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Concentrations of Perfluorooctanesulfonamides in Canadian Total Diet Study Composite Food Samples Collected between 1992 and 2004

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Canadian Total Diet Study composite samples collected from 1992 to 2004 ($n = 151$) were analyzed for a series of perfluorooctanesulfonamides that are likely breakdown products or manufacturing residuals associated with perfluorooctylsulfonyl phosphate esters. These esters have been incorporated into coatings for paper and paperboard used in food packaging. *N*-Ethylperfluorooctanesulfonamide (*N*-EtPFOSA), perfluorooctanesulfonamide, *N*,*N*-diethylperfluorooctanesulfonamide, *N*-methylperfluorooctanesulfonamide, and *N*,*N*-dimethylperfluorooctanesulfonamide were extracted using solvent extraction and quantified by gas chromatography−mass spectrometry. Perfluorooctanesulfonamides were detected in the picograms per gram to low nanograms per gram of wet weight range in all food groups tested—baked goods and candy, dairy, eggs, fast food, fish, meat, and foods to be prepared in packaging. The highest concentrations of total perfluorooctanesulfonamides were observed in fast food composites (from less than the method detection limit to 27300 pg/g of wet weight). Concentrations of *N*-EtPFOSA appeared to decrease over the sampling period (1992−2004) in French fries and other fast food composites; no such trend was apparent in freshwater fish, marine fish, and shellfish composites. A basic estimate of dietary exposure to perfluorooctanesulfonamides suggests that Canadians (>12 years old) are exposed to approximately 73 ng/person/day from these foods.

KEYWORDS: Food packaging; perfluorinated; dietary intake; human exposure

INTRODUCTION

Recent work has described levels of perfluorooctyl compounds, an emerging class of persistent organohalogen contaminants, in human sera and liver (*1*−*3*). These compounds—including perfluorooctanesulfonate ($C_8F_{17}SO_3^-$, PFOS), perfluorooctanoate ($C_8F_{17}CO_2^-$, PFOA), and perfluorooctanesulfonamide ($C_8F_{17}SO_2NH_2$, PFOSA)—were all used as surfactants in a wide variety of industrial and commercial applications, including fire-fighting foams, cleaning products, and water- and oil-repellent coatings for fabrics and paper (*4*). The perfluorinated compounds have been detected in tissues from children (*5*) and from both nonexposed and occupationally exposed adults in North America (*3*, *6*).

The ubiquitous presence of these perfluorooctyl compounds in the North American populace and biota sampled from locations around the world (*7*) led one of the primary manufacturers of fluorinated chemicals in North America to announce a cease in production of perfluorooctanesulfonyl compounds in 2000 (*8*). It was projected that from 2000 to 2002, the production of $C_8F_{17}SO_2$-containing compounds for U.S. Food and Drug Administration-approved uses would decrease from 1 520 000 to 0 kg.

The widespread occurrence of perfluorooctyl and perfluorooctanesulfonyl compounds in children and adults in North American suggests exposure is due to a source common to all age groups. The wide variety of industrial and consumer applications leads to numerous possibilities for the compounds' release into the environment and subsequent exposure to humans via environmental routes. However, there are also more direct routes, such as dietary exposure, by which humans may be exposed to perfluorinated compounds, particularly because perfluorinated compounds are used in food-packaging coatings (*4*). Substances containing perfluoroalkyl moieties have been approved or allowed for use as components of coated or uncoated food-contact surfaces of paper and paperboards for aqueous and fatty foods in the United States and Canada (*9*).

Some formulations that were used to form grease- and water-repellent coatings for paper and paperboard used in food packaging are mixtures of perfluorooctylsulfonyl phosphate esters (**Figure 1**). Perfluorooctylsulfonyl compounds may be present as manufacturing residuals in the coatings and migrate into the food upon contact. Laboratory studies also indicate that some perfluorooctylsulfonyl compounds can be metabolized to PFOS (*10*, *11*).

