DETERMINATION OF PERFLUORINATED ORGANIC COMPOUNDS IN FOOD AND DUST

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Introduction

Perfluorinated alkylated substances (PFAS) have been used since the 1950's because of their specific properties that include persistence, water, dirt and oil repellency and surface active behaviour[1]. At the beginning of the current millennium it became clear that people and environment have been exposed to these chemicals, because in blood of both humans and animals levels of certain PFAS were found. The common characteristic of PFAS is the fully fluorinated alkyl chain, which renders unique properties to these chemicals. PFAS have been found in animals from all over the globe, including from remote areas such as the Arctic. The general population is exposed to PFAS, for example levels of PFOS between 1 and 140 ng/mL, and of PFOA between 0.5 and 50 ng/mL, have been reported in human blood[2].
The present study is part of a Flemish government supported assessment of exposure routes and exposure levels of PFAS relevant for the general population, started in 2007 and running until 2010. In this assessment contaminant levels in food items and other potential sources of human exposure are being investigated in order to map their occurrence and evaluate their contribution to the overall exposure of the population to PFAS. The study will determine levels of a variety of PFAS in dietary items like vegetables, meat, fish, dairy products, beverages and indoor dust.
In the present paper the first results will be shown for a selection of food items and dust.

Materials and methods

Seventeen native standards of perfluoroalkanoic acids (C_4-C_{14}), PFOSA and perfluorosulfonic acids (C_4, C_6-C_8, C_{10}) were purchased from Wellington Laboratories (Canada). Eight labelled ^{13}C standards of perfluoroalkanoic acids (C_4, C_6, C_8, C_9-C_{12}), PFOS and deuterium labelled d_3-N-MePFOSA were a kind gift of Wellington Laboratories. ENVI-Carb 120/400 was obtained from Supelco (USA). All solvents used were analytical grade obtained from local suppliers. Polypropylene vessels were used where possible to avoid contamination or loss of analytes due to wall sorption.

Vegetables, meat, fish and dairy products were obtained from local supermarkets or growers in Flanders. House dust was collected with an ordinary vacuum cleaner, and sieved after removing visible non dust parts with a tweezer. Vegetables, meat and fish samples were homogenised in a blender. For vegetables a number of specimen were peeled (potato, apple), external leafs and roots removed (leek), and the specimen were subsequently pooled, and homogenised in a kitchen blender. In order to investigate the influence of homogenisation techniques, leek was also homogenised by freeze drying and grinding. Subsequently 1 g of homogenised sample, or 1g of collected dust was weighed in a polypropylene tube. Ten ml of methanol was added to the tube together with 40 µl of two solutions containing mixtures of internal standards (^{13}C-perfluoroalkanoic acids and ^{13}C-perfluoroalkane sulfonic acids, respectively). The contents of the tube were mixed thoroughly and then placed in an ultrasound bath during 10 min. The tubes were centrifuged at 2000 rpm during 10 min. The supernatant was transferred to a second polypropylene tube. The remaining pellet in the first tube was washed with 15 ml of methanol, shaken and treated with ultrasound, and centrifuged again. The supernatant was transferred to the second polypropylene tube. The second tube was placed on a water bath (45 ^oC) and the extract was concentrated in a gentle stream of N_2 to 1 ml.
100 mg of ENVI-carb was transferred to a polypropylene reaction vial and 50 µl of glacial acetic acid was added. Next the concentrated extract was added to the reaction vial, the polypropylene tube that contained the extract was washed twice with 250 µl of methanol and the washings were also transferred to the reaction vial. The contents of the reaction vial were shaken during 1 min, then centrifuged at 10,000 rpm during 10 min. The supernatant was transferred immediately into a new reaction vial containing 100 mg of Envicarb and 50 µl of acetic acid and the procedure was repeated. If the supernatant remained still coloured then the ENVI-carb clean up was repeated once more. If colourless then the supernatant was filtered over an Acrodisk LC 13 GHP-PALL luer 0.2 µm filter, using a methanol rinsed syringe.

