SURVEY OF PFOS AND RELATED FLUOROCHEMICALS IN FOOD

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SUMMARY

1. An improved analytical method was developed and validated for the determination of PFOS and related fluorochemicals. This method delivered reproducible analyses at low levels (1 µg/kg RL) in all foods for the 11 selected analytes.

2. This method was then applied to the analysis of an initial 199 individual food samples.

3. PFOS and PFCs were found mainly in the fish, shellfish, crustaceans and offal food groups.

4. A further 53 food samples of fish, crustaceans and offal were then obtained and analysed.

5. This survey of 11 fluorochemicals in each of 252 individual food items is almost certainly the largest single study of the occurrence and levels of PFOS and PFCs in foods undertaken to date.

6. No samples were found in this survey of UK food that might be considered to be 'highly contaminated' with PFCs.

7. The two highest contamination levels were for PFOS at 60 µg/kg in a sample of smoked eel, and at 40 µg/kg in a sample of whitebait. The highest level in an offal sample was 10 µg/kg in a wild Roe deer liver.

8. The 8 samples with total PFCs at >15 µg/kg were all in the fish group where contamination was expected (fish, shellfish, crustaceans). 5 samples (including a liver) contained 5-14 µg/kg. 14 samples (including liver and kidneys) contained 5-9 µg/kg. A further 26 samples (fish and offal) contained 3-4 µg/kg and 23 samples (including eggs, processed peas, popcorn and potatoes) contained 1-2 µg/kg.

9. Primary food produce such as meat, milk, cereals, vegetable and fish oils, fruits and vegetables were essentially free of PFC contamination.

1. List of Contents

INTRODUCTION

1.1 PFOS is now the generally accepted term referring to the individual chemical perfluorooctanesulfonic acid and any closely related compounds that contain the PFOS moiety ($C_8F_{17}SO_2$), including those that may potentially degrade to PFOS in the environment (Brooke 2004). This term is often used interchangeably with other similar acronyms: PerFluoroOrganic Substances (PFOS), PerFluoro Compounds (PFCs), or PerFluoroAlkylated Substances (PFAS). The chemicals under consideration are best described as an homologous series of fully-fluorinated carboxylic acids, and these can also be present as the sulfonic acids or as sulfonamide derivatives. Various larger 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 PFC 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 PFCs (Table 1).

1.2 PFCs are, or have been used extensively as surfactants and in the industrial polymers (Teflon®, SilverStone®), waterproofing agents (Gore-Tex®), stain repellents (ScotchGard, Stainmaster®), fire-fighting foams (AFFF) and in greaseproof food packaging materials (Zonyl®)(Figure 1).

1.3 While other molecular constituents can be removed by standard metabolic pathways, and there are believed to be important introversions of larger to smaller molecular weight PFCs (Figure 1). The high-energy carbon-fluorine covalent bond strength is too strong for metabolic processing. This means the core PFOS group is resistant to hydrolysis, photolysis, and microbial or mammalian metabolism. PFOS is therefore not degradable and bioaccumulates in the environment, probably by means of covalent protein binding.

1.4 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 (Prevedouros 2006). Various regulatory limits for acceptable levels of PFOS in the environment are being discussed.

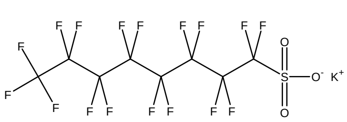
1.5 Although PFCs are only moderately toxic, they have been show to induce a number of adverse effects in experimental animals. PFCs are now known to also be endocrine disruptors (Leydig cell hyperplasia, lower testosterone levels) (Jensen 2008).

1.6 The monomers and low molecular weight products are liquid surfactants in solution, while the higher molecular weight oligomers, polymers and esters are used for treatment of solid surfaces such as fabrics and paper. *N*-Ethylperfluorooctanesulfonamide is also an insecticide (Sulfuramid) registered for use in the USA and New Zealand (Figure 1).

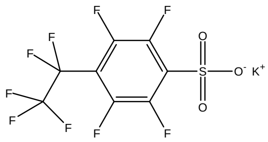
1.7 A number of new food-packaging fluorochemicals are replacing older, C_8-based PFCs. DuPont are the largest global manufactures and suppliers of fluorotelomer products and have recently announced the release of a new PFOS/PFOA replacement, the Capstone^{TM} product range with the concurrent elimination of residual C_8 contamination in all products and processes. This represents a complete switch to short-chain chemistry including C_6-sulfonic acid, acrylate, amine-oxide, and betaine products from the previous C_8 products. A selection of structures representing the diverse range of chemistry in use and the putative telomers from which they are derived is shown in Figure 2.

1.8 Much larger molecular weight products continue to be introduced to the global market place. As an example, of the complexity of these products, Ciba Lodyne 5100 is a poly-perfluoroalkylated polyamino acid, a fluoroprotein (FP) fire fighting foam. These products can contain: a protein hydrolysate, a fluorinated cotelomer that has a perfluoroalkyl radical, a polymerised chain consisting of units of an anionic hydrophilic monomer, a non-ionic hydrophilic monomer, and a fluorinated surface-active agent. These film-forming emulsifiers are effective against hydrocarbon fires and polar-liquid fires. The protein base provides a tough cohesive foam blanket with high resistance to heat that quickly smothers, cools, and seals. Fluorochemical surface-active agents combined with the protein base increase the fluidity and fuel repellency of the foam.

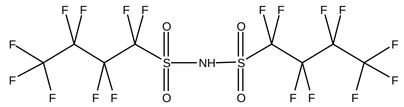
1.9 As an example of the technical difficulty of the ongoing phase out of PFOS, the aviation industry has been seeking to replace PFCs in hydraulic fluids, with little hope of success. Fire resistant hydraulic fluids based on phosphate ester chemistry were developed in 1948, resulting in a step change in aircraft safety, with the virtual elimination of hydraulic fluid fires in aircraft. Servo valves however experienced corrosion, and the use of additives such as the potassium salts of the perfluorinated anionic surfactants PFOS and it's isomer ρ-perfluoroethylcyclohexanesulfonic acid are critical in altering the electrical potential at the metal surface thus preventing electrochemical oxidation. It is understood that 2,500 alternatives, such as an oligomer of the smaller non-toxic C_4-homologue potassium bis(perfluorobutanesulfony)imide have so far been investigated.



PFOS-K



p-PF-EtcHxS-K

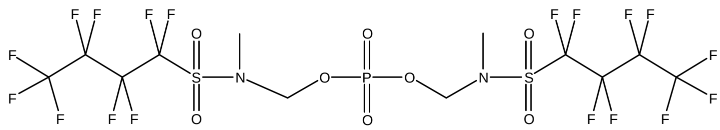


b(PFBSA)

1.10 Detailed knowledge relating to the final formulation chemistry and relative usage rates is scarce. In UK the main uses of PFCs in [400 t in 2001] were: waterproofing of textiles and fur products [195 t] and paper products [60 t], outdoor activities [70 t], flame retardants [65 t], others [10 t] (Brook 2004). Global usage peaked at *ca*. 3500t PFOS and 500t PFOA in 2000.

1.11 With the cessation of manufacture and sale of many PFC products, such as Class B fire fighting foam [AFFF], usage has reduced. The 2006 global usage survey suggest that in 2005 PFOS manufacture/import was reduced to no more than 162t, for industrial processes that are exempt from legislation. In order of relative importance, these were: sulfonyl fluoride [PFOS-F 90 t] as chemical intermediates, the tetraethyl ammonium salt [PFOS-TEA 50 t] and the potassium salt [PFOS-K] as mist suppressing agents in mining, the lithium salt [PFOS-Li 20 t], free PFOS as an antireflective agent in photography, and a sulfonamide [N-EtPFOSA 17 t] used as an insecticide. Other uses of less than 10t are photo-microlithography (semiconductors), hydraulic fluids, metal plating, and anti-foam agents in the fire-fighting industry. New uses of PFOS are still allowed and less than 1t of *N*-ethylheptadecafluoro-*N*-[3-(trimethoxysilyl) propyl] was reported to have been used as an additive in toner or printing inks (Figure 2, FC 405-60).

1.12 Up to 160 t of PFBS (C_4) based substances were used in 2005, these were based on the potassium salt [PFBS-K], the fluoride [PFBS-F] and 20-50 kg of a new oligomer (below).



bis-[2-(N-methylperfluorobutane sulfonamido)ethoxy] phosphoric acid

1.13 Use of perfluorocarboxylic acids, such as perfluorooctanoic acid (PFOA), remains higher than for PFOS.

1.14 Any global shift in the industry from C_8-chemistry to new products such as C_6- and C_4-based substitutes will be mirrored in human exposures, which will need to be assessed with new analytical methods for detection of both 'old' and 'new' PFC analytes.

Current knowledge of the occurrence of PFCs in food

1.15 To date there have been very few studies determining PFCs in the human diet. The current study is the most comprehensive to date.

1.16 The prevalence of PFOS and it's impact on the wider human food chain only became apparent when the 3M Multi-City Study reported four of the twelve positive food residues were from the control cities, i.e., those without a fluorochemical industry. Of the 200 individual foodstuffs; green beans, apples, cow's milk, bread and ground beef were found to contain PFOS/PFOA. While the highest individual measurement of PFOS was only 0.9 µg/kg, the widespread distribution of this contamination was immediately considered to be of major importance (3M Company, 2001).

Data accuracy

1.17 The technical difficulties in producing accurate data for these challenging analyses cannot be overstated. Even when examining peer-reviewed data, extreme caution should be exercised in judging the applicability of the methodology used for each analysis.

Dietary intake studies

1.18 The emerging data on the concentrations of PFCs in food throughout the world are forming a picture of a generally low-level contamination in the wider diet, but with individual "hot spots" occurring within the fish and offal food groups. A survey of Swedish total diet study (TDS) food composites focused on what were suspected as the four most likely food groups to be contaminated; meat products, dairy products, eggs and seafood. This survey did not turn up any positive residues and reported less than LOQ (2.2, 3.2 µg/kg PFOS and PFOA respectively) for all food samples surveyed. Individual fish samples were found to contain up to 23 µg/kg PFOS (Berger 2007). A Spanish survey of composite foodstuffs found numerous traces of PFOS with a maximum of 0.8 µg/kg (Ericson 2008). A larger Canadian TDS study reported a maximum level of 5 µg/kg perfluorononanoic acid (PFNA) in beefsteak. PFOS was measured at 2.7

µg/kg in beefsteak, 2.6 µg/kg in marine fish, 2.1 µg/kg in ground beef and 2.0 µg/kg in freshwater fish (Tittlemeir 2007). A large 7-day duplicate diet study in Germany reported the average values from 214 separate daily diets collected from 31 adults as 0.06 and 0.69 µg/kg for PFOS and PFOA, respectively (Fromme 2007). For adults consuming 2.5 kg of food (solid and liquid) this represented mean daily dietary intakes of 0.12 and 0.27 µg of PFOS and PFOA, respectively. The duplicate diet collection model was therefore not dissimilar in outcome to TDS model in the intake estimates. Of interest in this study was the detailed analysis of each day's food where just two PFOA values were unusually high. The larger of these was a concentration of 118 µg/kg in the daily diet. This one-off high value was undoubtedly from smaller portions of a single discrete foodstuff containing at least a one order of magnitude higher concentration. This again is consistent with the emerging knowledge on upper-end mg/kg contamination levels in some European freshwater fish from industrialised areas.