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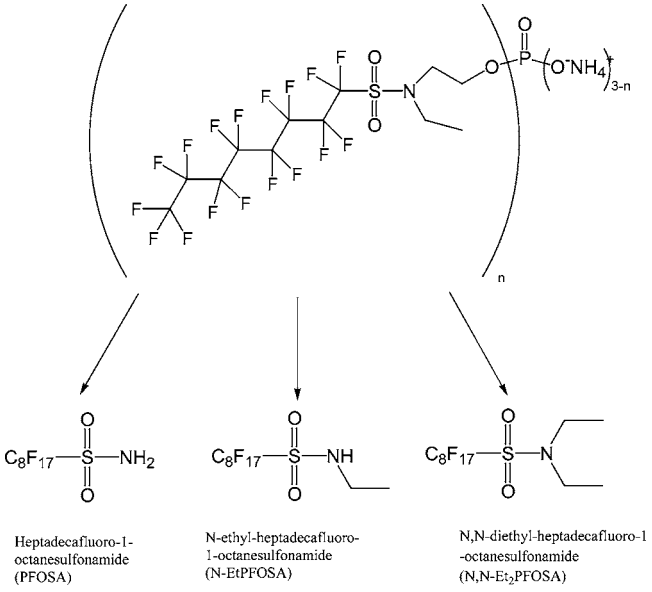

Figure 1. Structure of a fluoroalkyl phosphate ester used as a water and oil repellent in paper and paperboard food packaging and its possible manufacturing residuals or breakdown compounds.

The objectives of this study were to measure the concentrations of *N*-ethylperfluorooctanesulfonamide (*N*-EtPFOSA), perfluorooctanesulfonamide (PFOSA), *N*,*N*-diethylperfluorooctanesulfonamide (*N*,*N*-Et_2PFOSA), *N*-methylperfluorooctanesulfonamide (*N*-MePFOSA), and *N*,*N*-dimethylperfluorooctanesulfonamide (*N*,*N*-Me_2PFOSA) in food composites collected over 12 years (1992−2004) through the Canadian Total Diet Study and to estimate dietary exposure of Canadians over 12 years of age.

MATERIALS AND METHODS

Samples. The Canadian Total Diet Study is a market basket survey that samples foods comprising >1% of the average Canadian's diet (*12*). Over a 5-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 or kept in their original packaging. Replicate food items from the various grocery stores or restaurants are then combined and homogenized to form a composite sample. Composite samples are stored in chemically cleaned glass jars or polypropylene containers at −20 °C until analysis.

Individual composites (151 in total) from the 1992−2004 Total Diet Studies were analyzed for perfluorooctylsulfonyl compounds. The individual samples analyzed represented 43 unique foods (e.g., hamburger, whole milk, etc.; Supporting Information Table 1).

Chemicals. *N*-EtPFOSA (96%) was purchased from Interchim (Montluçon, France). PFOSA (>95%) was provided by Griffin LLC (Valdosta, GA). *N*,*N*-Et_2PFOSA was synthesized as described in Tittlemier et al. (*13*). *N*-MePFOSA (>98%), *N*-methyl-d_3-perfluorooctanesulfonamide (*N*-Me-d_3-PFOSA, >98% chemical and ≥98% isotopic purity), *N*,*N*-Me_2PFOSA (>98%), and *N*-ethyl-d_5-perfluorooctanesulfonamide (*N*-Et-d_5-PFOSA, >98% chemical and ≥98% isotopic purity) were obtained from Wellington Laboratories (Guelph, ON, Canada). Methyl perfluorotetradecanoate (MePFTeD, 95%) and methyl perfluorodecanoate (MePFD, 98%) were purchased from SynQuest Laboratories (Alachua, FL).

