CONCENTRATIONS OF PERFLUORINATED CARBOXYLATES AND RELATED COMPOUNDS IN CANADIAN TOTAL DIET STUDY FOOD COMPOSITES AND FOOD PACKAGING

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Introduction

The routes of human exposure to perfluorinated compounds 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 and water consumption. A number of perfluorinated compounds have been measured in air[1,2] and household dust.[3] Perfluorinated compounds 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.

A suite of perfluorosulfonates, perfluorocarboxylates, and unsaturated fluorotelomer carboxylates were measured in selected archived food composites and food packaging collected for the Canadian Total Diet Study to investigate the degree to which Canadians are exposed to these perfluorinated compounds via food consumption.

Materials and Methods

Samples. Twenty-seven composite samples from the 2004 Canadian Total Diet Study (TDS) were analyzed for a suite of conjugate bases of perfluorinated acids (PFAs), including perfluorosulfonates (PFSs), perfluorocarboxylates (PFCAs), and unsaturated fluorotelomer carboxylates (FTUAs). Over a five week period in 2004, various food items were purchased from four different grocery stores and fast food restaurants in Winnipeg, Manitoba. Foods were prepared as for consumption, and replicate food items from the various grocery stores or restaurants were combined and homogenized to form a composite sample. The composites analyzed are listed in Table 1. Samples of food packaging (Table 2) from fast food items collected as part of the TDS were also analyzed.

Analytical method. PFAs were extracted and analyzed according to the method outlined in Tittlemier et al.[5] Briefly, after spiking with recovery internal standard, PFAs were extracted from homogenized composite sample with methanol and centrifuged to obtain supernatant. For food packaging samples, 3 cm^2 subsamples of packaging from each of the four restaurants visited were combined into a composite sample and extracted. The extraction was repeated twice more, and the supernatants were combined and reduced in volume using N_2. An aliquot was taken and combined with an equal volume of purified water to make the solvent 1:1 (v/v) methanol/water. Instrument performance standards were added ($^{13}C_2$-perfluorooctanoic acid; Perkin Elmer, Boston, MA; $^{13}C_2$-perfluorononanoic acid, $^{13}C_2$-perfluorodecanoic acid, and $^{13}C_4$-perfluorooctanesulfonic acid; Wellington Laboratories, Guelph, ON), and the final solution was centrifuged. A portion of the final solution was transferred to a polypropylene autosampler vial prior to injection on the LC-MS/MS. Analyses were performed in the negative electrospray mode according to Tittlemier et al.[6] with some modifications. Confirmatory transitions were added for all native analytes (aside from PFHxA, 6:2 FTUA, and PFHpA), single transitions were added for the two new mass-labeled instrument performance standards ($^{13}C_2$-PFNA; $^{13}C_4$-

PFOS), and transitions were separated into 3 chromatographic windows in the multiple reaction monitoring program.

Results and Discussion

PFAs in TDS composites. PFAs were detected in 5 out of 29 composites analyzed. Average recovery (± standard deviation) of the recovery internal standard was 103 ± 22%. PFAs were identified and quantified if the signal to noise ratio was greater than 3, the correct primary and secondary transitions were recorded, and the retention time matched that of the analogous mass-labelled standard. PFOS was detected the most frequently (4/29 composites). PFNA and PFOA were the only other analytes to be detected in the TDS composites. Concentrations of the detected PFAs were in the low ng/g range – PFOA (2.6 ng/g), PFNA (4.5 ng/g), PFOS (2.0-2.7 ng/g). Average detection limits (estimated as the concentration required to produce a signal 3 times greater than the standard deviation of the noise) for the TDS composites ranged from 0.4 ng/g for PFHpA to 3.5 ng/g for PFTeDA.

