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AUTHORITY OF IRELAND

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MONITORING & SURVEILLANCE SERIES

Investigation into levels of perfluoroalkylated substances (PFAs) in meat, offal, fish, eggs, milk and processed products

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SUMMARY

The Food Safety Authority of Ireland FSAI in collaboration with the Department of Agriculture, Fisheries and Food and the Marine Institute have carried out a study of levels of perfluoroalkylated substances (PFAS) in meat, liver, eggs, fish and milk produced in Ireland. The study was undertaken because of awareness about the possible effects on human health of these biopersistent environmental contaminants, known to be present in a number of foodstuffs, notably fish. Furthermore the aim of this study also was to proactively monitor the Irish food supply for emerging new contaminants, with a view to aid national and international efforts in the management of these contaminants.

Perfluoroalkylated substances (PFAS) is the collective name for a very large group of fluorinated compounds, which consist of neutral and anionic surface active compounds with high thermal, chemical and biological inertness. Perfluorinated compounds are generally hydrophobic but also lipophobic. An important subset is the (per)fluorinated organic surfactants, to which perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) belong.

PFOS is extremely persistent and has substantial bioaccumulating and biomagnifying properties, although it does not follow the classic pattern of other POPs by partitioning into fatty tissues but instead binds to proteins in the blood and the liver. It has a capacity to undergo long-range transport and also fulfills the toxicity criteria of the Stockholm Convention on Persistent Organic Pollutants[1].

PFOS, PFOA and other perfluorinated organic compounds (PFCs) have been widely used in industrial and consumer applications including stain- and water-resistant coatings for fabrics and carpets, oil-resistant coatings for paper products approved for food contact, fire-fighting foams, mining and oil well surfactants, floor polishes, and insecticide formulations.

In this study, PFOS, PFOA and an additional 9 other PFAS were analysed in 100 different food matrices in accordance with available standards for analysis.

Trace levels of eight of the eleven compounds measured were detected in nineteen of the 100 separate food samples (9 fish, 9 livers and 1 egg). The highest individual measurements were 3 µg/kg of PFOS in two liver samples. The highest total PFCs measurement (sum of all individual) was 5 µg/kg, in a bovine liver. The study indicates that levels of perfluoroalkylated substances in the Irish food chain are low.

In 2008, the European Food Safety Authority (EFSA) derived a human Tolerable Daily Intake (TDI) for PFOS of 150 ng/kg bw per day and a ten-fold higher human TDI for PFOA of 1.5 µg/kg bw per day and concluded that the general population in Europe is unlikely to suffer negative health effects from PFOS and PFOA as the dietary exposure to these chemicals is below their respective TDIs. However, the expert panel recommended that further data on PFAS levels in food and in humans would be desirable, particularly with respect to monitoring trends in exposure and results from this survey have been forwarded to EFSA

Overall, the survey shows that Irish produce contains low amounts of the persistent bio-accumulative toxicants measured in this survey, however levels observed do not raise concern for human health.

[1] For further information see here: http://chm.pops.int/Convention/tabid/54/language/en-US/Default.aspx#convtext

ABBREVIATIONS

ABBREVIATION	FULL NAME
B.W.	body weight
BTBPA	Bis(246-tribromophenoxy)ethane
DAFF	Department of Agriculture, Fisheries and Food
EC	European Community
EFSA	European Food Safety Authority
FSAI	Food Safety Authority of Ireland
HSE	Health Service Executive
JECFA	FAO/WHO Joint Expert Committee Food Additives and Contaminants
K_{ow}	The octanol-water partition coefficient is the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature.
LOD	Limit of Detection
LOQ	Limit of Quantification/Quantitation
LOWER-BOUND	Analytical results reported below the LOD set at zero
MI	Marine Institute
NG	nanogram (0.000000001 g)
PG	picogram (0.000000000001 g)
PPB	parts per billion (equal to ng/g or µg/kg)
PTMI	Provisional Tolerable Monthly Intake
SCF	Scientific Committee of Food
SFPA	Sea Fisheries Protection Authority
TDI	Tolerable Daily Intake
TWI	Tolerable Weekly Intake
UPPER-BOUND	Analytical results reported below the LOD set at the LOD value
W.W.	wet weight or whole weight
MG	microgram (0.000001 g)
Σ	Sum

BACKGROUND

The Food Safety Authority of Ireland (FSAI) has a statutory responsibility to ensure the safety of food consumed, distributed, produced and sold on the Irish market. In this respect, the FSAI co-ordinates the collation of food safety surveillance information from laboratories run by its official agents, the Health Service Executive (HSE), the Department of Agriculture, Fisheries and Food, the Sea Fisheries Protection Authority, the Marine Institute and the local authorities. The FSAI also conducts targeted food safety surveillance in areas where potential safety issues have been identified and/or on food contaminants for which there are currently no testing facilities in Ireland. This report provides the results of a targeted surveillance study on levels of perfluoroalkylated substances (PFAS) in meat, offal, eggs and milk produced in Ireland.