Sample Extraction and Analysis. Samples were extracted and analyzed according to the method outlined in Tittlemier et al. (*13*). Briefly, a known amount of composite (generally about 10 g, but lower amounts were used for some dairy composites) was spiked with a recovery internal standard solution. Mass-labeled standards became available after a third of the samples had already been analyzed; thus, two different recovery internal standards (MePFTeD and *N*-Et-d_5-PFOSA) were used. Composites were extracted with 2 volumes of 2:1 (v/v) hexane/acetone using a mechanical homogenizer. Lipid content was determined via gravimetric analysis, and lipids were subsequently removed from the extracts by washing with concentrated sulfuric acid. The organic layer was reduced in volume and passed through a silica gel column containing 8 g of 40% acidified and 4 g of neutral silica gel using dichloromethane as an eluant. Performance internal standard (MePFD or *N*-Me-d_3-PFOSA) was added after the eluate was reduced in volume using a rotary evaporator. A sample containing Milli-Q-purified water was run through the method as a blank concurrently with each of the 15 sets of composites analyzed.

Samples were analyzed by gas chromatography−positive chemical ionization−mass spectrometry using an Agilent 5973N mass spectrometer coupled to a 6890 GC (Palo Alto, CA) fitted with a retention gap (1 m × 0.530 mm i.d., deactivated fused silica) and a DB-1701 (30 m × 0.25 mm i.d., 0.250 μm film thickness; Agilent) column. Methane (99.97%) was used as the reagent gas. The selected ion monitoring mode was used to monitor M^+ and $[M + H]^+$ ions of all fluorinated compounds. Quantitation was performed using the quasimolecular $[M + H]^+$ as target ions.

Data Analysis. Calibration curves constructed using relative responses of analytes in external standards prepared in isooctane were used to calculate concentrations of analytes in samples. Relative responses were calculated as the ratio of peak area of analyte to peak area of performance internal standard. Statistical analyses were performed using SigmaStat version 2.03 (SPSS Inc., Chicago, IL).

Dietary Exposure Estimate. Dietary exposure to perfluorooctanesulfonamides was estimated using the concentration data generated by this study and available food intake data (*12*). The Canadian Total Diet Study composites comprise foods ready for consumption; items are cleaned, otherwise prepared, and cooked prior to homogenization and compositing. Thus, the composites are representative of foods actually being consumed, and contaminant concentration data derived from these composites are more useful in estimating dietary exposure than data from unprepared and raw food items.

Because there was a variation over the sampling years of the composites analyzed for perfluorooctanesulfonamides, median concentrations from all available data were used in the dietary exposure estimate. It should be noted that this approach could over- or underestimate the current dietary intake of perfluorooctanesulfonamides if concentrations in food have been changing over time. In determining the average concentration, concentrations of zero were assigned to composites that were not analyzed and for instances when analyte was not detected above the detection limit.

RESULTS

Concentrations of Perfluorooctanesulfonamides in Total Diet Study Composites. Average blank and recovery corrected concentrations are given in **Table 1**. Individual data for the 151 composites are provided in Supporting Information Tables 1 and 2. Average percent recoveries (± standard deviation) of the two recovery internal standards were 73 ± 10% (n = 97) and 68 ± 8% (n = 54) for *N*-Et-d_5-PFOSA and MePFD, respectively. Only *N*-MePFOSA and *N*-EtPFOSA were detected in blanks. Average concentrations (for a 10 g blank sample) over the 15 sample sets were 31 ± 30 and 108 ± 72 pg/g for *N*-MePFOSA and *N*-EtPFOSA, respectively. The first four sets contained two blanks per set; concentrations in blanks from the same sets differed from each other by <25%. The amounts of *N*-MePFOSA and *N*-EtPFOSA detected in a blank were subtracted from the amount in composites extracted and analyzed concurrently in the same set.