Analysis was performed by HPLC-ESI-MS/MS[3] using a 4000QTrap (Applied Biosystems) triple quadrupole mass analyser connected to a Shimadzu HPLC system. For the HPLC analysis, a volume of 20 µl was injected in a HPLC system consisting of a Shimadzu pump (LC-20AD), autosampler (SIL-20A), and system controller (SCL-10A VP). The analytical column was a ACE 3 C18 (ID 2.1 mm; length 150 mm) with a particle diameter of 3 µm held at a temperature of 30 °C (column oven, CTO-20AC). The pre-column used for lowering the background of PFCs from the system was a Pathfinder 300 PS C18 (ID 4.6; length 50 mm) with a particle diameter of 3.5 µm. Gradient elution with a flow of 0.2 ml/min. was applied with the following solvent composition: A, 95:5 methanol:water and B: 40:60 methanol:water (both with 5 mM ammoniumacetate). After an equilibration time of 8 min., the solvent composition decreased from 100 % at the start of the analysis to 20% B at 8 min. and further decreased to 0% B at 17 min. After 20 min., the solvent composition increased to 100% B again until 22 min.
The MS/MS was tuned to record 51 transitions (in principle two for each analyte, one of which was used for quantitative purposes and the other for identity confirmation). The LC-MS/MS system was adapted to prevent PFAS contamination from tubing, by replacing polytetrafluoroethylene tubing, where possible, with stainless steel tubing, and by placing a C18 guard column in front of the 6 port injection valve, thus retaining any PFAS generated from the HPLC tubing. The transitions of the perfluorinated compounds were measured with the MS/MS operating in the negative ionization mode and are shown in Table 1.
Blank samples were run regularly throughout the processing of samples.

Table 1. Transitions used in triplequad MS/MS for identification and quantification of PFAS in this study

Compound	Q1 mass	Q3 mass	Transition	Retention time	Compound	Q1 mass	Q3 mass	Transition	Retention time
^{12}C PFBA	213	169	1	-	^{12}C PFDoA	613	569	1	14.10
$^{13}C_4$ PFBA	217	172	1	-		613	319	2	
^{12}C PFPeA	263	219	1	8.57	$^{13}C_2$ PFDoA	615	570	1	14.10
^{12}C PFHxA	313	269	1	9.85		615	369	2	
	313	119	2		^{12}C PFTrA	663	619	1	15.40
$^{13}C_2$ PFHxA	315	270	1	9.86		663	369	2	
	315	119	2		^{12}C PFTeA	713	669	1	16.90
^{12}C PFHpA	363	319	1	10.70		713	369	2	
	363	169	2						
^{12}C PFOA	413	369	1	11.30	^{12}C PFBS	299	80	1	8.84
	413	169	2			299	99	2	
$^{13}C_4$ PFOA	417	372	1	11.30	^{12}C PFHxS	399	80	1	10.70
	417	169	2			399	99	2	
^{12}C PFNA	463	419	1	11.80	^{12}C PFHpS	449	80	1	11.30
	463	219	2			449	99	2	
$^{13}C_5$ PFNA	468	423	1	11.80	^{12}C PFOS (K)	499	80	1	11.80
	468	219	2			499	99	2	
^{12}C PFDA	513	469	1	12.40	$^{13}C_4$ PFOS (Na)	503	80	1	11.80
	513	219	2			503	99	2	
$^{13}C_2$ PFDA	515	470	1	12.40	^{12}C PFOSA	498	78	1	12.90
	515	219	2			498	169	2	
^{12}C PFUnA	563	519	1	13.10	D_3 PFOSA	515	169	2	15.10
	563	269	2			515	219	1	
$^{13}C_2$ PFUnA	565	520	1	13.10	^{12}C PFDS	599	80	1	13.00
	565	269	2			599	99	2	

Results and discussion

Generation of PFAS by instrument tubing is an important source of contamination in PFAS analysis[4]. Fig. 1 shows the retardation of PFOA generated by instrument tubing. The retardation is a result of the use of the guard column placed between the LC instrument and the analytical column just prior to the injection port. Two different sample runs show distinct analyte peaks with different detector responses eluting earlier than the much wider retarded peak generated by the instrument which has a similar response in both runs. In our instrumentation this type of contamination was observed in particular for PFOA and 7H-PFHpA, a compound initially used as an internal standard.

