PERFLUORINATED CHEMICALS IN FOOD COMPOSITES FROM CATALONIA, SPAIN

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Abstract

Levels of perfluorinated chemicals (PFCs) were investigated in assorted food composites from Catalonia, Spain to assess possible exposure of PFCs through dietary intake. Levels of detected PFCs were low. PFOS was present in 24 out of 36 samples with levels ranging from <0.013 to 0.84 ng/g food composite on a fresh weight (fw) basis. PFOA and PFHpA were only present in two samples at 0.065 and 0.071 ng/g fw for PFOA, and 0.016 and 0.014 ng/g fw for PFHpA. Other PFCs, such as C4 and C6 perfluorinated sulfonates and C6 to C11 perfluorinated carboxylic acids, were below individually set limits of detection (LODs), ranging from 0.001 to 0.65 ng/g depending on sample type.

Introduction

PFCs are ubiquitous in the environment. They have unique properties such as chemical resistance and surfactant properties and have been used in a wide variety of industrial and consumer applications[1]. PFCs are present in biota and humans worldwide[2-4]. However, routes of exposure have not yet been fully established. To assess possible contamination linked to dietary habits a suite of different food items divided into 18 composite samples (two replicates) were investigated for PFCs. The food items represent dietary intake of Catalonians who have been shown to have low blood levels of PFCs in our earlier study[3]. In a study by Tittlemier et al, 2007, the dietary exposure of Canadians to PFCs was investigated. Only nine out of 54 Canadian food samples, prepared as for consumption, were shown to have detectable amounts of PFCs, with PFOS and PFOA detected most frequently at levels ranging from 0.5 to 4.5 ng/g[5].

Materials and Methods

A total of 36 samples composed by sub samples were purchased in local stores in the Tarragona County. For the preparation of all composite sub samples, the quantity of each food in every sub sample was included according to the dietary habits of the population of the area under evaluation. Samples were freeze-dried and kept in methanol cleaned polypropylene containers at -20°C until analysis. Upon analysis, one gram of freeze-dried samples of the composites was digested with sodium hydroxide and methanol according Powley et al, 2005[6]. After centrifugation the supernatant was cleaned up using solid phase extraction[7] and additional clean up was performed with ENVI-Carb bulk carbon[6] before analysis on LC-MSMS. Quantitation was done using ^{13}C-labeled PFOS and PFOA as internal standards for sulfonates and carboxylic acids respectively, calculating recovery against ^{13}C-labeled PFNA.

LC-MS/MS analysis
A total of 15 µl of the SPE extracts was injected into an HP 1100 LC system (Waldbronn, Germany) equipped with a tertiary pump, an automatic degasser and a thermostated column compartment that was kept at 25°C. Separation was achieved on a Waters Symmetry C18 (150 x 2.1 mm, 5µm) column. Water (A) and acetonitrile mobile phase (B), containing 10 mM ammonium acetate, was delivered with a flow rate of 300 µL/min. The gradient started at 35% B followed by a 10 min ramp to 90% B, a 5 min hold, and then reverting to initial conditions allowing 7 min stabilization time. Detection was performed using an API

5000 MS/MS system (Applied Biosystems/MDS Sciex, Canada) with a Turbo Ion Spray ion source operating in the negative electrospray mode.

Table I. MS/MS transitions for the PFCs analyzed.

Compound	Transistions		
PFBuS	298.9>80.0	298.9>99.0	298.9>82.9
PFHxS	398.9>79.9	398.9>99.0	398.9>118.9
PFOS	498.9>80.0	498.9>99.1	498.9>129.9
PFHxA	312.9>118.9	312.9>169.9	312.9>268.9
PFHpA	362.9>118.9	362.9>168.9	362.9>318.9
PFOA	412.9>168.9	412.9>218.9	412.9>368.8
PFNA	462.7>168.9	462.7>219.0	462.7>418.9
PFDA	512.9>218.9	512.9>268.9	512.9>468.9
PFUnDA	562.9>168.9	562.9>268.9	562.9>518.9
$^{13}C_4$PFOS	502.9>80.0	502.9>99.1	502.9>130.9
$^{13}C_4$-PFOA	416.9>168.9	416.9>218.9	416.9>371.8
$^{13}C_5$-PFNA	467.9>168.9	467.9>219.0	467.9>422.9

The most abundant transition was chosen for quantitation. The other transitions were used for confirmation and calculation of the identity ratio by calculating the ratio between secondary to primary transition in samples compared to the calibration standard.

Results and Discussion

All PFC levels present in the composite food samples were relatively low. PFOS was detected in 24 out of 36 samples with levels ranging from non detect to 0.84 ng/g food composite on a fresh weight basis, as shown in Table II. PFOA and PFHpA were the only other PFCs detected in two whole milk samples. Levels of PFOA were 0.065 and 0.071 ng/g fw and 0.016 and 0.014 ng/g fw for PFHpA. Other PFCs, such as C4 and C6 perfluorinated sulfonates and C6 to C11 perfluorinated carboxylic acids, were below individually set limits of detection (LODs), ranging from 0.010 to 0.65 ng/g depending on sample type.