Because the study spanned approximately 1 year, detection limits were estimated using instrument response and blank data from each set to describe the method sensitivity at the time a specific set of samples was analyzed. Detection limits for each set were estimated as twice the concentration of analyte detected in the blank (*N*-MePFOSA and *N*-EtPFOSA) or the concentration required to produce a signal >3 times the signal-to-noise

Table 1. Blank and Recovery Corrected Concentrations (Picograms per Gram of Wet Weight) of Various Perfluorooctanesulfonamides in Canadian Total Diet Study Composites (Grouped According to Food Type)

food type		*N*,*N*-Me_2PFOSA	*N*,*N*-Et_2PFOSA	*N*-MePFOSA	*N*-EtPFOSA	PFOSA
baked goods and candy	no. of positives/*n*[a]	0/11[b]	6/31	3/11	8/31	4/31
	av concn		98[c]	13	89	196
	range		nd[d]–1650	nd–62	nd–1240	nd–3070
dairy	no. of positives/*n*	0/2	0/10	1/2	2/10	0/10
	av concn			68	31	
	range			nd–135	nd–290	
eggs	no. of positives/*n*	na[e]	0/3	na	1/3	2/3
	av concn				150	260
	range				nd–450	nd–660
fast food	no. of positives/*n*	1/29	11/45	14/29	31/59	9/59
	av concn	3	340	30	1230	193
	range	nd–82	nd–3200	nd–250	nd–22600	nd–2540
fish and seafood	no. of positives/*n*	0/3	1/22	1/3	20/22	3/22
	av concn		29	16	110	74
	range		nd–645	nd–48	nd–590	nd–830
meat	no. of positives/*n*	0/5	2/15	5/5	8/15	4/15
	av concn		11	84	59	216
	range		nd–86	56–104	nd–414	nd–1490
foods to be prepared in packaging	no. of positives/*n*	0/1	2/11	1/1	8/11	1/11
	av concn		1660	258	1520	69
	range		nd–9860		nd–10500	nd–754

[a] *n* = number of composites analyzed. [b] Not all composites were analyzed for *N*,*N*-Me_2PFOSA and *N*-MePFOSA; these samples were analyzed prior to expansion of the method. [c] Averages were calculated by setting nondetects = 0. [d] nd = not detected. [e] na = not analyzed.

ratio for analytes that were not observed in blanks. Detection limits over the 15 sample sets analyzed averaged 25 (*N*,*N*-Me_2-PFOSA), 360 (*N*,*N*-Et_2PFOSA), 45 (*N*-MePFOSA), 160 (*N*-EtPFOSA), and 700 pg/g (PFOSA), but could vary among sample sets by as much as a factor of 26 due to variation in the mass of sample analyzed and blank or noise data from each specific sample set or sample.

The most frequently detected analyte was *N*-EtPFOSA, found in 78 of 151 composites, followed by *N*-MePFOSA (in 25 of 51) and *N*,*N*-Et_2PFOSA (in 22 of 137). Concentrations of *N*-EtPFOSA, *N*,*N*-Et_2PFOSA, and PFOSA were positively correlated (Spearman rank order correlation, $p < 0.032$).

The highest concentrations and frequency of detection of analytes occurred in the fast food composites, particularly French fries, egg breakfast sandwiches, and pizza. All food items that made up the fast food composites were prepared at commercial fast food outlets. They were not items available at grocery stores or markets for preparation by consumers in their homes. Maximum concentrations of total perfluorooctanesulfonamides analyzed (ΣPFOSAs) in fast foods ranged from 9720 pg/g for French fries to 27300 pg/g for pizza. Relatively high concentrations of individual analytes (i.e., ng/g levels) were also detected in cookies, Danish pastries, microwave popcorn, and wieners.

Dietary Exposure Estimate. The median dietary intake of ΣPFOSAs for Canadian teenagers and adults (>12 years old) was estimated to be 73 ng/person/day. Median intake estimates broken down by sex groups are listed in **Table 4**, along with the 10th and 90th percentile estimates.

DISCUSSION

Sources of Perfluorooctanesulfonamides in Food. There are various routes by which perfluorooctanesulfonamides can enter food. One possibility is exposure of food-producing animals or plants to these compounds via environmental routes, such as inhalation or adsorption from air or intake of contaminated water or food. Perfluorooctanesulfonamides have been detected in air (*14*−*16*) and water (*17*). They have also been detected in organisms of various food webs (*18*, *19*), although the bioaccumulation and biomagnification potential of all perfluorooctanesulfonamides has not been well characterized yet.

