Dietary Exposure As A Source of Perfluorinated Compounds For Canadians

Sheryl Tittlemier[1], Karen Pepper[1], Cathie Menard[1], John Moisey[1]

[1]Food Research Division, Health Canada

Introduction

The routes of human exposure to perfluorinated compounds, such as PFOS and PFOA, have not been well-characterized. Since these compounds are used in a wide variety of industrial and consumer applications, there is the opportunity of exposure to perfluorinated compounds from a large number of different sources. Likely exposure routes include inhalation and food consumption. A number of perfluorinated compounds have been measured in air[1;2] and household dust.[3] Precursors to PFOS have also been measured in food samples.[4]

The presence of perfluorinated compounds in foods can occur by different processes. Foods can become contaminated with perfluorinated compounds during contact with perfluoroalkyl-containing coatings on food packaging (eg. N-ethyl perfluorooctanesulfonamide phosphates). Foods, especially animal-derived items such as fish, can also become contaminated with perfluorinated compounds during environmental exposure.

Three perfluorooctanesulfonamides [N-EtPFOSA, PFOSA, and N,N-diethyl perfluorooctanesulfonamide (N,N-Et_2PFOSA)] and a suite of perfluorosulfonates and perfluorocarboxylates (Table 1) were measured in selected archived food composites collected for the Canadian Total Diet Study to investigate the degree to which Canadians are exposed to perfluorinated compounds via food consumption.

Materials and Methods:

Samples. The Canadian Total Diet Study samples all foods that comprise greater than 1% of the average Canadian's diet. Over a five week period each year, various food items are purchased from four different grocery stores and fast food restaurants in a selected Canadian city. Foods are prepared as for consumption, and replicate food items from the various grocery stores or restaurants are combined and homogenized to form a composite sample. The composites listed in Table 2 were analyzed for a suite of perfluorosulfonates (PFSs) and perfluorocarboxylates (PFCAs) after analysis of perfluorooctanesulfonamides (PFOSAs) revealed these samples as the containing the highest amounts of PFOSAs.

Analytical method. PFOSAs were analysed using a solvent extraction and column chromatographic clean-up followed by analysis using gas chromatography positive chemical ionization mass spectrometry[5].

After spiking with recovery internal standard (perfluoro-3,7-dimethyloctanoic acid, $PFMe_2OA$; SynQuest Labs, Alachua, FL), PFSs and PFCAs were extracted from 2g of homogenized composite sample with 4 mL of methanol following the method of Tomy et al.[6] The mixtures were centrifuged (10 min at 3600 x *g*) to obtain supernatant. The extraction was repeated twice more with 2 mL volumes of methanol, and the supernatants were combined and reduced in volume at 37^{o}C to 2.5 mL using N_2. A 250 mL aliquot was taken and combined with 240 mL of purified water [Milli-Q water (Millipore, Billerica, MA) passed through a glass column containing Amberlite XAD-7 resin (Aldrich, Oakville, ON) to remove any possible perfluorinated contaminants] to make the solvent approximately 1:1 (v/v) methanol/water. Instrument performance standard was added (10 mL, $^{13}C_2$-perfluorooctanoic acid; Perkin Elmer, Boston, MA; $^{13}C_2$-perfluorodecanoic acid; Wellington Laboratories, Guelph, ON), and the final solution was centrifuged at 14 000 x *g* for 10 min. A portion of the final solution was transferred to a polypropylene autosampler vial prior to injection on the LC-MS/MS.

PFSs and PFCAs were analyzed using LC-MS/MS in the negative electrospray mode. Analysis was performed according to Tittlemier et al.[7] with the addition of transitions for the two mass-labeled instrument performance

standards (m/z 415→369.8 $^{13}C_2$-PFOA; m/z 515→469 $^{13}C_2$-PFDA) and minor modifications to the HPLC gradient program. In addition, an interference was observed in the m/z 499→80 PFOS transition with the "chicken nuggets" matrix, thus the m/z 499→99 transition was used for quantitation. No other interferences were observed for the other analytes and matrices.

Results and Discussion

Analytical considerations - recoveries. To evaluate the newly developed methanol extraction method, recoveries and matrix effects were examined. Replicates of chicken burger (n=3) and organ meat (n=3) composites were fortified with PFCAs, PFSs, and $PFMe_2OA$ at 10 ng/g extracted, and compared to post-extraction fortified chicken burger and organ meat extracts. Average recoveries (± standard deviation, n=3) were 93 ± 24%, 81 ± 8%, and 94 ± 4% for PFCAs, PFSs, and $PFMe_2OA$, respectively. Individual PFCA and PFS recoveries were not significantly different from the recovery of $PFMe_2OA$, suggesting that this compound would act as a suitable recovery internal standard for these analytes. Method detection (MDL) and quantitation limits (MQL) were estimated on a sample-specific basis as the lowest concentration of analyte in a sample that would produce a signal three and ten times greater than surrounding baseline noise, respectively. The MQL ranged from approximately 0.3 – 0.8 ng/g for PFOS and PFHpA through PFTeDA; MQLs for PFBS and PFHxA were about 1.8 and 1.6 ng/g, respectively.