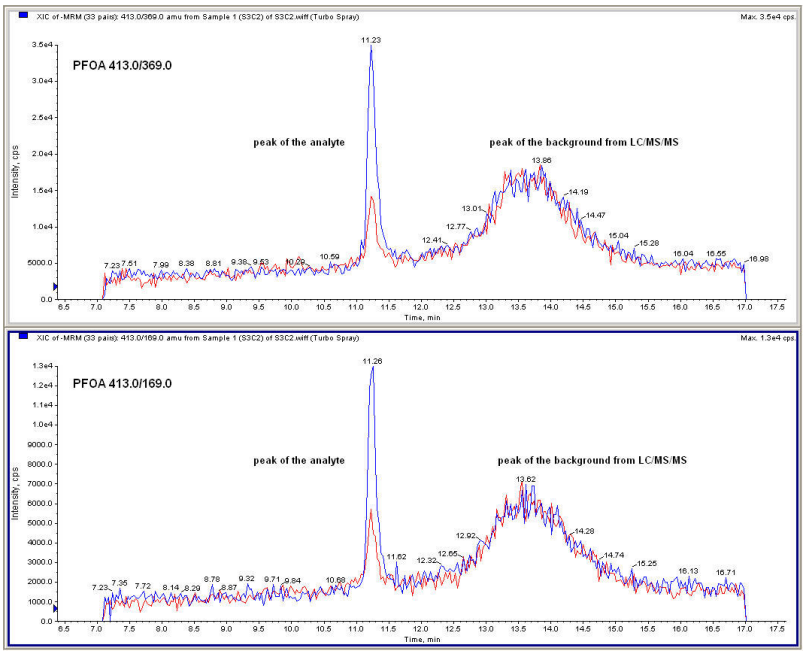

Figure 1. Ion chromatograms of two water samples (in blue and red) showing background peak of PFOA retarded by guard column (for explanation, see text).

Tables 2 and 3 show the results for alkanoic acids and for sulfonic compounds respectively. House dust contains all analytes determined. PFOA (150 ng/g) and PFOS (54 ng/g) are the most abundant perfluorinated organics in house dust. The total amount of perfluoroalkanoic acids in dust amounts to ~ 200 ng/g and the total of sulfonic compounds to 60 ng/g. These values agree with other published data. In a recent study in house dust in the USA, PFOS and PFOA were the most prominent compounds detected, occurring in over 95% of the samples at median concentrations of 201 and 142 ng/g of dust, respectively[5]. In house dust collected in Japan mean levels of PFOS and PFOA of 200 and 380 ng/g, respectively, were reported[6]. In dust collected from homes in Ottawa, mean levels of PFOS, PFOA and PFHxS amounted to 440, 106 and 390 ng/g[7], respectively.

Table 2. Concentrations of perfluoroalkanoic acids (in ng/g of -wet- material) in several dietary items and in house dust