Another probable route of perfluorooctanesulfonamide entry into food is via transfer from items involved in food preparation and storage, particularly food packaging. Perfluorinated compounds have been incorporated into coatings used on paper products for food packaging to render packaging oil resistant. Fluoroalkyl compounds are often present in these paper products in the tens of milligrams per gram of dry weight of fiber range (*4*, *20*). Any small molecular weight manufacturing residuals, or breakdown products of the larger fluoroalkyl compounds such as perfluorosulfonamides, could potentially migrate from the coated packaging into the food contained within.

Data generated during this study suggest that migration from food packaging occurred. The *N*-ethyl compounds (*N*-EtPFOSA and *N*,*N*-Et_2PFOSA), which were incorporated into products primarily used for paper products (*21*), were detected at the highest concentrations in the food composites, up to 22600 pg/g. Concentrations of *N*-EtPFOSA and *N*,*N*-Et_2PFOSA were also significantly correlated (correlation coefficient = 0.562), suggesting a common source. The analogous *N*-methyl compounds, which were primarily used for fabric coatings, including carpeting (*21*), were observed at much lower concentrations (maximum observed concentration was 258 pg/g). This difference in concentration may be indicative of the use patterns of the *N*-ethyl and *N*-methyl compounds.

In addition, the highest concentrations of ΣPFOSAs were all found in foods with relatively high fat contents (>5% extractable lipid content by weight). The 10 highest ΣPFOSAs concentrations were all observed in composites of fast food and foods to be prepared in packaging (**Table 2**). These are all foods that are stored in oil-resistant packaging; thus, there is the opportunity for these foods to be in contact with perfluorooctyl sulfonyl-treated material.

Temporal Trends of *N*-EtPFOSA in Composites. There were eight different foods analyzed for which composites representing at least six different years were available. The

Table 2. Top 10 Composites Containing the Highest Concentrations (Picograms per Gram of Wet Weight) of Perfluorooctanesulfonamides

composite	year	ΣPFOSAs	% lipid
pizza	1998	27300	11
microwave popcorn	1998	18900	21
microwave popcorn	1999	15300	30
egg breakfast sandwich	1998	11900	8.6
French fries	1992	9720	14
French fries	1994	8330	16
French fries	1993	6730	19
chicken nuggets	1999	5870	9.3
French fries	1999	4110	13
fish burger	1998	3820	4.5

Table 3. Changing Concentrations of *N*-EtPFOSA (Picograms per Gram of Wet Weight) in Total Diet Study Composites Sampled over Various Years[a]

year	chicken burger	chicken nuggets	French fries	wiener	pizza	fish, fresh-water	fish, marine	shrimp
1992			6700		0[b]			
1993			6730		3190	70	34	168
1994			8330		576		43	173
1995						135[c]	77[c]	0[c]
1998	106	1660	1390	148	22600	204	107	139
1999	98	4920	1160	0	192			
2000	0	382	280	79	138		0	
2001	83	571	586	0	0	70	61	62
2002	69	69	0	77	109	144		
2003	0	0	0	0	0	82		49
2004	0	0	0	0	0			

[a] Blank cells indicate composite was not analyzed for that particular year. [b] Values of 0 indicate that *N*-EtPFOSA was not detected above the MDL. [c] Average of concentrations detected in summer and winter samples.

Table 4. Dietary Exposure Estimates (Nanograms per Person per Day) for Canadian Teenagers and Adults by Age and Sex Groupings

group (age, years)	median	10th percentile	90th percentile
female (12–19)	81	12	420
female (20–39)	68	12	310
female (40–64)	44	9	200
female (>65)	29	8	150
male (12–19)	120	16	610
male (20–39)	120	18	580
male (40–64)	76	14	360
male (>65)	41	10	220

results detailing concentrations of *N*-EtPFOSA, the most frequently detected analyte, are presented in **Table 3**. Concentrations of *N*-EtPFOSA appear to be decreasing for all of the fast foods. There is no apparent trend for *N*-EtPFOSA concentrations in shrimp, freshwater fish, or marine fish.