Analytical considerations – matrix effects. Two mass-labelled instrument performance standards were used to try to account for matrix effects on analyte ionization, since it was not feasible to prepare matrix-matched standard calibration curves for all 9 different matrices. The ratios of slopes from organ meat matrix-matched and solvent standard calibration curves for each analyte were similar amongst the two $^{13}C_2$-labelled PFCAs, PFSs, and all PFCAs except for perfluorododecanoate and perfluorotetradecanoate. Aside from these two exceptions, all perfluorinated compounds experienced signal enhancement from co-extracted materials. The similarities in slope ratios suggest that normalization of responses to those of $^{13}C_2$-PFOA and $^{13}C_2$-PFDA can account for co-extracted signal enhancement of most perfluorinated analytes.

Concentrations of PFOSAs, PFSs, and PFCAs in Total Diet Study composites. Wet weight concentrations of perfluorinated compounds measured in the composites are given in Table 1. No PFCs were detected above the MDLs in any of the blanks. Average percent recoveries of the recovery internal standards were 95 ± 24% (n = 22), and 71 ± 8% (n = 19) for $PFMe_2OA$ and N-Et-d_5-PFOSA, respectively.

Within this selection of composite samples, PFOSAs were detected the most frequently, and at the highest concentrations. **Σ**PFOSA concentrations were always greater than **Σ**PFS and **Σ**PFCA. N-EtPFOSA and N,N-Et_2PFOSA were the most abundant of the PFOSA compounds, and were generally observed in the low ng/g range. PFSs and PFCAs were detected above the MDL in 11 out of the 21 samples, but only above the MQL in 3 of the samples. PFHpA (3/21 samples), PFOA (2/21), PFOS (1/21), and PFTeDA (1/21) were detected the most frequently above the MQL in the low ng/g range. PFNA was also detected, but was below the MQL.

The presence of a variety of PFCs in Canadian Total Diet Study composites indicates that food is one source of these compounds for the Canadian population. However, since only a small number of various foods have been analyzed up to this point, the relative significance of diet as a source of PFCs compared to other possible sources such as air[1;2], dust[3], and drinking water[8] is unclear.

Acknowledgement

This work was partially supported by the Strategic Science Fund, Office of the Chief Scientist, Health Canada.

Reference List

1. Martin JW; Muir DCG; Moody CA; Ellis DA; Kwan WC; Solomon K; Mabury SA. *Anal.Chem.* **2002,** *74*, 584-90.

2. Shoeib M; Harner T; Ikonomou M; Kannan K. *Environ Sci Technol.* **2004,** *38*, 1313-20.

3. Moriwaki H; Takata Y; Arakawa R *J Environ Monitor.* **2003,** *5*, 753-57.

4. Tittlemier SA; Edwards L; Pepper K. *Org.Comp.* **2003,** *62*, 315-18.

5. Tittlemier SA; Pepper K; Edwards L; Tomy G. *J Chromatogr.A* **2005,** *1066*, 189-95.

6. Tomy G; Halldorson T; Tittlemier SA. 2005.

7. Tittlemier SA; Ryan JJ; Van Oostdam J. *Org.Comp.* **2004,** *64*, 4009-14.

8. Harada K; Saito N; Sasaki K; Inoue K; Koizumi A. *Bull Environ Contam Toxicol* **2003,** *71*, 31-36.

Table 1. Results of Total Diet Study composite analyses for total PFOSAs, PFCAs, and PFSs (ng/g wet weight).

Composite	Year	ΣPFOSAs	ΣPFSs	ΣPFCAs
microwave popcorn	1999	15.3	0.98	6.7
pizza	1993, 1994, 1998, 1999, 2001	0.847 – 13.9	nd[a] – trace[b] (0.25)	nd – 2.7
french fries	1992, 1993, 1994, 1998, 1999, 2001	1.60 – 12.4	nd - trace (0.21)	nd – trace (0.32)
egg breakfast	1998, 1999	nd – 11.8	nd	trace (0.33) – trace (0.87)
chicken burger	1999	0.097	nd	nd
wieners and sausages	2004	1.50	trace (0.24)	nd
hamburger	1992, 1994	0.791 – 1.32	nd	nd – trace (0.25)
fish burger	1999, 2000	1.24	nd	nd – trace (1.03)
luncheon meats, cold cuts	2004	0.923	trace (0.49)	trace (0.85)

[a]not detected above the method detection limit

[b]detected above method detection limit, but below method quantitation limit