1.19 In order to put European and UK data into context, recent work in Japan (Guruge 2008) reported cattle, pig and chicken livers to contain mean PFOS concentrations of 34, 54 and 67 µg/kg, respectively, with the highest individual PFOS value at 92 µg/kg in a chicken liver. Chinese chicken eggs were all found to contain PFOS in the range of 45-87 µg/kg (Wang 2008)

PFOS in European fish

1.20 Evidence from a number of papers demonstrates that fish is probably the primary source of dietary exposure to PFCs. There is now a wide range of literature covering concentrations in predatory birds and animals from the highest trophic levels, particularly those from the polar-regions where fish is a key component of their diet. Data on retail products is still rather sparse. EFSA have recently completed a scientific opinion of PFOS/PFOA contaminants in the food chain (EFSA-Q-2004-163, 2008), some of which has been summarised in the following two paragraphs.

1.21 PFOS concentrations in shrimps in the Western Scheldt and the Belgian part of the North Sea ranged from 19–520 µg/kg, the highest mean concentration (319 µg/kg) being in samples taken from the Western Scheldt, close to Antwerp. The mean PFOS concentrations in crab (*Carcinus maenas*) tissues ranged from 93 to 292 µg/kg. In bib (*Trisopterus luscus*) the highest value of 111 µg/kg, was for specimens caught in the Western Scheldt. The PFOS concentration in samples from the coastal region were higher than in those from open water. Fillet of flounder (*Platichthys flesus*), again from the Western Scheldt, appeared to be the most contaminated with PFOS levels in the range of 93–230 µg/kg. Pikeperch (*Sander lucioperca*) fillets from two areas of water in the Netherlands contained PFOS in the range 40–150 µg/kg. In North Sea herring (*Clupea harengus*) and mackerel (*Scomber scombrus*), PFOS levels were 7.8–51 and 7–22 µg/kg, respectively. PFOS was detected in mussels (*Mytilus galloprovincialis*) from Portugal estuaries in the range of 39–126 µg/kg. PFOS was found in several fish specimens from Lake Vättern (Sweden) and the Baltic Sea, where the levels fell within the ranges 1–23 and 0.5–3 µg/kg, respectively.

1.22 PFOS has been reported in liver samples abstracted from several fish species from different European areas. High PFOS levels, up to 3800 µg/kg were found in livers from sea bass (*Dicentrarchus labrax*), from the Western Scheldt. Plaice and flounder livers from the Western Scheldt also contained PFOS at 730 and 540 µg/kg, respectively, whilst sole (*Sola sola*) liver from the North Sea contained 130 µg/kg. In livers of several marine and fresh water fish species from the Nordic regions, PFOS varied widely from 0.85–551 µg/kg. Liver samples from perch (*Perca fluviatilis*) and pike (*Esox lucius*) caught in Swedish and Finnish waters, showed PFOS at levels >100 µg/kg. Mediterranean fish livers were also quite wide ranging from <1–87 µg/kg.

1.23 In Belgium, PFOS has been measured in eel livers between 1024-9031µg/kg from the Ieperlee canal at Boezinge, downstream of the industrial zone of Ypres. Carp livers from the Blokkersdijk pond nature reserve in the vicinity of a fluorochemical production facility contained 250-781 µg/kg PFOS (Hoff 2005). In both eel and carp the PFOS concentrations in the livers correlated with a biomarker for hepatic damage; serum alanine transferase activity, suggesting these European freshwater fish have been exposed to sufficiently high levels of PFOS to induce liver damage.

1.24 Wood mice from this same area, the Blokkersdijk nature reserve, were severely contaminated, with the liver from one mouse found to contain 178,550 µg/kg of PFOS, the highest naturally incurred level recorded to date (Hoff 2004).

1.25 Seafood has been found to highly influence human body burden of PFHxSH, PFOS, PFOSA, PFHxA, PFHpA, PFNA, PFDA, PFUnA, and PFDoA, and to a lesser extent PFOA. Individuals with a high fish intake in their diet (mainly Baltic fish), on average had the highest levels of all 10 fluorochemicals when compared with the other subpopulations (Falandysz 2005).

Temporal trends

1.26 Increases in exposure levels globally, has led to elevated circulatory concentrations of PFOS in mammalian plasma. This upward trend is believed to have been apparent for some decades. Aside from industrial exposure, it is not yet clear as to the exact mechanisms of exposure to specific chemicals and their precursors (Figures 1 & 2), or their relative significance, e.g. via household and consumer products *vs* food. 3M, the major producer, had reduced PFOS production by 98% at the end of 2000 (equivalent to an 88% reduction global production), with cessation in 2002 (Olsen 2008, Spliethoff 2008).

1.27 An elegant experiment demonstrating a temporal trend in the human food chain, used guillemot eggs obtained from a Baltic island. This island was free of local contamination. The guillemots feed on fish from the Baltic Sea. The Baltic Sea has a large terrestrial drainage basin, with high anthropogenic input and a low outflow, thus the concentration of PFOS in the eggs reflects the general level of contamination in the Baltic region. The concentration increasing from 17 μg/kg in 1968 to 623 μg/kg in 2003. This follows an almost linear rise of 18 μg/kg/per year between 1968-2003. This suggests an almost constant input over the 35 years resulting in a 30-fold increase and is one of the clearest examples of a temporal trend of increasing PFOS concentration in commodities, both fish and gulls eggs, that are caught and collected for human consumption (Holmstrom 2005).

1.28 The global regulation of PFOS/PFOA together with the voluntary change to alternative products that is already well underway in Westernised countries, should result in a decline in environmental contamination and hence human exposure. However, as yet there are no global data that can be used to demonstrate such a downward trend. However, in the last few months the first localised declines in human exposure have been published. American blood samples were once the most highly contaminated in the world. For American Red Cross blood donors (Olsen 2008) and in new born infants in New York State. (Spliethoff 2008), PFOS levels appear to have peaked, and are now declining rapidly in line with the previously reported half-lives from occupational exposure studies.

Declining human exposure

1.29 Declines in US exposure to PFCs appear to have quickly followed the fall in US production. However this is not the case globally. PFOS levels appear to be continuing to increase in blood taken from Chinese citizens. It is thought that PFOS is still manufactured in China. Chinese chicken eggs (pools of eight samples from eight cities) were all found to contain PFUnA and PFOS, 75% contained PFOA and half contained PFDA (Yuan 2007).

Literature methodology

Extraction methods from the literature

1.30 Methods for the analysis of PFCs were reviewed recently (de Voogt 2006). The majority of environmental analyses conducted to date have used an ion-pairing extraction method (Hansen 2001, Guruge 2008). An aqueous homogenate with basic ion pairing extraction reagent (IPE) is partitioned into MTBE. This may be complemented with further clean-up steps such as sonication and shaking with methanol and activated carbon. This can be followed by dilution of the methanol extract and before weak anion exchange SPE (Yeung 2008). Lipid removal by normal phase SPE can be used if PFOSA is not required (Orata 2008). Simple extractions using aqueous ammonium acetate have been used for samples from single food groups, such as liver, followed by molecular weight cut-off filtration and these have been shown to work well for some analytes in biota (Berger 2005).

1.31 Food samples, especially composites, may be exceptionally problematic and it is widely recognised that these often require a more extensive clean-up and matrix removal than when dealing with, for example, individual wildlife samples. For animal livers, the IPE solution was analysed without further cleanup (Guruge 2008). The Canadian TDS study used a simple methanol extraction and ultracentrifugation without cleanup (Tittlemeir 2007). The German Duplicate Diet Study used sequential aqueous and methanol extractions, a five-fold dilution of the combined extracts with water and weak anion exchange SPE (Fromme 2007). The Swedish TDS study used acetonitrile extraction, acetic acid and carbon treatment of the acetonitrile extract. A dilution and precipitation with aqueous ammonium acetate was conducted before analysis of food extracts (Berger 2007). The Spanish TDS study involved aqueous sodium hydroxide treatment of freeze dried foods, followed by a methanol extraction, neutralisation, centrifugations and dilution with water before SPE. The basic eluent from the anion exchange SPE was pH adjusted and treated with carbon (Ericson 2008).

Future approaches: Exhaustive Fluorine Characterisation

1.32 Fluorine analysis can be used to show that only a modest portion of the ion-pair reagent-MTBE extractable organic fluorine (EOF) in liver is accountable as the sum of the measurement of the individual PFC analytes. Meaning that most of the PFCs present are not actually being measured by the target analyte approach (Yeung 2008A EP). A study of seawater from coastal Japan 60-90% of the measured organic fluorine was unaccounted as individual PFCs (Miyake 2007). Human blood show high variability with known PFCs accounting for >80% of EOF in the US and Japan. In the Jintan region of China the proportion of measured vs EOT was only 30%, suggesting the presence of unmeasured fluorinated organic components (Yeung 2008B EST). This novel approach has huge potential to be coupled with HPLC fractionation and TOF-MS for conducting exhaustive fluorine characterisation of highly contaminated samples. This knowledge will be particularly useful in identifying which analytes are of importance and should be included in the next generation of MS/MS measurement methods.

METHOD DEVELOPMENT, VALIDATION AND SURVEY CONDUCT

Instrumentation

Chromatographic separation

2.1 A number of HPLC columns have been reported in the literature for the separation of PFCs. However, most authors have restricted the scope of their methods to a few key analytes. The standard C_{18} phases retain the larger, e.g. C_{18} acids, but these are often not adequately eluted using a 100% organic mobile phase. Where they do not fully elute with an 100% organic mobile phase, peak-broadening reduces LC-MS sensitivity and hinders accurate quantification. Changing to specific C_8 phases allows these larger acids to be eluted earlier using an aqueous to organic gradient with less peak broadening. For example, the Waters BEH phase was selected for use in our earlier project.

2.2 Two new fluorinated stationary phases; perfluorooctyl (Benskin 2007) and pentafluorophenyl-ethyl are now available. These separate analytes by fluorine content, as well as conventional reverse phase mechanisms. The perfluorooctyl phase was used in all current analyses, unless stated otherwise. Problem samples, which required a different elution order of the matrix interferences and analytes were reanalysed using a C_8, pentafluorphenyl-ethyl phase column.

2.3 It is critical that pure solvents, especially the aqueous phase are used to prevent any on-line concentration effects that could result in analytes concentrating on the front end of the analytical column during equilibration, which are then released when the organic content is increased during the elution cycle.

2.4 A chromatographic method was developed which retains and separates all of the perfluorinated carboxylic acids (from C_6-C_{12}) and the other selected analytes. The HPLC and guard columns chosen were Fluorosep RP Octyl (5 µm, 60 Å, 2.1 x 150 mm) thermostatically operated at 30 ^{o}C. The injection volume was generally 10 µl. The gradient programme (methanol: aqueous ammonium formate, 5 mM, pH 4) was: 10% methanol increasing to 30% at 0.1 min (linear gradient), to 75% at 7 min and 100% methanol at 10 min, this was held for 5 min (column washing), then decreased to 10% methanol at 15.1 min, and held for 4.9 min at 10% methanol (column re-conditioning). The eluate was diverted to the mass spectrometer between 7 and 19.5 min, and from 0-7 and 19.5-20 min it was diverted by valve switching to waste in order to protect the ion source. The retention times for analytical standards are given in Table 2.

Detection and Determination

2.5 A CTC Pal autosampler (Presearch, UK) and an HP1100 HPLC system with column oven (Agilent, UK) were coupled to an API4000 triple quadrupole mass spectrometer (MDS Sciex Instruments, UK). Analyst 1.4.2 software was used for instrument control, file acquisition and data processing. The MS detector was used in MRM with a Turbo Ion Spray source for quantitative analysis. All transitions were acquired simultaneously. The primary and qualifying ions are presented in Table 2. Data acquisition was conducted in one simultaneous acquisition schedule without separation into chromatographic acquisition windows. The instrumental parameters of the MS detector were optimized by infusing standard solutions (1 µg/ml in 1:1 methanol: aqueous ammonium formate 5 mM, pH 4). Final Turbo Ion Spray (TIS) conditions were; turbo-gas 50 psi, curtain-gas 12 psi, nebuliser-gas 50 psi, desolvation temperature 450 ^{o}C.