PFAs in fast food packaging composites. PFAs were detected in all fast food packaging composites analyzed. All samples contained at least 50% of the analytes. For analytes that did not have mass-labelled standards available, sample extracts were fortified with native analyte to confirm peak identity after quantitation. The perfluorocarboxylates with perfluoroalkyl chain length of C_9 and shorter, along with PFOS, were detected in all 6 fast food packing composites. PFOA and PFHpA were the individual analytes detected at the highest concentrations, ranging from 25 to 3490 ng/g and 8.3 to 2240 ng/g, respectively. The observed range of PFOA concentrations encompasses those reported for microwave popcorn bags (6 to 290 ng/g) by Begley et al.[7]; however they did not observe PFOA above the 1 ng/g detection limit in a french fry box, sandwich wrapper, or hamburger wrapper. PFOS ranged from 13 to 283 ng/g. The FTUCAs were detected at the lowest concentrations, ranging from < 1.3 to 66 ng/g.

Implications of fast food composite results. The general lack of detection of PFAs in fast food composites coupled with the detection of all PFAs (at μg/g concentrations in some instances) in the corresponding fast food packaging strongly suggests that the PFAs present in the food packaging generally do not migrate to detectable levels in the foods stored within this packaging. This is consistent with results from other studies that have examined the migration of perfluorinated compounds from treated products. Begley et al.[7] found PFOA concentrations at 6 to 290 ng/g on microwave popcorn bags, but < 1 ng/g in Miglyol, a food oil simulant, which was heated in the bags. Powley et al. observed no migration of PFOA from PTFE-coated frying pans.[8]

The data suggest that food packaging is not a source of PFAs in food, and thus not a vector of human exposure. However it is possible that the food packaging containing PFAs are a source of PFAs to the environment as these products degrade in landfills, or are recycled. It is conceivable that the PFAs can make their way back into the human food web via accumulation in fish, cattle, and other food-producing animals.

Estimate of relative importance of dietary intake during human exposure to PFAs. A basic estimate of Canadians' exposure to PFAs was made using the 2004 TDS PFA data, concentrations of PFAs in dust[3], concentrations of PFAs in Lake Ontario surface water[9], and reasonable maximum exposures to treated carpet and apparel.[10] The food intake PFA exposure estimate of 200 ng/day (for a 60 kg adult) was on the same order of magnitude as the estimated exposure to PFAs via dust, water, and treated carpet and apparel (all estimated using maximum reported concentrations, and reasonable maximum exposure scenarios). This estimate suggests that food is an important route of direct exposure to PFAs.

References

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Table 1. Concentrations of total PFAs in Total Diet Study composites analyzed.

Total Diet Study Composite	ΣPFAs (ng/g wet weight)
beef, steak	7.2
beef, roast	2.6
beef, ground	2.1
pork, fresh	nd[b]
pork, cured	nd
veal, cutlets	nd
lamb	nd
luncheon meats, cold cuts	trace
luncheon meats, canned	nd
organ meats	nd
wieners + sausages	trace
eggs	nd
poultry, chicken + turkey	nd
poultry, liver pâté	nd
fish, marine	2.6
fish, freshwater	2.0
fish, canned	nd
shrimp	nd
popcorn, microwave	nd
frozen entrée	nd
hot dog	nd
french fries	nd
pizza	nd
hamburger	nd
chicken burger	nd
chicken nuggets	nd
infant food, dinner: cereal + vegetable + meat	nd
infant food, meat, poultry, or eggs	nd
infant food, dinner: meat or poultry + vegetable	nd

[a]limit of detection < concentration detected < limit of quantitation
[b]not detected

Table 1. Concentrations of total PFAs in packaging of fast food samples.

Fast food	Packaging analyzed	ΣPFAs (ng/g wet weight)
pizza	cardboard boxes + paper liners	124
french fries	cardboard boxes + paper bag	7170
hamburger	paper wrapper + paper-lined foil wrapper	180
chicken burger	paper wrapper + paper-lined foil wrapper	301
hot dog	cardboard boxes + paper-lined foil wrapper	7810
chicken nuggets	cardboard boxes + paper bag + foil-lined cardboard	3900