Reported less than values were calculated from the actual peak area in samples, having a corresponding blank area > 50 % of the amount in the sample. These values can vary even for the same sample type due to differences in water content of the samples. The recovery of the labeled standards ($^{13}C_4$- PFOS and $^{13}C_4$-PFOA) ranged between 32-74% for $^{13}C_4$- PFOS and 61-130% for $^{13}C_4$-PFOA. Quantitation was based on solvent based calibration standards. A matrix matched calibration curve in extracted egg was prepared to study ion enhancement or reduction due to matrix effects. It was not feasible to prepare matrix matched calibration curves for all 18 matrices present. Originally, instrumental analysis was performed using an LC single quadropole MS instrument. However, this technique proved to be insufficiently selective and coelution at m/z 499, when monitoring PFOS, occurred. Identity confirmation of quantification trace (primary transition) was performed by calculating the ratio of secondary to primary MS/MS transition in samples compared to the calibration standard according to the method suggested by the Commission of the European Communities[8]. The identity was within 30% of the calibration standards for all detected concentrations except for one egg sample, as shown in table II.

Table II. Individual PFOS and PFOA concentrations (ng/g fresh weight) in 36 composite food samples.

	PFOS	**PFOA**	**PFHpA**
Food composite	Fresh weight (ng/g)	Fresh weight (ng/g)	Fresh weight (ng/g)
vegetables	0.026	<0.016	<0.002
vegetables	0.018	<0.039	<0.006
beans and peas	<0.026	<0.036	<0.006
beans and peas	<0.028	<0.054	<0.011
bread, spaghetti, rice	<0.067	<0.073	<0.015
bread, spaghetti, rice	<0.071	<0.088	<0.002
white fish	0.35	<0.045	<0.005
white fish	0.46	<0.085	<0.004
shellfish	0.15	<0.030	<0.004
shellfish	0.15	<0.028	<0.002
canned tuna, sardine, mussel	0.25	<0.17	<0.009
canned tuna, sardine, mussel	0.29	<0. 85	<0.005
fresh salmon, sardine, tuna	0.82	<0.15	<0.001
fresh salmon, sardine, tuna	0.49	<0.11	<0.020
assorted meat	0.065	<0.036	<0.004
assorted meat	0.024	<0.071	<0.007
chicken	0.020	<0.071	<0.005
chicken	0.021	<0.063	<0.003
veal	0.023	<0.053	<0.004
veal	0.032	<0.015	<0.003
lamb	0.040	<0.10	<0.020
lamb	0.040	<0.040	<0.006
eggs	0.088[a]	<0.057	<0.005
eggs	0.077	<0.053	<0.005
dairy products	0.16	<0.038	<0.007
dairy products	0.086	<0.042	<0.008
whole milk	<0.014	0.055	0.016
whole milk	<0.013	0.058	0.014
milk	0.026	<0.013	<0.003
milk	<0.013	<0.043	<0.007
fruit	<0.018	<0.039	<0.004
fruit	<0.016	<0.032	<0.004
margarine	<0.036	<0.10	<0.013
margarine	<0.032	<0.13	<0.015
oil	<0.12	<0.097	<0.018
oil	<0.075	<0.40	<0.054

Samples reported as less than values have a corresponding blank area larger than 50% of targeted compound area.
[a] Ratio primary to secondary transition was >30% but < 50%.

Concentrations found in Spanish food items are comparable or somewhat lower than previous dietary studies of PFCs in assorted foods. In a UK 2004 total diet study, PFOS was found in four out of 20 different food groups at 1 ng/g fresh weight in eggs and sugars & preserves, and at 2 and 10 ng/g fw in canned vegetables and potatoes, respectively. PFOA was found in one sample, 1 ng/g fw in potatoes. Detection limits for other food groups in the English study were significantly higher and in the range of 0.5 to 20 ng/g for PFOS[9]. In our study PFOS was detected at levels of 0.017-0.84 ng/g fw. As noted by Tittlemeir et al, 2007, concentrations of PFCs in composite samples are generally lower than in individual food items since PFC-free food items in the same composite can dilute the total concentration of PFCs[5]. Generally, highest concentrations were found in marine food composites indicating this food group as the most important for dietary exposure of PFCs to humans. Individuals with a high fish intake diet have

previously been shown to have higher blood levels of PFCs than other subpopulations[10]. PFOS has also been found in seafood collected in China with concentrations ranging from 0.3 to 13.9 ng/g fw[11]. In this study PFOA and PFHpA were only found in two whole milk samples at low concentrations. The low levels found in the food are in agreement with the levels of PFOS and PFOA in blood for residents in the same area, which were similar or lower than in other European countries[3].

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