2.6 Detection parameters for each individual analyte were determined and are summarised in Table 2.

Samples

2.7 The sampling plan for this survey was drawn up by Ventress Technical Limited (VTL 2008), who also supplied the samples for Phases 1 and 2. Two hundred fresh food samples were provided for analysis (Phase 1). These were split between linked FSA projects. For the work reported here *ca*. 400 g of each was homogenised and portions were extracted without further treatment such as freeze-drying. Subsequently a second set of 53 samples was provided (Phase-2).

2.8 These foods are briefly described in Tables 5 & 6. Phase–1 was selected to cover all the foods where PFOS might be present. Phase-2 sampling was designed to target only those groups or individual foods where contamination was found in Phase-1 to confirm and expand on the Phase-1 results.

2.9 All other food samples and reference materials referred to in this report were obtained locally by the authors and were used for method development and validation.

Chemicals

2.10 A summary of the chemicals used as analytical standards, their common names, abbreviations, molecular weights, suppliers and stated purities are given in Table 1. As the purities were all stated as being >95%, no correction was necessary. The 17 chemicals measured (11 analytes plus 6 internal standards) were checked for any cross-contamination and the results are presented in Table 3.

2.11 Any other solvents and chemicals were of reagent or specific LC-MS grade.

Extraction method

2.12 After numerous experiments it was concluded that no one simple procedure was adequate for all types of samples. As we believed the sodium hydroxide digestion and anion exchange treatment of the basic aqueous extract to be a major advance in sample clean-up, over the more widespread ion-pairing extraction process, we pursued this approach (Taniyasu 2005). Thus the sample extraction and presentation to SPE became a multi-step. It was eventually found that extraction into methanol, drying down the methanol and reconstituting in the sodium hydroxide digestion reagent was a suitable generic approach for most foods.

2.13 Our final method was as follows: Quadruple 10 g portions of each food were weighed out into 50 ml Falcon tubes, (the various internal standard (IS) and standard additions were added at this point) in order to prepare two blank portions, one overspiked at the reporting level (RL = 1 µg/kg), and one portion at 10-times the RL (10 x RL =10 µg/kg). These portions were homogenised in 20 ml of methanol with an Ultra Turrax (T25 basic with S25N blade). When homogenised, more methanol was added (*ca.* 40 ml in total) and mixed. Samples were shaken vigorously overnight (16 hr), and then centrifuged (15 min, 5000 rpm) (Tittlemier 2007). For eggs and milk, heating at 70 ^{o}C for 2 hr was required to induce protein precipitation. The supernatant methanol extract was dried under a nitrogen stream (80 ^{o}C) just to dryness and the residues were re-dissolved in aqueous KOH (25 ml, 0.01 M, and sonicated for 10 min). The aqueous solutions were centrifuged (15 min, 5000 rpm). Where floating matter/fat were present, the supernatants were poured in one continuous gentle movement, to avoid disturbing the sediment or breaking up the floating material, into a funnel connected onto the top of a preconditioned SPE cartridge (weak anion exchange)(Taniyasu 2005). Where clear solutions with no floating matter were obtained, these were simply added in repeated ca. 5 ml portions to the cartridges as the eluent went through (to *ca*. 1 ml remaining). Cartridges were loaded at a constant flow rate by increasing from gravity feed to full vacuum as required. After loading, cartridges were washed with ammonium acetate (2 x 6 ml, 25 mM, pH 4.5) and eluted with basic methanol (4 ml, 0.1% ammonia). The eluates were dried under a stream of nitrogen gas (30 ^{o}C), until just dry, and the residues taken up in methanol (400 µl, sonicated for 10 min). Extracts were transferred into silyanised glass microvials (300 µl) for determination by LC-MS/MS.

2.14 Analysis of these extracts, using an API400 LC-MS/MS system generally gave the low limits of quantification (RL 1 µg/kg) required.

Fluorous liquid-liquid extraction

2.15 The analysis of cheeses was particularly problematic, due to the excessive amount of material (*ca*. 50 mg) left after the standard clean-up. This resulted in poor chromatography and blockages. The clean-up method was therefore extended. The residue was halved by utilising the elution of neutral amides off the SPE in methanol (4 ml, neutral pH), and then treating this fraction as separate extracts. Acids, both sulfonic and carboxylic were then eluted as before, using basic methanol (4 ml, 0.1% ammonia). Each fraction still contained *ca*. 25 mg of coextractives.

2.16 A fluorous solvent mixture was then used to partition fluorinated from non-fluorinated materials by liquid-liquid extraction (F-LLE). Residues from the weak anion exchange SPE (neutral or basic) steps were dried under a stream of nitrogen gas (30 ^{o}C), until just dry, and then redissolved in dichloromethane (10 ml, DCM saturated with water) by sonicating for 10 min. Trifluoroethanol (7.5 ml) and perfluorohexane (FC-72, 2.5 ml) were added, and the mixture was shaken (1 min) then sonicated for 10 min. When the residues were in solution, this triphasic system was heated to 80 ^{o}C for one hour to achieve a monophasic mixture. The mixtures were then cooled to –70 ^{o}C for one hour and the upper 10 ml of DCM was pipetted out and discarded as the non-fluorinated fraction. The lower two fluorous layers were pipetted out together and dried under a stream of nitrogen gas (30 ^{o}C), until just dry, and the residues taken up in methanol (400 µl, sonicated for 10 min). Extracts were transferred into silyanised glass microvials (300 µl) for determination by LC-MS/MS.

Contamination control

2.17 Constant care was required throughout the whole method in order to minimise possible contamination. PFOS can in be present in fluorinated plastics, cleaning products and dust. Contamination readily transfers, by both deposition from the air, and surface-to-surface contact.

2.18 The extraction and clean up procedures prior to LC-MS/MS determination were all conducted in a dedicated laboratory. The preparation and storage of stock solutions, dilution of these to working solutions of mixed standards and the overspiking and low-level food extraction processes were performed on separate laboratory benches. All glassware was scrupulously cleaned. Large items and volumetric flasks by repeatedly washing with methanol, whilst all smaller items including beakers, vials and Pasteur pipettes by muffling (wrapping in aluminium foil and baking to volatilise any organic matter by heating to 500 ^{o}C for 16 hr). Clean glassware was kept stoppered or wrapped in foil until required. All contact with samples was with glass Pasteur pipettes in place of spatulas, e.g. for weighing out reagents and food. All vial tops, plastic disposable pipette tips, single use polypropylene tubes (50 ml) were kept sealed at all times when not in use. Chemical bottles and Winchesters of solvent were reserved for this project only, and were only sampled by direct decanting or intermediate transfer from muffled glassware.

2.19 A procedure for preparing concentrated stock solutions, assessing these for the absence of contamination and preparing dilutions of these as required, eliminated the majority of sample batches becoming contaminated. Any abnormal results were usually single sample contaminations, and when these occurred the appropriate samples were rehomogenised and reanalysed until repeatability was achieved.

Analytical quality control

2.20 Stock standard solutions were prepared at 1 mg/ml in methanol and stored at ambient temperature. Dilutions of these were prepared fortnightly to minimise any possible binding to the surface of the glassware, or concentration effects due to solvent evaporation.

2.21 Working solutions of mixed standards were prepared at 5 and 0.5 µg/ml in methanol for spiking. Foods (10 g) were spiked at 1 and 10 µg/kg (ppb) by addition of 20µl of 0.5, or 5 µg/ml working standard solutions. Tetrahydro-

PFOS (TH-PFOS), $^{13}C_4$-PFOA, $^{13}C_4$-PFOS, $^{13}C_2$-PFDeA, D_9-*n*-Et-FOSE and D_3-*n*-Me-FOSEA were used as internal standards by addition of 200 μl of 0.5 μg/ml of a mixed solution, a spiking level of 10 μg/kg.

2.22 Each food sample was analysed in duplicate and taken through the entire extraction procedure to ensure that laboratory contamination was not mistaken for the presence of native analyte. Each sample was also overspiked at two concentrations (1 & 10 μg/kg). In order to prove the absence of a given analyte, the relevant internal standard had to be demonstrated to be present in all extracts; the blank extract had to be PFC free, and the overspiked extracts had to produce a peak for the target analyte at the appropriate retention time. As the different foods behave differently with respect to extraction, recovery of analytes through the SPE stages, and matrix induced suppression of ionisation, a single LOQ for all foods or all analytes was not achievable, even though the same extraction procedure was used. An inspection of each chromatogram was undertaken to estimate an LOQ for each individual target PFC. The LOQ's varied considerably for the different PFCs within a single food type and between different food types (Table 2).

Method validation

2.23 Linearity of instrument response was excellent for all target PFCs. For replicate injections of the same sample of the MS instrument, RSD's of <10% were achieved.

2.24 The various extraction and cleanup sets were assessed for robustness.

2.25 Volatility was assessed by heating and concentration of methanol solutions under a stream of nitrogen gas.

2.26 SPE was assessed by studying other similar cartridges and assessing which gave quantitative recovery of each of the analytes. Any deviation of >10% from nominal was considered unacceptable.

RESULTS AND DISCUSSION

Misreporting of taurodeoxy cholic acid (TDCA)

3.1 Although LC-MS quantification of PFOS is now a common procedure, ionisation suppression problems and coelution issues with liver, and particularly egg extracts, make it difficult to report precise and accurate concentrations. There is still systematic misreporting of interferences for PFOS and possibly PFHxS. Care has been taken in this work to eliminate the possibility of missidentifying any known interferences as PFCs.

3.2 Hansen (2001) noted that the *m/z* 499/80 transition ($[M-H]^- \rightarrow 80\ [SO_3]^-$) provided a stronger signal than the *m/z* 499/99 transition ($[M-H]^- \rightarrow 99\ [SO_3F]^-$) for PFOS in animal tissues, but an unidentified interferent was also present and therefore the transition *m/z* 499/99 was used. As PFOS is measured at *m/z* 498.905 and TCDA at *m/z* 498.286, a difference of 0.619 Da, even low resolution TOF MS instruments are able to discriminate between these two compounds (de Voogt 2006). The co-eluting interferent of PFOS was identified as the bile salt taurodeoxycholic acid (TDCA). Both compounds are sulfonic acids with an *m/z* 499/80 transition (Benskin (2007). We have confirmed this assigment (Figure 10). As the primary cause of this quantification difficulty was co-elution, when this interference was identified, an alternative separation procedure was developed using a linear perfluorooctyl (PFO) stationary phase to ensure separation before quantification.

3.3 The optimal sensitivity of PFOS using LC-MS/MS is achieved using the $[M-H]^- \rightarrow 80$ transition $[SO_3]^-$. Specificity at the expense of sensitivity is achieved through the use of the less responsive $[M-H]^- \rightarrow 99\ [SO_3F]^-$ transition, which is more specific and can only arise from fragmenting a fluorinated molecule.

3.4 As an illustration of how PFOS values of *ca.* 200 μg/kg are being missreported [American Chemical Society, 23 July 2008, 10.1021/es800770f], Figure 10 shows the chromatograms of resolved PFOS and TDCA peaks obtained using the perfluorooctyl stationary phase. We first confirmed the identities of TDCA and PFOS, and then the presence of TDCA in eggs by a separate LC-TOF-MS experiment using authentic analytical standards of each. With LC-MS/MS using the qualifying ions, the relative size differences between the true PFOS peak responses [naturally incurred and overspiked] at 11.85 min in both the channels 499/80 and 499/99, and the true PFOS concentration of 0.2 μg/kg was calculated and confirmed. The response of the +10 overspiking level is then used in a single point comparison to obtain an estimated value of 215 μg/kg for “missreported” PFOS. Laboratories relying on a standard C_8 or C_{18} stationary phase column and an LC-MS instrument lacking the specificity of MS/MS, or high resolution MS (TOF), will therefore, in this example, invariably missreport TDCA as 215 ppb of PFOS.