The study was undertaken because of awareness about the possible effects on human health of these biopersistent environmental contaminants, known to be present in a number of foodstuffs, notably fish. Furthermore the aim of this study also was to proactively monitor the Irish food supply for emerging new contaminants, with a view to aid national and international efforts in the management of these contaminants.

Perfluoralkylated substances (PFAS)

Perfluoroalkylated substances (PFAS) is the collective name for a very large group of fluorinated compounds, including oligomers and polymers, which consist of neutral and anionic surface-active compounds with high thermal, chemical and biological inertness. Perfluorinated compounds are generally hydrophobic but also lipophobic and will therefore not accumulate in fatty tissues as is usually the case with other persistent halogenated compounds. An important subset is the (per)fluorinated organic surfactants, to which perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) belong.

PFOS, PFOA and other perfluorinated organic compounds have been widely used in industrial and consumer applications including stain- and water-resistant coatings for fabrics and carpets, oil-resistant coatings for paper products approved for food contact, fire-fighting foams, mining and oil well surfactants, floor polishes, and insecticide formulations. A number of different perfluorinated organic compounds have been widely found in the environment[1].

PFOS has global biospheric distribution, bioaccumulation and biomagnification patterns similar to other persistent organic pollutants (POPs). A recent review provides an up to date reference for sources, fate and transport of perfluorocarboxylates[2] .

The chemicals under consideration are best described as a homologous series of fully-fluorinated carboxylic acids, which can also be present as the sulfonic acids or as sulfonamide derivatives. Various higher molecular weight compounds from which these persistent contaminants are believed to derive in the environment also need consideration. The actual list of chemicals that require monitoring as contaminants or as source pollutants is therefore in the order of 200 individual compounds. Measuring every possible PFAS is unrealistic at this time. The list of priority analytes is generally restricted to the simple carboxylic acids, the sulfonic acids and the amides. In this work we have been restricted by the availability of standards, which led to a selected analyte list of 11 individual PFAS (see Materials and Methods).

For PFOS and PFOA, the European Food Safety Authority (EFSA) derived a human Tolerable Daily Intake (TDI) of 150 ng/kg bw and 1.5 µg/kg bw per day respectively (EFSA 2008).

MATERIALS AND METHODS

Study outline

The present study was undertaken to investigate the current levels of PFAS in Irish meat, offal, eggs, fish, milk and processed products.

For this survey the following types of food samples were collected (Table 1)

Table 1 Food Samples included in this survey

Sample Type/Species	Matrix	Number of Samples	Number of sub-samples per sample
Avian	Meat	6	3-4 retail packets
	Liver	3	10-40 tissue samples
	Eggs	20	24 units
Bovine	Meat	5	2-5 retail packets
	Liver	2	10 tissue samples
	Milk	32	1 (tanker samples)
Ovine	Meat	5	3-5 retail packets
	Liver	3	10 tissue samples
Porcine	Meat	5	2-5 retail packets
	Liver	2	10 tissue samples
Equine	Liver	2	10 tissue samples
Vegetables	Potatoes	2	1kg composite
	Cabbage	1	4 units
	Tomatoes	1	22 units
	Mushrooms	1	5*250g
Processed Vegetables	Baked Beans (canned)	1	5 cans
	Canned Sweetcorn	1	6 cans
	Canned tomato puree	1	12 cans
Cereals	Oatflakes	1	5 retail packets
	Cornflakes	1	5 retail packets
	Bread	1	5 retail packets
	Rice (microwaveable)	1	4 retail packets
Processed Meat	Ham	1	8 retail packets
	Sausages	1	4 retail packets
Dairy products	Butter	5	5 retail packets
	Cheese	1	4 retail packets
Fish	Salmon	5	1 INDIVIDUAL
	Mackerel	3	50 INDIVIDUALS
	Trout	3	44-50 INDIVIDUALS
	Oysters	5	50-100 INDIVIDUALS

Offal, milk and egg samples were supplied by officers of the Department of Agriculture, Fisheries and Food at production level (slaughterhouse: liver, farm/dairy tanker: milk, packing station: eggs), fish and oysters were supplied by the Marine Institute and the remainder taken by officers of the Food Safety Authority of Ireland at retail level.

Analysis of the samples was undertaken by Food and Environment Research Agency (FERA (formerly the Central Science Laboratory (CSL)), York, UK, during 2007-2008 under contract to FSAI.

