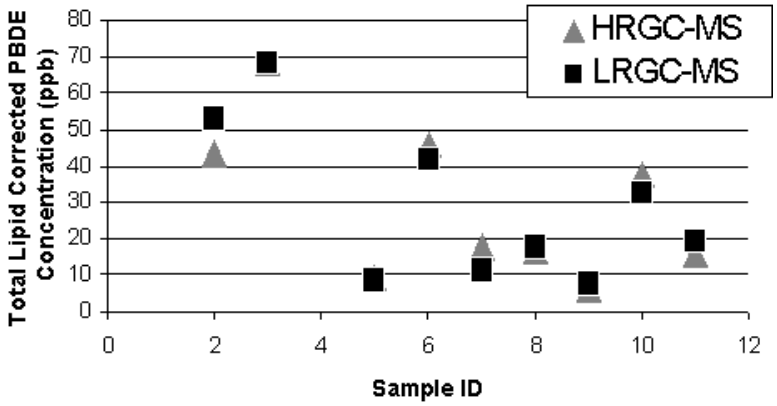


**Figure 1. Comparison of HRGC-MS and LRGC-MS results**

The current levels of PBDEs do not represent a known health risk, however, the temporal trend of PBDEs in the environment and biota is alarming. Ikonomou et al.[8] suggest that PBDEs may become the most prevalent organohalogen contaminant by 2050, assuming concentrations of PBDEs continues to rise at their current rate. The ubiquity of PBDEs in the arctic and sub-arctic regions suggests that a monitoring program should be developed and implemented. Also, the collection and analysis of human milk samples and blood plasma from various regions in the arctic and sub-arctic over time will help determine whether PBDE congeners are increasing in those areas compared to other regions. The need for monitoring in arctic and sub-arctic regions is particularly important because these areas may become sinks for PBDEs, as has happened with other POPS. The results of this report illustrates the importance for monitoring of PBDEs in humans, especially in arctic and sub-arctic areas, and the need for further investigation relating to possible health effects as a consequence of PBDE exposure.

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