3.5 We observed large isobaric interferences [TDCA] in all liver, kidney, chicken, beef, lamb, whitebait, sardines, herring, mackerel, and cod-liver oil samples. Other foods such as vegetables, eel, salmon, shellfish, butter, pork and milk contained much lower levels of intereferences and other foods were generally free of this interference. It is therefore essential to use the perfluorooctyl (PFO) stationary phase when determining PFOS in animal and fish products.

Other recent studies

3.6 The current work should be viewed in the context of other recent UK work. The Greenpeace survey of European eel livers followed up the ion-pairing-extractions (IPE) with a silica defatting clean-up (Law 2008, Greenpeace 2006). The normal phase defatting process removes neutral amides, such as PFOSA.. LOQs ranged from 16-162 μg/kg. PFBS could not be quantified due to analytical interferences. Unusually high PFHxS values were reported (up to 583 μg/kg), with a proviso that there is a possibility that these may be analytical intereferences. The detection system for PFHxS was a single MS (SIM), not MS/MS. The method failed on the Italian eel sample. The UK pooled eel livers from Canvey Island in the Thames were reported to contain 248 μg/kg PFOS, 83 μg/kg PFHxS and 92 μg/kg PFDoA. As a number of the eel samples in this current work (Tables 7 & 8) were found to be free of PFCs, it would appear to be a localised problem specific to certain contaminated in-land waterways.

Method validation

3.7 Linearity of instrument response (normalised) was excellent for all analytes. For replicate injections of the same test solutions of the MS instrument, RSD's of <10% were achieved for all analytes. However, the actual raw area responses varied greatly by analyte and this was affected by even the simplest matrix changes (Figures 3 & 4). Food matrix, while consistent within a given sample, dramatically alters the response making internal calibration by standard additions essential (Figure 5).

3.8 The various extraction and cleanup sets were assessed for robustness. The Strata XAW weak anion exchange SPE step was assessed against a number of other equivalent SPE products. With solvent standard solutions at a 100 μg/kg equivalence loading, Oasis HLB & WAX and Isolute SAX gave quantitative recovery of all analytes (Taniyasu 2005). Other phases where less suitable. For example, Isolute ABN gave a lower (68%) recovery for PFOSA. ENV+ gave a lower (74%) recovery for PFBSH. IST C_8 gave a lower (1, 4, 68%) recovery for PFBSH, PFHxA and PFHpA, IST M-M gave a lower (1, 50, 46, 1, 15) recovery for PFBSH, PFHxSH, PFOS, PFHxA and PFHpA. Silicycle Si-amine did not give quantitative recoveries for any of the analytes under the same elution conditions.

3.9 Heating and concentration of methanol solution under a stream of nitrogen gas was studied carefully to assess the extent of losses due to volatility. It was found that both carboxylic and sulfonic acids were resistant to losses, even under extreme conditions, i.e. heating at 100 ^{o}C when dry for 2 hours. The neutral PFOSA exhibited some volatility under the test conditions, but this was minimal (Figure 3).

3.10 The amides, D_9-*n*-Et-FOSE and D_3-*n*-Me-FOSEA, that were used as internal standards (IS) were also volatile and this affected reproducibility and hence their suitability for use. PFOSA is therefore the most difficult analyte to quantify accurately, primarily due to the lack of a suitable IS that mimics the actual recovery of PFOSA across different matrices.

3.11 In practice the best choice of IS was determined empirically from the available candidates by calulating the correlation coefficent of the normalised standard addition line. The data set with the better r^2 fit was used to produced the more accurate estimation of PFOSA content.

3.12 The final method validation was a reproducibility assessement of a number of naturally contaminated foods. These were analysed, often many months apart to asess inter-batch reproducibilty. The primary aim was qualitative, to obtain the same screening result, both negative samples to remain negative and positive results to be confirmed over repeated analyses. The secondary aim, was to obtain a similar quantitative result. Both qualitative and quantitative data were considered acceptable and are presented in Table 4. Insufficient data is available to calculate either coefficients of variation or measurement uncertainty for individual analytes and foods. A fixed percentage value of 20% should be used as an estimate of measurement uncertainty.

3.13 The choice of HPLC column for the separation had a large effect on the measured LOQs (Figure 6, Table 2). Where quantification to the RL was proving problematic, an alternative stationary phase was used to produce a more suitable separation/matrix combination.

3.14 Standard addition using multi-point calibration and two ion channels was used to confirm any positive residues (Figure 7).

3.15 Analytical recoveries were investigated by comparing standard addition and standards prepared in matrix extracts for all of the key food groups (Figures 8 & 9).

3.16 These are unequivocal, as the identity of peaks were in each instance confirmed by use of other secondary transitions and the quantitation was by standard addition.

Data

3.17 An initial survey of 199 individual food samples was then followed up with a second phase involving a further 53 food samples. No samples were found that contained high enough levels to have warranted immediate reporting to the FSA. The data are consistent with other recent European food surveys (Fromme 2007, Tittlemier 2007, Ericson 2008, Berger 2007).

3.18 The two highest levels of PFOS observed in this survey were *ca*. 60 µg/kg in a smoked eel and 40 µg/kg in a whitebait sample. This survey included both UK-produced and imported foods. In general, a higher level of contamination was found in imported fish.

3.19 A number of food samples appear to contain trace levels of PFOS and other PFCs above the reporting limit of 1 µg/kg. These positive results were all in food groups where predicted, i.e. fish, shellfish, crustaceans and offal. Other primary produce foods, such as, fish and vegetable oils, meat, milk, eggs, cereals, fruits and vegetables, were essentially free from contamination (Tables 7 & 8, Figures 11 &12). For the contaminated food types a summary of the numbers of each food tested, the number of positive samples, the range of PFC concentrations and the mean values are provided as an overall summary (Table 9). A separate figure showing the contributions of the individual PFCs such as PFOS and PFOSA is provided (Figure 13). There were no observable trends seen due to different farming or husbandry practices, although the data upon which to base this conclusion are limited..

3.20 A sample of potato waffles proved anomolous with an unusual contamination profile. As some 10 g portions were free of any contamination it was unclear if this was a sub-sampling problem. After four analysis had produced inconsistent results, the whole sample was rehomogenised and repotted after which it proved consistently negative.

3.21 Packaging information suggests that a number of the whitebait were in fact from the same location. Food and Agriculture Organisation of the UN major fishing subarea 37.4 the Black Sea area [Marmara Sea 37.4.1, Azov Sea 37.4 and Black Sea 37.4.3]. Some of these fish would appear to have been packaged in the same factory in Bulgaria. A similar profile of PFOS/PFOSA was observed in these fish with an absence of carboxylic acids. The two NE altlantic whitebait where more contaminated (higher PFOS) and also contained a range of carboxylic acids.

3.22 PFCs can be present at much higher levels in both environmental samples and foods where a specific contamination event is known to have occurred.

3.23 Crustaceans (excluding prawns) were all UK caught and showed a consistent profile of carboxylic acids, sulfonic acids and PFOSA.

3.24 According to the manufacturers addvertising material, the smoked eel sample with 60 µg/kg PFOS was smoked in-house, at Chelmsford Essex. Fresh eel fillets from a local freshwater reservoir had been brined in sea salt and smoked over Beech and Oak chips without the use of preservatives, dyes or any other chemicals.

3.25 Carp were from France and Holland and were generally contaminated with PFOS.

3.26 Both venison liver samples had higher PFOS levels than any of the other species tested; sheep, pig, cow, chicken. The highest level in an offal was 10 µg/kg of PFOS, a liver sample from a Roe deer liver. After corresponding with the vendor, this deer was believed to have been shot from a well-managed wild population of Roe deeer living on an area of low lying arable land with mixed woodland, climbing gradually to higher moorland terrain on Lord Barnard's Estate - Castle Raby, Staindrop, Darlington, County Durham DL2 3AH.

3.27 The overall pattern was that PFOS was the most prevalent contaminant, and in the samples where it was found, it was often accompanied by lower levels of other PFC contaminants. Of the 199 Phase-1 samples, PFCs were found in 41. PFOS was found in 31 samples, at concentrations from 1-59 µg/kg, other PFCs found inn these 31 samples were: PFOSA[n=9], PFBSH[n=3], PFHxA[n=3], PFHpA[n=3], PFOA[n=3], PFNA[n=2], PFDeA[n=1] and PFUnA[n=1] PFDoA[n=1]. Of the 53 Phase-2 samples, PFCs were found in 38 samples. PFOS was found in 35 samples at concentrations from 1-40 µg/kg, other PFCs found in these 35 samples were PFOSA[n=11], PFHxSH[n=2], PFOA[n=8], PFNA[n=5], PFUnA[n=4] and PFDoA[n=1].

CONCLUSIONS

4.1 A sensitive, reliable and robust analytical method for determining PFOS and 10 associated PFCs in food has been established. The method is both repeatable and reproducible, and capable of measuring PFOS down to 1 µg/kg in all the food types surveyed in this report.

4.2 A number of food samples were found to contain trace levels of PFOS and other PFCs close to the reporting limit of 1 µg/kg. These positive results were all in food groups as predicted: fish, shellfish, crustaceans, offal. Other primary produce foods such as, vegetable and fish oils, meat, milk, eggs, cereals, fruits and vegetables were essentially free of contamination.

4.3 The two highest contamination levels observed were for PFOS at *ca*. 60 µg/kg in a smoked eel sample, and at *ca*. 40 µg/kg in a whitebait sample. The highest contamination in an offal sample was 10 µg/kg of PFOS in a liver sample from a wild roe deer.

4.4 There were no high residues requiring immediate notification to the FSA. It was concluded that these data are consistent with other recent European and Canadian food surveys (Fromme 2007, Tittlemier 2007, Ericson 2008, Berger 2007) and our Irish Survey.