Sample type	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTrA	PFTeA
apple	<0.9	<0.07	<0.6	<0.1	<0.3	<0.12	<0.06	<0.08	<0.03	<0.03	<0.04
potato	9.4±1.5	0.4±0.2	<0.6	<0.1	<0.3	<0.12	<0.06	<0.08	<0.03	<0.03	<0.04
leek	<0.9	<0.07	<0.6	<0.1	<0.3	<0.12	<0.06	<0.08	<0.03	<0.03	<0.04
milk	<0.9	<0.07	<0.6	<0.1	<0.3	<0.12	<0.06	<0.08	<0.03	<0.03	<0.04
beef	<0.9	<0.07	<0.6	<0.1	<0.3	<0.12	<0.06	<0.08	<0.03	<0.03	<0.04
pork	<0.9	<0.07	<0.6	<0.1	<0.3	<0.12	<0.06	<0.08	<0.03	<0.03	<0.04
cod	<0.9	<0.07	<0.6	<0.1	<0.3	0.14±0.02	0.09±0.02	0.35±0.08	0.06±0.01	0.24±0.06	<0.04
dust	3.4±0.7	1.3±0.2	15.2±2.4	7.3±0.6	150±12	3.2±0.3	11.9±0.9	1.3±0.2	6.3±0.3	1.4±0.1	7.0±0.6

A relatively high concentration of C_4 and C_5 acids was found in potato. Further work as to the origin of these samples will be conducted in order to explain these levels. Cod appears to bioaccumulate the longer alkanoic acids. The general trend observed in the literature that levels in biota of alkanoic acids with uneven chain lengths are higher than their preceding even chain length homologue is also observed in cod (for C_8-C_{13}) in this study. In dust, however this trend seems to be reversed.

In a UK survey of PFAS in food[8], levels of PFOS and PFOA were generally below LODs, except for potatoes (10 ng/g of PFOS and 1 ng/g of PFOA), canned vegetables (2 ng/g PFOS) and eggs 1 ng/g PFOS). LODs in that study were generally 1 tot 2 orders of magnitude higher than in the present one. In a Canadian total diet study[9] levels of PFAS were determined in composite foods made of food items. PFOS was detected most frequently, followed by PFOA, at levels up to 3 ng/g. PFOS levels in beef and fish in that study correspond well to those found in the beef and cod samples analysed in the present study.

Table 3. Concentrations of perfluorosulfonic acids and perfluorosulfonamide (in ng/g of -wet- material) in several dietary items and in house dust

Sample type	PFBS	PFHxS	PFHpS	PFOS	PFDS	PFOSA
Apple	<0.15	<0.03	<0.02	<0.25	<0.02	<0.01
Potato	<0.15	<0.03	<0.02	<0.25	<0.02	<0.01
Leek	<0.15	<0.03	<0.02	<0.25	<0.02	0.02±0.01
Milk	<0.15	<0.03	<0.02	1.2±0.1	<0.02	0.01±0
Beef	<0.15	<0.03	<0.02	4.8±0.7	<0.02	0.02±0
Pork	<0.15	<0.03	<0.02	<0.25	<0.02	<0.01
Cod	<0.15	<0.03	<0.02	2.6±0.3	<0.02	0.24±0.03
Dust	0.73±0.02	0.85±0.17	0.15±0.02	53.8±10.0	0.50±0.08	1.5±0.2

For a provisional calculation of the daily exposure of humans to PFAS we can use the data from Tables 2 and 3 and multiply these with daily intakes of fruit, vegetables, meat, fish and milk. Assuming the latter to be 60, 100, 100, 50 and 50 g/d, respectively, we would obtain daily intakes of PFOS of < 15, <25, 480, and 130 ng from food and 60 ng from milk, or ~ 700 ng/person/d in total. Assuming a dust ingestion rate of 0.05 g/d, an additional 3 ng/d of PFOS would be taken up from this route and 2 ng/d from dermal contact with dust[2]. For PFOA dust would be the only significant contributor to human exposure from the media investigated in this study, leading to an estimated intake of 8 ng/d by dust swallowing and 6 ng/d from dermal contact with dust. These figures relate favourably to the recommended TDI for PFOS of 150 ng per kg bodyweight per day and 1.5 µg/kg bw/d for PFOA proposed recently by the European Food Safety Authority[2]. Obviously, these figures do not take into account other food items and other routes of exposure such as drinking water and inhaled air. Furthermore, contributions from precursors other than PFOSA that may give rise to body burdens of selected perfluoroalkanoic acids or sulfonates have not been the subject of this initial investigation, and will be further evaluated during the course of the project.

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