Analytes included in the survey

PFAS Congeners

No	Class	Abbrev.	Code	Name
1	Amide	C8 Amide	PFOSA	Perfluorooctane sulfonylamide
2	Sulfonates	C4 Sulfonate	PFBS	Perfluorobutane sulfonate
3		C6 Sulfonate	PFHxS	Perfluorohexane sulfonate
4		C8 Sulfonate	PFOS	Perfluorooctane sulfonate
5	Acids	C6 Acid	PFHxA	Perfluorohexanoic acid
6		C7 Acid	PFHpA	Perfluoroheptanoic acid
7		C8 Acid	PFOA	Perfluorooctanoic acid
8		C9 Acid	PFNA	Perfluorononanoic acid
9		C10 Acid	PFDeA	Perfluorodecanoic acid
10		C11 Acid	PFUnA	Perfluoroundecanoic acid
11		C12 Acid	PFDoA	Perfluorododecanoic acid

Analytical methods

Sample preparation

The pooled samples were provided frozen by the Food Safety Authority of Ireland and sent to FERA. The homogenates of the samples were freeze-dried by the laboratory and further homogenized by means of grinding.

Sample Analysis

Samples were analysed by FERA using high pressure liquid chromatography-mass spectrometry following extraction and cleanup using the method of Taniyasu[3]. Full details of the analytical methodology have been published by Lloyd *et al* in 2009[4]. The inclusion of fluorinated chemicals other than PFOS and PFOA was limited by the availability of internal analytical standards.

RESULTS

Table 2 presents concentrations of PFAS congeners measured during this study. Results are expressed as µg/kg fresh weight. PFAS were only detected in 1 egg sample, 9 fish samples and 9 liver samples, and individual results are displayed for these samples.

Table 2 Concentration of PFAS in food expressed as µg/kg fresh weight

Type		N	PFHxA	PFHpA	PFOA	PFNA	PFDeA	PFUnA	PFDoA	PFBS	PFHxS	PFOS	PFOSA	ΣPFCs
Milk		32	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
Egg		20	<1	<1	<1	<1	<1	<1	<1-**1**	<1	<1	<1	<1	**1**
Fish	Mackerel	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	<1	**1**
	Mackerel	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	**1**	**2**
	Mackerel	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**2**	<1	**2**
	Mackerel	1	<1	<1	**2**	<1	<1	<1	<1	<1	<1	**1**	<1	**3**
	Oyster	5	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
	Salmon	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
	Salmon	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	<1	**1**
	Salmon	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
	Salmon	1	<1	<1	<1	<1	<1	<1	<1	**1**	<1	<1	<1	**1**
	Salmon	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
	Trout	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**2**	<1	**2**
	Trout	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**2**	<1	**2**
	Trout	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	<1	**1**
Liver	Avian	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	**1**
	Avian	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	**1**
	Avian	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
	Bovine	1	<1	<1	<1	**1**	**1**	<1	<1	<1	<1	**3**	<1	**5**
	Bovine	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**2**	<1	**2**
	Equine	1	<1	<1	<1	<1	<1	**1**	<1	<1	<1	**2**	<1	**3**
	Equine	1	<1	<1	<1	<1	<1	**1**	<1	<1	<1	**2**	<1	**3**
	Ovine	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**3**	<1	**3**
	Ovine	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**2**	<1	**2**
	Ovine	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
	Porcine	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	**1**	**2**
	Porcine	1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
Meat	Ovine	5	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
	Avian	6	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
	Porcine	5	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
	Bovine	5	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
Processed Meat		2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
Vegetables		8	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
Cereals		4	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0
Dairy		6	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0

A Limit of Quantification (LOQ) of 1 µg/kg (ppb) was achieved for all analytes in all samples. Trace levels of eight of the listed eleven perfluoro target analytes were detected across nineteen of the separate food samples (9 fish, 9 livers and 1 egg). The highest individual measurements were 3 µg/kg of PFOS in two liver samples.

The highest total PFAs measurement (sum of all individual analytes and setting non-detects at zero) was 5 µg/kg, in a bovine liver.

DISCUSSION/CONCLUSIONS

These measurements indicate a low level of contamination by PFAS in the Irish food chain and are comparable to other countries that have conducted similar studies[5,6,7,8].

In 2008, the European Food Safety Authority (EFSA) derived a human Tolerable Daily Intake (TDI) for PFOS of 150 ng/kg bw per day and a ten-fold higher human TDI for PFOA of 1.5 µg/kg bw per day and concluded that the general population in Europe is unlikely to suffer negative health effects from PFOS and PFOA as the dietary exposure to these chemicals is below their respective TDIs. However, the expert panel recommended that further data on PFAS levels in food and in humans would be desirable, particularly with respect to monitoring trends in exposure and results from this survey have been forwarded to EFSA. The collected data will be collated, analysed and summarised by EFSA into an intermediate report (January 2011) and a final report (May 2012).

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Abbey Court,
Lower Abbey Street,
Dublin 1.

Advice Line: 1890 336677
Telephone: +353 1 817 1300
Facsimile: +353 1 817 1301
Email: info@fsai.ie
Website: www.fsai.ie