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TABLES

Table 1. Names, masses, abbreviations, purity and suppliers of standards

Class	Abbrev	Formulae	Name	Isotopic MW	CAS number	Supplier	Purity
Amides	PFOSA	C8F17SO2NH2	Perfluorooctane sulfonamide	498.95	754-91-6	ABCR	97%
Sulfonates	PFBSH	C4F9SO3H	Perfluorobutane sulfonic acid	299.95	375-73-5	sigma	97%
	PFHxSK	C6F13SO3K	Perfluorohexane sulfonate potassium salt	437.9	3871-99-6	fluka	98%
	PFOSK	C8F17S03K	Perfluorooctane sulfonate potassium salt	537.89	2795-39-3	fluka	98%
Acids	PFHxA	C5F11COOH	Perfluorohexanoic acid	313.98	307-24-4	fluka	97%
	PFHpA	C6HF13COOH	Perfluoroheptanoic acid	363.98	375-85-9	sigma	99%
	PFOA	C7HF15COOH	Perfluorooctanoic acid	413.97	335-67-1	sigma	96%
	PFNA	C8HF17COOH	Perfluorononanoic acid	463.97	375-95-1	sigma	97%
	PFDeA	C9HF19COOH	Perfluorodecanoic acid	513.97	335-76-2	sigma	98%
	PFUnA	C10F21COOH	Perfluoroundecanoic acid	563.96	2058-94-8	sigma	95%
	PFDoA	C11F23COOH	Perfluorododecanoic acid	613.96	307-55-1	sigma	95%

Table 2. Summary of analytical standards

	Primary Ions		Qualifier Ions		MeOH LOQs		Matrix based LOQs µg/kg[a]			
Test analyte	Transition	Product ion	Transition	Product ion	Rt	µg/kg[a]	Milk	Jam	Veg Oil	Salmon
PFHxA	313.1>269.1	$[M\text{-}CO_2]^-$	313.1>119.1	$[C_2F_5]^-$	11.25	0.01	0.025	0.1	0.05	0.3
PFHpA	363.1>319.1	$[M\text{-}CO_2]^-$	363.1>169.1	$[C_3F_7]^-$	11.92	0.005	0.01	0.05	0.02	0.01
PFOA	413.1>369.1	$[M\text{-}CO_2]^-$	413.1>169.1	$[C_3F_7]^-$	12.43	0.005	0.025	0.01	0.05	0.01
PFNA	463.1>419.1	$[M\text{-}CO_2]^-$	463.1>219.1	$[C_4F_9]^-$	12.86	0.001	0.05	0.02	0.05	0.02
PFDeA	513.1>469.1	$[M\text{-}CO_2]^-$	513.1>219.1	$[C_4F_9]^-$	13.26	0.001	0.025	0.02	0.02	0.05
PFUnA	563.1>519.1	$[M\text{-}CO_2]^-$	563.1>319.1	$[C_6F_{13}]^-$	13.66	0.001	0.025	0.02	0.01	0.02
PFDoA	613.1>569.1	$[M\text{-}CO_2]^-$	613.1>269.1	$[C_5F_{11}]^-$	14.02	0.001	0.025	0.02	0.02	0.05
PFBSH	299.1>80.1	$[SO_3]^-$	299.1>99.1	$[SO_3F]$-	10.05	0.01	0.05	0.05	0.01	0.05
PFHxS	399.1>80.1	$[SO_3]^-$	399.1>99.1	$[SO_3F]$-	11.64	0.01	0.05	0.02	0.05	0.1
PFOS	499.1>80.1	$[SO_3]^-$	499.1>99.1	$[SO_3F]$-	12.59	0.01	0.1	0.1	0.05	0.1
PFOSA	498.1>78.0	$[SNO_2]^-$	498.1>169.1	$[C_3F_7]^-$	13.96	0.002	0.025	0.02	0.1	1
THPFOS	427.1>407.1	$[M\text{-}HF]^-$	-	-	12.34	-	-	-	-	-
$^{13}C_2$-PFDeA	515.1>470.1	$[^{12}C_8{}^{13}C_1F_{19}]^-$	-	-	13.26	-	-	-	-	-
$^{13}C_4$-PFOA	417.1>372.1	$[^{12}C_2{}^{13}C_3F_{11}]^-$	-	-	12.42	-	-	-	-	-
$^{13}C_4$-PFOS	503.1>801	$[SO_3]^-$	-	-	12.57	-	-	-	-	-
D_9-*n*-Et-FOSE	639.1>59.0	$[CH_3CO_2]^-$	-	-	14.81	-	-	-	-	-
D_3-*n*-M-FOSEA	515.1>169.1	$[C_3F_7]^-$	-	-	14.68	-	-	-	-	-

Summary of MRM transitions, retention times and solvent based LOQs of PFC analytical standards.

[a]Concentration expressed as ng/kg food equivalent, matrix matched. Uses 10 g food matrix concentrating the extract 25-fold into 0.4 ml methanol. Methanol based LOQs were all <10 ng/kg (0.25 ng/ml).

Table 3. Purity estimates for PFC analytical standards

		Measured percentage content [% purity]																		
Test analyte	Code	PFHxA	PFHpA	PFOA	PFNA	PFDeA	PFUnA	PFDoA	PFBS	PFHxS	PFOS	PFOSA	THPFOS	$^{13}C_4$-PFOS	$^{13}C_2$-PFDeA	$^{13}C_4$-PFOA	D_9-n-EFOSE	D_3-n-MFOSEA	Calculated	Nominal
Perfluorohexanoic acid	PFHxA	99.5	0.2	0.3	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	-	-	-	-	-	100	97%
Perfluoroheptanoic acid	PFHpA	1.1	98.6	0.1	<0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	-	-	-	-	-	99	99%
Perfluorooctanoic acid	PFOA	<0.1	0.1	99.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	-	-	-	-	-	100	96%
Perfluorononanoic acid	PFNA	<0.1	2.1	0.5	97.3	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	-	-	-	-	-	97	97%
Perfluorodecanoic acid	PFDeA	<0.1	<0.1	0.2	0.9	98.6	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	-	-	-	-	-	99	98%
Perfluoroundecanoic acid	PFUnA	<0.1	0.2	0.7	1.0	1.0	96.5	0.5	<0.1	<0.1	<0.1	<0.1	-	-	-	-	-	-	97	95%
Perfluorododecanoic acid	PFDoA	<0.1	0.4	1.5	2.2	3.8	1.1	90.9	<0.1	<0.1	<0.1	<0.1	-	-	-	-	-	-	91	95%
Perfluorobutanesulphonic acid	PFBSH	<0.1	<0.1	<0.1	0.1	0.1	<0.1	0.1	95.9	<0.1	2.6	1.2	-	-	-	-	-	-	96	97%
Perfluorohexanesulfonic acid	PFHxSH	<0.1	<0.1	<0.1	0.1	0.1	<0.1	<0.1	0.2	99.5	<0.1	0.1	--	--	--	--	--	--	100	98%
Perfluorooctanesulfonic acid	PFOSH	<0.1	<0.1	0.1	0.1	<0.1	0.1	0.1	0.1	0.2	99.4	<0.1	-	-	-	-	-	-	99	98%
Perfluorooctanesulfonyl amide	PFOSA	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	99.9	-	-	-	-	-	-	100	97%
TetrahydroPFOS	THPFOS	0.1	0.7	<0.1	<0.1	<0.1	<0.1	<0.1	0.9	0.1	<0.1	<0.1	98.2	-	-	-	-	-	98.2	-
$^{13}C_4$-PFOS	$^{13}C_4$-PFOS	<0.1	<0.1	0.2	0.2	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	99.7	<0.1	<0.1	<0.1	<0.1	100	98%
$^{13}C_2$-PFDeA	$^{13}C_2$-PFDeA	<0.1	<0.1	0.3	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	99.4	<0.1	<0.1	<0.1	99	98%
$^{13}C_4$-PFOA	$^{13}C_4$-PFOA	<0.1	<0.1	0.2	0.5	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	0.1	<0.1	<0.1	0.2	98.5	<0.1	<0.1	99	98%
D_9-n-Et-FOSE	D_9-n-Et-FOSE	0.1	0.2	2.7	0.7	0.9	0.3	0.3	0.0	0.3	1.0	0.8	<0.1	<0.1	<0.1	<0.1	92.5	<0.1	93	98%
D_3-n-M-FOSEA	D_3-n-M-FOSEA	0.1	<0.1	0.2	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	99.6	100	98%

Purity estimates by self-content of the measured chemicals. All calculations were performed without conducting purity corrections.

Table 4. Method reproducibility information

	Measured analyte concentration µg/kg										
Sample	PFBS	PFHxS	PFOS	PFHxA	PFHpA	PFOA	PFNA	PFDeA	PFUnA	PFDoA	PFOSA
S07-013418 Herring	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
S07-013355 Whole Mackerel			1[2]								1[1]
S07-013354 P-1 Valid Dressed crab			6[4]			9[8]	1[2]				1[1]
S07-013480 Whitebait			11[15]								10[27]
S07-013521 Whitebait IQF			12[9]								6[4]
S07-013543 Whitebait		1[1]	48[40]			4[5]			1[2]		
S07-013546 Cromer crab		1[2]	14[12]			4[4]	2[1]	1[1]			1[2]
S07-013519 Spider crab			13[9]			5[6]					
S07-013538 Wild roe deer liver			10[11]			3[6]	1[2]				
Carp roe QC			765[757]								

Interbatch reproducibility data for repeat analysis of naturally incurred PFC containing food sample.

First determination, followed by second determination in parenthesis.

ND = not determined <1 µg/kg in both batches.

Table 5. Food sampling information. Phase-1 samples

No	Type	LIMS	Product	Source	Code
1	Fish	S07-013309	Morrisons R. Trout	Morrison's Fishmonger	15314
2		S07-013357	Tesco, Welsh Whole R. Trout	Tesco Fish Counter	15391
3		S07-013460	Mirror carp	C J Newnes	15554
4		S07-013481	Carp	A A Lyons	15563
5		S07-013310	Morrisons Organic Salmon Scottish	Morrison's	15315
6		S07-013420	Farmed Salmon Fillet	Alexander Crawford	15452
7		S07-013456	Wild Atlantic Salmon	The Chelsea Fishmonger	15511
8		S07-013482	Wild Salmon	Wren & Hines	15564
9		S07-013356	Tesco Wild Alaskan Salmon	Tesco Fish Counter	15398
10		S07-013454	Smoked Eel	Maldon Oysters	15508
11		S07-013506	Wild English Eels	Dutch Eel Company	15654
12		S07-013341	Eastwood Lemon sole	Eastwoods	15403
13		S07-013434	Dover Sole	Miller's Farm Fish Stall	15498
14		S07-013363	Sainsbury Wild Alaskan Salmon	Sainsbury's Fresh Meat	15363
15		S07-013400	Waitrose Plaice fillets	Waitrose	15427
16		S07-013435	Plaice Fillets	Miller's Farm Fish Stall	15499
17		S07-013342	Eastwood Cod	Eastwoods	15404
18		S07-013419	Cod	Alan Beveridge	15451
19		S07-013397	Youngs Haddock Fillets	Young's	15424
20		S07-013421	Haddock	Alexander Crawford	15453
21		S07-013483	Sprats	J Bennett Jnr	15566
22		S07-013479	English Sprats	Barton & Hart	15567
23		S07-013480	Whitebait	J Bennett Jnr	15565
24		S07-013461	Whitebait (Sprattus) ocean caught	Ocean Catch	15555
25		S07-013399	Waitrose Whole Herring	Waitrose Wet Fish	15426

No	Type	LIMS	Product	Source	Code
26		S07-013418	Herring	Alan Beveridge	15450
27		S07-013371	Crystal Waters Mackerel	Crystal Waters	15369
28		S07-013355	Whole Mackerel Fishmongers Cardiff	E Ashton	15397
29		S07-013446	Waitrose Cornish Sardines	Waitrose Wet Fish	15516
30		S07-013447	Fishworks Cornish Sardines	Fish Works	15512
31		S07-013380	Dressed Crab	Fish Box Foods	15377
32		S07-013354	Dressed Crab	E Ashton	15393
33	Crustaceans	S07-013457	Youngs Langoustine Fillets	Young's	15514
34		S07-013462	Crayfish	Barton & Hart	15562
35		S07-013378	Crystal Water whole shell-on prawns	Crystal Waters	15375
36		S07-013396	ASDA N. Atlantic Prawns	Asda	15423
37	Shellfish	S07-013455	Pacific Oysters	Maldon Oysters	15517
38		S07-013458	Fishworks Pacific Oysters	Fish Works	15515
39	Fish oil	S07-013326	Boots Cod Liver Oil	Boots	15342
40		S07-013404	Valupak Cod Liver Oil Capsules	Valupak	15486
41		S07-013327	H &B Salmon Oil Caps	Holland & Barrett	15356
42		S07-013501	Wellicene Health- Tuna cap	Wellcene Health	15578
43	Veg Oils	S07-013496	Brahams oil of Cold-Pressed Hemp seed	Braham & Murray	15575
44		S07-013333	Sainsbury's Olive Oil	Sainsbury's	15347
45		S07-013428	Napolins Olive Oil	Napolina	15406
46		S07-013323	Mazola Corn Oil	Mazola	15328
47		S07-013437	Flora Pure Sunflower Oil + Vitamin E	Flora	15503
48		S07-013409	Trex Sunflower Oil	Trex	15441
49	Offal	S07-013474	Tesco British Pork Sliced Liver	Tesco	15530
50		S07-013471	McKay Pork Liver	McKay Family Butchers	15527

