

PERFLUORINATED COMPOUNDS IN THE UK 2004 TOTAL DIETMortimer DN¹, Clarke DB², Gem M¹, Rose M²

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Introduction

Perfluorooctane sulphonate (PFOS) belongs to a group of fluorinated chemicals often referred to as perfluoroalkyl substances (PFAS). Other chemicals in this group are homologues of PFOS and derivatives such as perfluorooctanesulphonyl fluoride (POSF), amines, amides, carboxylates and perfluorooctane sulphonamide (PFOSA). PFOA refers to the anion and salts of perfluorooctanoic acid as well as the acid itself.

PFOS and PFOA are used to provide soil, oil and water resistance to apparel and leather, fabric/upholstery and carpets. They are also used as surfactants, food contact materials and in fire fighting foams. These chemicals are not manufactured directly in the UK although they are imported and used in a variety of manufacturing processes such as those listed above. They are very resistant to both chemical and biological attack and are therefore persistent in the environment, although they may degrade slowly under certain conditions. PFOS in particular appears to be ubiquitous. The Organisation of Economic Co-operation and Development (OECD) has concluded

Table 1: Fluorinated chemicals measured

Chemical	Abbr.	Number > LOD
Perfluorooctanesulphonylamide	PFOSA	1
Perfluorobutane sulphonate	PFBS	2
Perfluorohexane sulphonate	PFHxS	1
Perfluorooctane sulphonate	PFOS	4
Perfluoropentanoic acid	PFPeA	0
Perfluorohexanoic acid	PFHxA	1
Perfluoroheptanoic acid	PFHpA	0
Perfluorooctanoic acid	PFOA	1
Perfluorononanoic acid	PFNA	1
Perfluorodecanoic acid	PFDeA	1
Perfluoroundecanoic acid	PFUnA	1
Perfluorododecanoic acid	PFDoA	1
Perfluorotetradecanoic acid	PFTdA	1
Perfluorohexadecanoic acid	PFHdA	0
Perfluorooctadecanoic acid	PFOdA	0

that risk reduction measures are needed for these chemicals, and some have already been put into place in the UK.^{1,2}

PFOS and PFOA have some potential to bioaccumulate in the food chain, although they tend to bind to certain proteins rather than concentrating in fat as do other persistent organic pollutants. Accordingly, they may be found in the blood and liver rather than the fatty components of foods. There have been relatively few reported occurrences of PFOS and even fewer of PFOA in food. Most of these have been in the blood and liver of fish.³⁻⁷ PFOS has also been detected occasionally in milk and ground beef, and PFOA in bread, apples and beans.⁸ Both chemicals have been detected in human milk.⁹ Other PFAS

only appear to have been measured and reported in the liver of cattle, chicken and pigs in a Japanese study of farm animals in which PFOS and PFOA were also analysed.¹⁰ The Food Standards Agency is not aware of any estimates of dietary intakes of PFOS or PFOA in other countries, but work is in progress in Germany.¹¹

This work represents the first extensive survey for fluorinated organic chemicals in food in the UK.

Materials and Methods

The Total Diet Study models the typical UK diet and is based on food consumption surveys conducted as part of the national Expenditure and Food Survey (EFS).^{12,13,14} Food items representing all parts of the diet were purchased during 2004 from retail outlets located in several towns and cities around the UK. The foods, allocated to one of 20 food groups, were prepared and cooked where appropriate before being combined into composite samples representing the following food groups: bread, cereals, carcass meats, offal, meat products, poultry, fish,

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oils and fats, eggs, sugars and preserves, green vegetables, potatoes, other vegetables, canned vegetables, fresh fruit, fruit products, beverages, milk, milk products and nuts.

Portions (5g) of the composites were digested with potassium hydroxide and centrifuged and the supernatant cleaned up using solid phase extraction following the method of Taniyasu.^{15,16} The analysis was carried out by reversed phase high performance liquid chromatography-mass spectrometry using a C8 column coupled to a triple quadrupole mass spectrometer with electrospray operated in the negative ion mode. For analytical quality

Table 2: Concentrations of PFOS and PFOA ($\mu\text{g}/\text{kg}$) in samples from the 2004 Total Diet Study