The decrease in fast food *N*-EtPFOSA concentrations was not an artifact of desiccation of older composites during long-term storage. Moisture content was determined in triplicate from thawed and homogenized composites. Aliquots were dried on preweighed aluminum pans in an oven at 75 °C for 5 days, until a constant mass had been reached. The average moisture content of the French fry composites was calculated for each year from the three aliquots. The average moisture content of the French fry composites collected from 1992 to 2004 did not differ significantly with time (ANOVA, $p > 0.05$; data not shown). Because the other fast food composites had been stored in a manner similar to that used for the French fries, it is unlikely that there was any inconsistent drying of these composites while stored in the freezers either.

The decrease in concentrations of *N*-EtPFOSA in fast foods is likely due in part to the cessation in production of perfluorooctyl sulfonyl compounds that began in 2000 (*8*). *N*-EtPFOSA was not detected in any of the fast food samples collected after the final phase-out of production in 2002, suggesting that the cessation in production resulted in a decrease in the use of perfluorooctyl sulfonyl compounds in food packaging (**Table 3**). The presence of *N*-EtPFOSA in a few composites collected after 2002 (e.g., Danish 2004, ΣPFOSAs = 2210 pg/g) may be attributed to the use of stockpiled paper/paperboard coating or packaging materials purchased prior to the phase-out of perfluorooctyl sulfonyl production. This trend also supports the hypothesis that the detection of perfluorooctyl sulfonyl in fast foods was likely a result of migration from the packaging used to store the foods.

It is more difficult to discern trends of *N*-EtPFOSA concentrations in shrimp, freshwater fish, and marine fish because fewer composites collected after 2002 have been analyzed. However, a lack of apparent decrease in concentration may indicate exposure of fish and shrimp via environmental routes, as opposed to via food packaging. Fish and shrimp items forming the Total Diet Study composites were mainly packaged on polystyrene trays and plastic cling wrap or in polyethylene bags, rather than paper, which may have been treated. *N*-EtPFOSA and PFOSA, a metabolite of *N*-EtPFOSA (*10*, *11*), have been detected in aquatic organisms including fish (*19*, *22*, *23*).

Dietary Exposure to Perfluorooctanesulfonamides. The median dietary intakes of ΣPFOSAs for Canadian male and female teenagers and adults (>12 years old) were estimated to be 90 and 55 ng/person/day, respectively. Shoeib et al. estimated the median exposure of adults to the predominant perfluorooctyl sulfonyl compounds in indoor air and dust (*N*-methyl- and *N*-ethyl perfluorooctane sulfonamidoethanol) to be 20 ng/person/day via dust ingestion and 40 ng/person/day via inhalation (*16*). Concentrations of *N*-EtPFOSA were about 15−30 times lower than those of the two sulfonamidoethanols measured, and *N*-EtPFOSA was not detected above the method detection limit in dust. The combined estimate for exposure to perfluorooctylsulfonyl compounds via indoor dust and air is of the same order of magnitude as the dietary exposure estimates, suggesting that food may be an important route of exposure to this family of compounds.

Conclusions. The results of this study demonstrate that Canadians have been exposed to perfluorooctanesulfonamides in foods. Because perfluorooctanesulfonamides can be biotransformed to the more persistent perfluorooctanesulfonate (*10*, *11*), it is very likely that dietary exposure to perfluorooctanesulfonamides has also been an indirect route of exposure of Canadians to perfluorooctanesulfonate. The most significant dietary sources of perfluorooctanesulfonamides were foods that were packaged in paper products that were often treated with perfluoroalkyl compounds for oil resistance, such as French fries and pizza. A basic estimate of dietary exposure of Canadians to these compounds suggests that this route has been an important source of perfluorooctanesulfonamides. However, as concentrations in certain foods decrease with time, dietary exposure to perfluorooctanesulfonamides may become less significant.

Supporting Information Available: Canadian Total Diet Study composite samples analyzed for perfluorooctanesulfonamides and the sample-specific concentrations found. This material is available free of charge via the Internet at http://pubs.acs.org.

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