No	Type	LIMS	Product	Source	Code
51		S07-013308	Co-op Lambs Liver	Co-op	15313
52		S07-013402	Lambs Liver	Andrews Quality Meats	15429
53		S07-013433	Lambs Liver	P & J Butchers	15496
54		S07-013487	ASDA Lambs Liver	Asda	15560
55		S07-013478	Chicken Liver	Gregory's Meats	15534
56		S07-013473	Tesco Chicken Liver	Tesco	15529
57		S07-013351	Ox Liver	J T Morgan	15395
58		S07-013485	Ox Liver	Eric Tennant Butchers	15557
59		S07-013436	Venison Liver	Denham Estate	15500
60		S07-013445	Organic pig kidney	Longwood Organic Farm	15553
61		S07-013500	Pig Kidney	Powters	15579
62		S07-013379	Ox Kidney	Cherrytree Butchers	15376
63		S07-013352	Ox Kidney	R T Perkins	15396
64		S07-013432	Lambs Kidney	P & J Butchers	15501
65		S07-013470	McKay Lambs Kidney	McKay Family Butchers	15526
66		S07-013311	Lambs Hearts	Flackie's Meat	15316
67		S07-013353	Lambs Hearts	R T Perkins	15394
68		S07-013367	Country Park Foods Black Pudding	Country Park Foods	15402
69		S07-013410	Black Pudding	W P Tulloch	15442
70		S07-013488	Asda duck liver pate	Asda	15558
71		S07-013504	Castle MacLellan Chicken liver Pate	Castle MacLellan	15582
72		S07-013376	Newmarket Sausages Natural Casings	Musk's	15373
73		S07-013317	Sherbourne Lincolnshire Sausages	Sherbourne	15322
74	Meats	S07-013381	Boneless shoulder of lamb	Meat Inn	15378
75		S07-013412	Shoulder of Lamb	W P Tulloch	15444

No	Type	LIMS	Product	Source	Code
76		S07013315	Morrisons Boneless Leg of Pork	Morrison's	15320
77		S07-013395	Waitrose British Pork Boneless Leg Roast	Waitrose	15422
78		S07-013312	Morrisons B. Steak	Morrison's	15317
79		S07-013411	Rump Steak for Braising	W P Tulloch	15443
80		S07-013472	McKay Fresh Chicken Legs	McKay Family Butchers	15528
81		S07-013502	Boneless chicken thighs	Powters	15580
82		S07-013382	Meat Inn Turkey Breast	Meat Inn	15379
83		S07-013394	Asda British Turkey Breast Joint	Asda Good For You	15421
84		S07-013403	Andrews Venison Fillet	Andrews Quality Meats	15430
85		S07-013413	Venison Haugh Joints	Charles Frazer	15445
86		S07-013350	Scotch beef quarterpounders	Stoddarts of Scotland	15400
87	Milk	S07-013377	Countrylife Organic whole milk	Country Life	15374
88		S07-013343	Calon Wen Organic Whole Milk	Calon Wen	15392
89		S07-013408	Morrisons Fresh Whole Milk	Morrison's	15440
90		S07-013425	Yarty Valley - Whole Milk	Yarty Valley Dairies	15494
91		S07-013469	Strathray Whole Milk	Strathroy	15525
92		S07-013468	Ballyrashane Whole Milk	Ballyrashane	15524
93		S07-013498	Delamere Dairy Fresh Goats milk	Delamere Dairy	15559
94		S07-013505	Woodlands Sheeps milk powder	Woodlands	15583
95		S07-013459	Ewe tree Farm Sheep's Milk	Ewe Tree Farm Dairy	15513
96		S07-013401	Waitrose Fresh Full Cream Goats Milk	Waitrose	15428
97		S07-013484	Raw sheep milk Boydells Dairy Farm	Boydells Dairy Farm	15556
98	Cheese	S07-013318	Pilgrims Choice Cheese	Pilgrims Choice	15323
99		S07-013344	Tesco, Welsh Medium Cheddar	Tesco	15390
100		S07-013453	Waitrose Duddleswell Cheese	High Weald	15510

No	Type	LIMS	Product	Source	Code
101		S07-013438	Somerset Brie	Complete Meats	15493
102		S07-013398	Cornish Brie Wedges	Cornish Country Larder	15425
103		S07-013439	Wensleydale Sheeps Cheese	Complete Meats	15495
104		S07-013362	Sainsbury Organic Goat Cheese	Sainsbury's So Organic	15362
105		S07-013335	Somerset Goat Cheese	Capricorn	15349
106		S07-013452	M & S Medium Half Fat Cheese Slices	Marks & Spencer	15509
107		S07-013372	Primula Cheeese Spread	Primula	15401
108	Eggs	S07-013495	Elliots Eggs Free Range	Elliott's Eggs	15574
109		S07-013368	Tesco Free Range Eggs Organic	Tesco Organic	15366
110		S07-013337	Budgens Free Range Eggs	Budgens	15351
111		S07-013476	Skea Eggs Free Range	Skea Eggs	15532
112		S07-013422	Scottish Free Range Eggs	Scotlay	15454
113		S07-013393	Farmhouse Freedom Eggs Free Range Organic	Farmhouse Freedom	15420
114		S07-013448	Barrington Park Estates Organic Free Range Eggs	Barrington Park Estate	15507
115		S07-013451	Rookery Farm Organic Free Range Eggs	Rookery Farm	15506
116		S07-013316	Bitteswell Browns Eggs Caged	Bitteswell Browns	15321
117		S07-013383	Birds big English Fresh Eggs Caged	Birds	15380
118		S07-013338	Tesco Free Range Duck Eggs	Tesco Finest	15389
119		S07-013405	Free Range Duck Eggs	Miller's Farm Shop	15487
120	Vegetables	S07-013320	Morrisons Baby Potatoes [Maris Peer]	Morrison's The Best	15325
121		S07-013477	Baby New Potatoes [Charlotte]	Wilson's Country Ltd	15533
122		S07-013336	Somerfield White Potatoes (Osprey)	Somerfield	15350
123		S07-013348	Tesco Loose Potatoes	Tesco	15385
124		S07-013390	Waitrose organic baby new potatoes(Carlingford)	Waitrose Organic	15417
125		S07-013441	Potatoes [Marfona]	Miller's Farm Shop	15492

No	Type	LIMS	Product	Source	Code
126		S07-013465	Whitepark Bay McCurdy's [Queens] Potatoes	McCurdy's	15521
127		S07-013321	Bartlett Rooster Potatoes (Rooster- Red)	Bartlett	15326
128		S07-013359	Sainsbury Baking potatoes(Harmony)	Sainsbury's	15359
129		S07-013414	Fresh Potatoes (Epicure)	Cunninghams of Paisley	15446
130		S07-013364	Sainsbury Crispy Oven Fries	Sainsbury's	15364
131		S07-013486	Asda Crispy Home Style Chips [frozen]	Asda	15561
132		S07-013366	Aunt Bessies, Homestyle Crispy Roast	Aunt Bessie's	15399
133		S07-013424	Tesco 12 Waffles	Tesco	15497
134		S07-013339	Kettle Crisps	Kettle	15388
135		S07-013440	Walkers Cheese and Onion Crisps	Walkers	15405
136		S07-013430	Weightwatchers Mini Loops	Weight Watchers	15409
137		S07-013423	Mini Pringles (Original)	Pringles	15488
138		S07-013494	Sweet Potatoes	Asda	15573
139		S07-013503	Bugdens Sweet Potatoes	Budgens	15581
140		S07-013322	Morrisons Carrots	Morrison's	15327
141		S07-013346	Tesco British Carrots	Tesco	15386
142		S07-013370	Tesco British Parsnips	Tesco	15368
143		S07-013491	ASDA British Parsnips	Asda	15570
144		S07-013358	Sainsbury Half Swede	Sainsbury's	15358
145		S07-013347	Tesco Swede	Tesco	15383
146		S07-013442	Celeriac	Miller's Farm Shop	15491
147		S07-013492	ASDA British celeriac	Asda	15571
148		S07-013385	John Wedder Beetroot (bunch)	John Wedder	15382
149		S07-013444	Beetroot	Miller's Farm Shop	15490
150		S07-013415	Baby Turnips	Cunninghams of Paisley	15447

No	Type	LIMS	Product	Source	Code
151		S07-013443	Baby Turnips	Miller's Farm Shop	15489
152		S07-013313	String Beans	G H Ratcliffe	15318
153		S07-013387	Asda Runner beans	Asda	15414
154		S07-013365	Fresh Broad Beans in Pod	John Wedder	15365
155		S07-013314	Broad Beans	G H Ratcliffe	15319
156		S07-013384	John Wedder Whole Cabbage	John Wedder	15381
157		S07-013389	Waitrose Spring Greens	Waitrose	15416
158		S07-013388	Waitrose Spinach	Waitrose	15415
159		S07-013490	ASDA Spinach	Asda	15569
160		S07-013375	M&S Scottish Broccoli	Marks & Spencer	15372
161		S07-013416	Broccoli Florets	Imrie Fruit	15448
162		S07-013307	Co-op Cauliflower	Co-op	15312
163		S07-013386	M&S Cauliflower	Marks & Spencer	15413
164		S07-013349	Leeks, Cardiff	The Fruit Bowl	15387
165		S07-013417	Whole Leeks (Fresh)	Cunninghams of Paisley	15449
166		S07-013334	Sainsbury Red Onions	Sainsbury's	15348
167		S07-013489	Asda Onions	Asda	15568
168		S07-013374	M&S Tomatoes	Marks & Spencer	15371
169		S07-013493	Jersey Jewel Tomatoes on vine	Tesco Finest	15572
170		S07-013345	Cherry Tom on the vine	Tesco	15384
171		S07-013360	Sainsbury British Watercress	Sainsbury's	15360
172		S07-013306	Co-op Mushy Peas	Co-op	15311
173		S07-013464	Batchelors Bigga Marrowfat Processed Peas	Batchelors	15520
174		S07-013324	D'Aucy Sweetcorn (Canned Vac packed)	D'aucy	15329
175		S07-013426	Princes sweetcorn in brine	Princes	15410

No	Type	LIMS	Product	Source	Code
176		S07-013340	Tarantella Organic Chopped Tomatoes	Tarantella	15411
177		S07-013467	Sainsburys Chopped Tomatoes	Sainsbury's	15523
178		S07-013475	Crosse & Blackwell Broad Beans in water	Crosse & Blackwell	15531
179		S07-013499	Freshcan Broad Beans	Fresh Can	15577
180		S07-013332	Waitrose Jersey Potatoes	Waitrose	15346
181		S07-013497	ASDA Jersey new potatoes [canned]	Asda	15576
182		S07-013463	Costcutter New Potatoes in water with mint	Costcutter	15519
183	Grains/Bread	S07-013329	Mornflake Superfast Oats	Mornflake	15344
184		S07-013429	Quaker Oats organic	Quaker Oats	15408
185		S07-013407	Hamlyns Scottish Oatmeal	Hamlyns of Scotland	15439
186		S07-013449	Infinity Foods Organic Oatmeal	Infinity Foods Organics	15505
187		S07-013466	Sunblest White Medium Sliced Bread	Sunblest	15522
188		S07-013361	Hovis Squre White Loaf	Hovis	15361
189		S07-013391	Doves Farm Organic Wholemeal Bread	Doves Farm	15418
190		S07-013319	Warburtons Wholemeal Bread	Warburtons	15324
191		S07-013325	Chicago Joes Toffee Popcorn	Chicago Joes	15330
192		S07-013328	Butterkist Pop Corn	Butterkist	15343
193		S07-013369	Orv. Red. Pop Corn	Orville Redenbacher's	15367
194		S07-013427	Cinema Sweet Pop Corn	Cinema Sweet	15407
195	Fruit/Jam	S07-013330	Duchy Orig. Strawberry Jam Organic	Duchy Originals	15345
196		S07-013406	Robertsons Blackcurrant Jam	Robertson's	15438
197		S07-013373	Mackays Raspberry Pres.	Mackays	15370
198		S07-013331	Tiptree Strawberry Conserve	Tiptree	15357
199		S07-013392	Waitrose Blackcurrant Coulis	Waitrose	15419
200		S07-013450	The English Provender Co. Raspberry Coulis	The English Provender	15504

LIMS is the CSL unique sample identifying code used in our Laboratory Information Management System (LIMS).