Food Group	Concentrations (microgram/kg fresh weight)							
					Sum PFAS		Sum PFAS	
	PFOS		PFOA		Lower bound		Upper bound	
Bread	<20	\pm <4	<5	\pm <1	0	\pm -	172	\pm 30
Miscellaneous cereals	<10	\pm <2	<5	\pm <1	0	\pm -	165	\pm 29
Carcass meats	<10	\pm 2	<2	\pm <0.4	0	\pm -	154	\pm 27
Offal	<20	\pm <4	<2	\pm <0.4	0	\pm -	232	\pm 36
Meat products	<10	\pm <2	<2	\pm <0.4	0	\pm -	126	\pm 21
Poultry	<10	\pm <2	<2	\pm <0.4	0	\pm -	153	\pm 27
Fish	<5	\pm <1	<3	\pm <0.6	0	\pm -	92	\pm 17
Oils and fats	<0.5	\pm <0.1	<1	\pm <0.2	1	\pm 0.2	78	\pm 15
Eggs	1	\pm 0.2	<1	\pm <0.2	1	\pm 0.2	86	\pm 16
Sugars & preserves	1	\pm 0.2	<1	\pm <0.2	1	\pm 0.2	86	\pm 16
Green vegetables	<3	\pm <0.6	<1	\pm <0.2	0	\pm -	105	\pm 20
Potatoes	10	\pm 2	1	\pm 0.2	58	\pm 11	120	\pm 23
Other vegetables	<3	\pm <0.6	<10	\pm <2	1	\pm 0.2	80	\pm 16
Canned vegetables	2	\pm 0.4	<5	\pm <1	2	\pm 0.4	138	\pm 27
Fresh fruit	<2	\pm <0.4	<5	\pm <1	0	\pm -	118	\pm 23
Fruit products	<1	\pm <0.2	<5	\pm <1	0	\pm -	126	\pm 25
Beverages	<0.5	\pm <0.1	<0.5	\pm <0.1	0	\pm -	13	\pm 2.5
Milk	<0.5	\pm <0.1	<0.5	\pm <0.1	0	\pm -	24	\pm 4.7
Dairy products	<5	\pm <1	<5	\pm <1	0	\pm -	299	\pm 56
Nuts	<2	\pm <0.4	<5	\pm <1	0	\pm -	171	\pm 32

control, food samples were over-spiked with a mixture of standards for the compounds of interest, using tetrahydro-PFOS as an internal standard.¹⁷ The compounds measured are listed in Table 1. The inclusion of fluorinated chemicals other than PFOS and PFOA was limited by the availability of analytical standards. Analysis of these samples was carried out in conjunction with participation by CSL in the 1st Worldwide Interlaboratory Study on Perfluorinated Compounds in Environmental and Human Samples, which formed part of a method validation exercise.¹⁸

Results and Discussion

Table 1 lists the compounds measured and the number of food groups that contained them above the limit of detection. PFOS was detected most often, in four groups. The results for PFOS and PFOA are presented in Table 2 and are a summary of the full results which can be found in reference 16. The uncertainties associated with concentrations of the individual chemicals were 20%. The uncertainties associated with *upper bound* PFAS concentrations have been estimated by summing the uncertainties associated with the concentrations or limits of determination (LODs) of the constituent chemicals in a given food group. For *lower bound* results the uncertainties are assumed to be zero where a chemical was not detected.

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PFOS was detected at concentrations above the limit of determination in the potatoes, canned vegetables, eggs and sugars & preserves food groups. PFOA was detected only in the potatoes food group. Five of the fluorinated chemicals measured were not detected in any of the food groups, and the others were detected only occasionally.

Table 3: Estimated upper bound dietary intakes

Age group	Estimated average dietary intakes (microgram/kg bodyweight/day)					
	Upper bound			Lower bound		
	PFOS	PFOA	PFAS	PFOS	PFOA	PFAS
Senior citizens - living at home	0.1	0.05	1.9	0.02	0.001	0.09
Senior citizens - in old peoples' homes	0.1	0.06	2.3	0.02	0.002	0.09
Adults	0.1	0.07	2.5	0.01	0.001	0.1
Schoolchildren:						
4-6 years	0.3	0.1	5.2	0.05	0.004	0.3
7-10 years	0.2	0.1	4.1	0.04	0.004	0.2
11-14 years	0.1	0.07	2.8	0.03	0.003	0.2
15-18 years	0.1	0.06	2.2	0.02	0.002	0.1
Toddlers:						
1.5-2.5 years	0.3	0.2	6.1	0.05	0.004	0.3
2.5-3.5 years	0.3	0.1	5.5	0.05	0.004	0.2
3.5-4.5 years	0.2	0.1	5.1	0.05	0.004	0.2

Ten fluorinated compounds were detected in the potatoes food group. The potatoes group comprises not only fresh potatoes either baked, boiled or microwaved with or without skin but also prepared and processed products such as instant potato, chips, crisps and other potato snacks, croquettes and hash browns and potato salad. This group will require further study in order to understand the high results.

Dietary intakes of PFOS, PFOA and PFAS by different age groups were estimated using food consumption data from various dietary surveys.¹⁹⁻²² The estimated average upper bound dietary intakes of fluorinated chemicals by adults from the whole diet in 2004

were 0.1 microgram/kg bodyweight per day for PFOS and 0.07 microgram/kg bodyweight per day for PFOA (Table 3). The data on exposure was submitted to the UK independent scientific Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) for assessment during a meeting in May 2006.

The Total Diet Study allows a good assessment of overall dietary exposure. However, a drawback of the approach is that the wide range of foods included in each group means that significant contamination will only be found if the group is generally affected, for example in the case of dioxins in fish, meat and eggs. Other than the investigations into the results for the potato group, future work will therefore be directed towards individual foods for which literature reports indicate possible contamination, such as fish and offals.

Acknowledgements

This work was funded by the Food Standards Agency, United Kingdom. The authors also wish to thank all participating staff of Central Science Laboratory for their input and support in this survey.

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