Table 6. Food sampling information. Phase-2 samples

No	Type	LIMS	Product	Source	Code
1	Fish	S07-013507	Haddock portions	Morrison's	16140
2		S07-013508	Fresh carp (cyprinus carpio)	Morrison's	16141
3		S07-013520	Mirror carp	J Bennett, Billingsgate Ltd.	16153
4		S07-013514	Common carp	C J Newness	16147
5		S07-013509	Cod loin	Asda Extra Special	16142
6		S07-013523	Bideford cod	David Felce Daughter & Son	16156
7		S07-013515	Frozen sprats	John Koch	16148
8		S07-013516	Cornish sardines	Ocean Catch	16149
9		S07-013552	Sardines	James Knight of Mayfair	16185
10		S07-013534	Whitebait	Holmes whitebait	16167
11		S07-013543	Whitebait	Aldus	16176
12		S07-013521	Whitebait IQF	World Seafood Direct	16154
13		S07-013525	Whole trout organically farmed	Sainsburys So Organic	16158
14		S07-013527	2 whole rainbow trout	The Fishmonger	16160
15		S07-013528	Haddock fillet	Iceland	16161
16		S07-013529	Salmon fillets	Tesco Value, Norway	16162
17		S07-013526	Lochmuir Scottish salmon portions	Marks and Spencer	16159
18		S07-013536	2 prime boneless salmon fillets	Youngs farmed in Norway	16169
19		S07-013551	Whole mackerel (gutted by	James Knight of Mayfair	16184
20		S07-013533	Whole Cornish mackerel	E P Fisheries	16166
21		S07-013553	Herring (filleted by fishmonger)	Selfridges - James Knight of	16186
22		S07-013554	Smoked eel	Selfridges	16187
23		S07-013513	Traditional jellied eels	Bradley's	16146
24		S07-013517	Jellied eels	Micks Eel Supply Ltd	16150
25		S07-013518	Smoked eel	Micks Eel Supply Ltd	16151

26		S08-009817	Herring Harvey Nichols	Harvey Nichols	16189
27		S08-009818	Whitebait	Interseafish	16190
28		S08-009819	Carp	Covent Graden Fishmongers	16191
29		S08-009820	Sardines wholefoods market	Wholefoods Market	16192
30		S08-013024	Sardines Sainsburys	Sainsbury Fishmongers	16250
31	Crustaceans	S07-013542	Crab (whole)	H. Boldock	16175
32		S07-013522	Brown crab (whole)	C+A Seafoods	16155
33		S07-013546	Cromer crab (dressed)	Waitrose Fishmonger	16179
34		S07-013519	Spider crab (whole)	R+G Shellfish	16152
35	Offal	S07-013524	Beef liver	Kimber's Traditional Farm Produce	16157
36		S07-013530	Halal beef liver	Alnoor	16163
37		S07-013541	Ox liver	S & M Foods	16174
38		S07-013547	Pigs liver	Park Road Butchers	16180
39		S07-013549	Pigs liver (outdoor reared)	Grasmere Farm	16182
40		S07-013538	Wild roe deer liver	Teesdale Game & Poultry	16171
41		S07-013539	Farmed red deer liver	Round Green Farm Venison Co	16172
42		S07-013532	Wild venison liver	Parson’s nose	16165
43		S07-013535	Lambs liver	Dickenson	16168
44		S07-013540	Lambs liver	S & M Foods	16173
45		S07-013510	Traditional lamb sliced liver	Sainsbury's	16143
46		S07-013555	Irish pigs liver	ASDA	16188
47		S07-013511	Beef kidney	Sainsbury's	16144
48		S07-013548	Lambs kidney	Park Road Butchers	16181
49		S07-013531	Lambs kidney	Parson’s nose	16164
50		S07-013544	Ox kidney	Battys Family Butchers	16177
51		S07-013545	Pigs kidney	Battys Family Butchers	16178
52		S07-013550	2 pigs kidney (outdoor reared)	Downland Produce	16183
53		S07-013537	8 Cumberland pork sausages	Budgens	16170

Table 7. Food analysis data - Phase-1 samples

No	Type	LIMS	Product	Measured analyte concentration µg/kg										
				PFHxA	PFHpA	PFOA	PFNA	PFDeA	PFUnA	PFDoA	PFBS	PFHxS	PFOS	PFOSA
1	Fish	S07-013309	Morrisons R. Trout [UK, Farmed]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1
2		S07-013357	Tesco, Whole R. Trout [UK, Wales]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1
3		S07-013460	Mirror carp [France]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
4		S07-013481	Carp [Holland]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**8**	< 1
5		S07-013310	Morrisons Salmon [UK, Shetlands]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
6		S07-013420	Farmed Salmon Fillet [UK, Scotland]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
7		S07-013456	Wild Atlantic Salmon [UK, River Tay]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
8		S07-013482	Wild Salmon [UK, Exmouth]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
9		S07-013356	Tesco Wild Alaskan Salmon	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
10		S07-013454	Smoked Eel [UK, Essex]	< 1	<1	< 1	< 1	**2**	**2**	< 1	< 1	< 1	**59**	< 1
11		S07-013506	Wild English Eels	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**2**	< 1
12		S07-013341	Lemon sole [British Channel]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
13		S07-013434	Dover Sole [UK, Lyme bay]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
14		S07-013363	Sainsbury Wild Alaskan Salmon	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr	nr
15		S07-013400	Plaice fillets [Iceland, NE Atlantic]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1
16		S07-013435	Plaice Fillets [UK, Brixham]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
17		S07-013342	Eastwood Cod [Norway, farmed]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
18		S07-013419	Cod [North Sea]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**2**	< 1
19		S07-013397	Youngs Haddock Fillets [NE Atlantic]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1
20		S07-013421	Haddock [UK]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
21		S07-013483	Sprats [UK, Brixham]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	**4**
22		S07-013479	English Sprats [UK, Brixham]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	**2**
23		S07-013480	Whitebait [NE Atlantic]	**7**	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**15**	**27**
24		S07-013461	Whitebait ocean caught [Black Sea]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**9**	**6**
25		S07-013399	Whole Herring [Scotland NE Atlantic]											

26		S07-013418	Herring [Scotland North Sea]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
27		S07-013371	Crystal Waters Mackerel [UK]	**2**	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1
28		S07-013355	Whole Mackerel Cardiff [UK]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**2**	**1**
29		S07-013446	Waitrose Cornish Sardines [UK]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	**2**
30		S07-013447	Fishworks Cornish Sardines [UK]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**2**	**3**
31		S07-013380	Dressed Crab [UK, Whitby]	< 1	<1	**4**	**1**	< 1	<1	< 1	< 1	< 1	**4**	**2**
32		S07-013354	Dressed Crab [NE Atlantic]	< 1	<1	**8**	**2**	< 1	<1	< 1	< 1	< 1	**4**	**1**
33	Crustaceans	S07-013457	Langoustine Fillets [Scotland]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
34		S07-013462	Crayfish [England]	< 1	<1	< 1	< 1	< 1	< 1	**2**	< 1	< 1	< 1	< 1
35		S07-013378	Whole shell-on prawns [Greenland]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1	< 1
36		S07-013396	N. Atlantic Prawns [Greenland]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1
37	Shellfish	S07-013455	Pacific Oysters [UK, Essex, farmed]	< 1	**1**	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
38		S07-013458	Pacific Oysters [UK, Cornwall]	< 10	**1**	< 1	< 1	< 1	< 1	< 1	< 10	< 10	< 10	< 1
39	Fish oil	S07-013326	Boots Cod Liver Oil	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1	< 1
40		S07-013404	Cod Liver Oil Capsules [UK]	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1
41		S07-013327	H &B Salmon Oil Caps [USA]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1
42		S07-013501	Tuna cap [Australia]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1
43	Veg Oils	S07-013496	Oil of hemp seed [UK, Devon]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1
44		S07-013333	Sainsbury's Olive Oil [Spain]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1
45		S07-013428	Napolins Olive Oil [EU	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1
46		S07-013323	Mazola Corn Oil	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
47		S07-013437	Flora Pure Sunflower Oil + Vitamin E	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1
48		S07-013409	Trex Sunflower Oil	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1
49	Offal	S07-013474	Tesco British Pork Sliced Liver [UK]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1
50		S07-013471	McKay Pork Liver [N Ireland]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**4**	< 1
51		S07-013308	Co-op Lambs Liver [NZ]	< 1	<1	**1**	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1
52		S07-013402	Lambs Liver [UK]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**4**	< 1
53		S07-013433	Lambs Liver [UK, West country]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**2**	< 1

54		S07-013487	ASDA Lambs Liver [UK]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**2**	< 1
55		S07-013478	Chicken Liver [N Ireland]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
56		S07-013473	Tesco Chicken Liver [UK]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
57		S07-013351	Ox Liver [UK]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**5**	< 1
58		S07-013485	Ox Liver [England]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1
59		S07-013436	Venison Liver [UK, Suffolk]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**7**	< 1
60		S07-013445	Organic pig kidney [England]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1
61		S07-013500	Pig Kidney [England]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1
62		S07-013379	Ox Kidney [England]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**3**	< 1
63		S07-013352	Ox Kidney [UK]	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**2**	< 1
64		S07-013432	Lambs Kidney [UK, West country]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
65		S07-013470	McKay Lambs Kidney [N Ireland]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
66		S07-013311	Lambs Hearts	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
67		S07-013353	Lambs Hearts	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
68		S07-013367	Country Park Foods Black Pudding	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
69		S07-013410	Black Pudding	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
70		S07-013488	Asda duck liver pate	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
71		S07-013504	Castle MacLellan Chicken liver Pate	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
72		S07-013376	Newmarket Sausages Natural	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
73		S07-013317	Sherbourne Lincolnshire Sausages	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
74	Meats	S07-013381	Boneless shoulder of lamb	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
75		S07-013412	Shoulder of Lamb	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
76		S07013315	Morrisons Boneless Leg of Pork	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
77		S07-013395	Waitrose British Pork Boneless Leg	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
78		S07-013312	Morrisons B. Steak	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
79		S07-013411	Rump Steak for Braising	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
80		S07-013472	McKay Fresh Chicken Legs	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
81		S07-013502	Boneless chicken thighs	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1

82		S07-013382	Meat Inn Turkey Breast	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
83		S07-013394	Asda British Turkey Breast Joint	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
84		S07-013403	Andrews Venison Fillet	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
85		S07-013413	Venison Haugh Joints	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
86		S07-013350	Scotch beef quarterpounders	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
87	Milk	S07-013377	Countrylife Organic whole milk	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
88		S07-013343	Calon Wen Organic Whole Milk	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
89		S07-013408	Morrisons Fresh Whole Milk	< 1	<2	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
90		S07-013425	Yarty Valley - Whole Milk	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
91		S07-013469	Strathray Whole Milk	< 1	<2	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
92		S07-013468	Ballyrashane Whole Milk	< 1	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
93		S07-013498	Delamere Dairy Fresh Goats milk	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
94		S07-013505	Woodlands Sheeps milk powder	< 1	<2	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
95		S07-013459	Ewe tree Farm Sheep's Milk	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
96		S07-013401	Waitrose Fresh Full Cream Goats	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
97		S07-013484	Raw sheep milk Boydells Dairy Farm	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
98	Cheese	S07-013318	Pilgrims Choice Cheese	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
99		S07-013344	Tesco, Welsh Medium Cheddar	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
100		S07-013453	Waitrose Duddleswell Cheese	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
101		S07-013438	Somerset Brie	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
102		S07-013398	Cornish Brie Wedges	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
103		S07-013439	Wensleydale Sheeps Cheese	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
104		S07-013362	Sainsbury Organic Goat Cheese	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
105		S07-013335	Somerset Goat Cheese	< 1	< 1	< 1	< 1	< 10	< 10	< 10	< 1	< 1	< 10	< 1
106		S07-013452	M & S Medium Half Fat Cheese	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
107		S07-013372	Primula Cheese Spread	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
108	Eggs	S07-013495	Elliots Eggs Free Range	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
109		S07-013368	Tesco Free Range Eggs Organic	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1

110		S07-013337	Budgens Free Range Eggs	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
111		S07-013476	Skea Eggs Free Range	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
112		S07-013422	Scottish Free Range Eggs	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
113		S07-013393	Farmhouse Freedom Eggs Free	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
114		S07-013448	Barrington Park Estates Organic	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
115		S07-013451	Rookery Farm Organic Free Range	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1
116		S07-013316	Bitteswell Browns Eggs Caged [UK]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
117		S07-013383	Birds big English Fresh Eggs Caged	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
118		S07-013338	Tesco Free Range Duck Eggs	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
119		S07-013405	Free Range Duck Eggs [UK], Dev.]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
120	Vegetables	S07-013320	Morrisons Baby Potatoes [Maris, UK]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**1**	< 1	< 1	< 1
121		S07-013477	Baby New Potatoes [Charlotte]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
122		S07-013336	Somerfield White Potatoes (Osprey)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
123		S07-013348	Tesco Loose Potatoes	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
124		S07-013390	Waitrose organic baby new	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
125		S07-013441	Potatoes [Marfona]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
126		S07-013465	Whitepark Bay McCurdy's [Queens]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
127		S07-013321	Bartlett Rooster Potatoes (Rooster-	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
128		S07-013359	Sainsbury Baking	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
129		S07-013414	Fresh Potatoes (Epicure)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
130		S07-013364	Sainsbury Crispy Oven Fries	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
131		S07-013486	Asda Crispy Home Style Chips	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
132		S07-013366	Aunt Bessies, Homestyle Crispy	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
133		S07-013424	Tesco 12 Waffles	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
134		S07-013339	Kettle Crisps	< 1	<2	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
135		S07-013440	Walkers Cheese and Onion Crisps	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
136		S07-013430	Weightwatchers Mini Loops	< 1	<2	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
137		S07-013423	Mini Pringles (Original)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1

138	S07-013494	Sweet Potatoes	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
139	S07-013503	Bugdens Sweet Potatoes	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
140	S07-013322	Morrisons Carrots [UK]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
141	S07-013346	Tesco British Carrots	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
142	S07-013370	Tesco British Parsnips	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1	< 1	< 1	< 1
143	S07-013491	ASDA British Parsnips	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
144	S07-013358	Sainsbury Half Swede	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
145	S07-013347	Tesco Swede	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
146	S07-013442	Celeriac	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
147	S07-013492	ASDA British celeriac	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
148	S07-013385	John Wedder Beetroot (bunch)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
149	S07-013444	Beetroot	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
150	S07-013415	Baby Turnips	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
151	S07-013443	Baby Turnips	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
152	S07-013313	String Beans	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
153	S07-013387	Asda Runner beans	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
154	S07-013365	Fresh Broad Beans in Pod	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
155	S07-013314	Broad Beans	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
156	S07-013384	John Wedder Whole Cabbage	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
157	S07-013389	Waitrose Spring Greens	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
158	S07-013388	Waitrose Spinach	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
159	S07-013490	ASDA Spinach	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
160	S07-013375	M&S Scottish Broccoli	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
161	S07-013416	Broccoli Florets	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
162	S07-013307	Co-op Cauliflower	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
163	S07-013386	M&S Cauliflower	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
164	S07-013349	Leeks, Cardiff	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
165	S07-013417	Whole Leeks (Fresh)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1

166		S07-013334	Sainsbury Red Onions	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
167		S07-013489	Asda Onions	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
168		S07-013374	M&S Tomatoes	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
169		S07-013493	Jersey Jewel Tomatoes on vine	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
170		S07-013345	Cherry Tom on the vine	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
171		S07-013360	Sainsbury British Watercress	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
172		S07-013306	Co-op Mushy Peas	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
173		S07-013464	Batchelors Bigga Marrowfat	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**2**	< 1	< 1	< 1
174		S07-013324	D'Aucy Sweetcorn (Canned)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
175		S07-013426	Princes sweetcorn in brine	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
176		S07-013340	Tarantella Organic Chopped	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
177		S07-013467	Sainsburys Chopped Tomatoes	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
178		S07-013475	Crosse & Blackwell Broad Beans in	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
179		S07-013499	Freshcan Broad Beans	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
180		S07-013332	Waitrose Jersey Potatoes	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
181		S07-013497	ASDA Jersey new potatoes(canned)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
182		S07-013463	Costcutter New Potatoes in water	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
183	Grains/Bread	S07-013329	Mornflake Superfast Oats	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
184		S07-013429	Quaker Oats organic	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
185		S07-013407	Hamlyns Scottish Oatmeal	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
186		S07-013449	Infinity Foods Organic Oatmeal	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
187		S07-013466	Sunblest White Medium Sliced Bread	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
188		S07-013361	Hovis Square White Loaf	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
189		S07-013391	Doves Farm Organic Wholemeal	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
190		S07-013319	Warburtons Wholemeal Bread	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
191		S07-013325	Chicago Joes Toffee Popcorn [UK]	< 1	< 1	< 1	< 1	< 1	< 1	< 1	**2**	< 1	< 1	< 1
192		S07-013328	Butterkist Pop Corn	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
193		S07-013369	Orv. Red. Pop Corn	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1

194		S07-013427	Cinema Sweet Pop Corn [UK]	< 1	**1**	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
195	Fruit/Jam	S07-013330	Duchy Orig. Strawberry Jam Organic	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
196		S07-013406	Robertsons Blackcurrant Jam	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
197		S07-013373	Mackays Raspberry Pres.	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
198		S07-013331	Tiptree Strawberry Conserve	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
199		S07-013392	Waitrose Blackcurrant Coulis	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
200		S07-013450	The English Provender Co.	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1

nr = no result. While the sample was received at CSL, A wet [non-freeze dried] portion was not available for PFOS analysis.

LIMS is the CSL unique sample identifying code used in our Laboratory Information Management System (LIMS)

Table 8. Food analysis data- Phase-2 samples

No	Type	LIMS	Product	PFHxA	PFHpA	PFOA	PFNA	PFDeA	PFUnA	PFDoA	PFBSH	PFHx	PFOS	PFOSA
				Measured analyte concentration μg/kg										
1	Fish	S07-013507	Haddock portions [France, NE Atlantic]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	<1
2		S07-013508	Fresh carp [France, farmed]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**6**	<1
3		S07-013520	Mirror carp [France]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**8**	<1
4		S07-013514	Common carp [France, Wild]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**6**	<1
5		S07-013509	Cod loin [Norway, NE Atlantic]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
6		S07-013523	Bideford cod [UK, Devon]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**2**	**2**
7		S07-013515	Frozen sprats [UK, Cornwall]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**4**	**4**
8		S07-013516	Cornish sardines [UK, NE Atlantic]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	<1
9		S07-013552	Sardines [UK Cornwall]	<1	<1	<1	<1	<1	**2**	<1	<1	<1	**3**	**2**
10		S07-013534	Whitebait [Bulgaria]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**9**	**7**
11		S07-013543	Whitebait [Holland, NE Atlantic]	<1	<1	**5**	<1	<1	**2**	<1	<1	**1**	**40**	**14**
12		S07-013521	Whitebait IQF [Bulgaria]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**9**	**7**
13		S07-013525	Whole trout organically farmed [Scotland]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
14		S07-013527	Whole rainbow trout [UK, farmed]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
15		S07-013528	Haddock fillet [China, NE Atlantic]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	<1
16		S07-013529	Salmon fillets [Norway, farmed]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
17		S07-013526	Lochmuir salmon portions [Scotland]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
18		S07-013536	Boneless salmon fillets [Norway, farmed]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
19		S07-013551	Whole mackerel [UK, Cornwall]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
20		S07-013533	Whole Cornish mackerel [UK, Cornwall]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
21		S07-013553	Herring (filleted by fishmonger) [UK]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
22		S07-013554	Smoked eel [Englang]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
23		S07-013513	Traditional jellied eels	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
24		S07-013517	Jellied eels [NI Lough Neagh]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
25		S07-013518	Smoked eel [Holland]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	<1
26		S08-009817	Herring Harvey Nichols [UK, Cornwall]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	<1

27		S08-009818	Whitebait [Netherlands, Bulgaria]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**5**	**3**
28		S08-009819	Carp [Holland]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**4**	<1
29		S08-009820	Sardines wholefoods market [NE Atlantic]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**2**	**1**
30		S08-013024	Sardines Sainsburys [NE Atlantic]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**3**	**1**
31	Crustaceans	S07-013542	Crab [UK, Filey]	<1	<1	**5**	**1**	<1	**1**	**1**	<1	<1	**2**	**3**
32		S07-013522	Brown crab [Scotland]	<1	<1	**6**	**3**	<1	<1	<1	<1	<1	**3**	**2**
33		S07-013546	Cromer crab [UK, Cromer]	<1	<1	**4**	**1**	<1	**1**	<1	<1	**2**	**12**	<1
34		S07-013519	Spider crab [UK, Penzance]	<1	<1	**6**	**1**	<1	<1	<1	<1	<1	**13**	<1
35	Offal	S07-013524	Beef liver [UK, West Country]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**3**	<1
36		S07-013530	Halal beef liver [Scotland]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**3**	<1
37		S07-013541	Ox liver [England]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	<1
38		S07-013547	Pigs liver [UK, Yorkshire]	<1	<1	**2**	<1	<1	<1	<1	<1	<1	**4**	<1
39		S07-013549	Pigs liver [UK ,Lincolnshire]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
40		S07-013538	Wild roe deer liver [UK, Teeside]	<1	<1	**3**	**1**	<1	<1	<1	<1	<1	**10**	<1
41		S07-013539	Farmed red deer liver [UK Barnsley]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**2**	<1
42		S07-013532	Wild venison liver [Scotland]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	<1
43		S07-013535	Lambs liver [UK]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**3**	<1
44		S07-013540	Lambs liver [England]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
45		S07-013510	Lamb liver [UK, West Country]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**5**	<1
46		S07-013555	Irish pigs liver [Ireland]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
47		S07-013511	Beef kidney [UK]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	<1
48		S07-013548	Lambs kidney [UK]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**2**	<1
49		S07-013531	Lambs kidney [UK]	<1	<1	<1	<1	<1	<1	<1	<1	<1	**1**	<1
50		S07-013544	Ox kidney [UK]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
51		S07-013545	Pigs kidney [UK]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
52		S07-013550	Pigs kidney [UK Wiltshire]	<1	<1	**1**	<1	<1	<1	<1	<1	<1	**4**	<1
53		S07-013537	Cumberland pork sausages [UK]	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

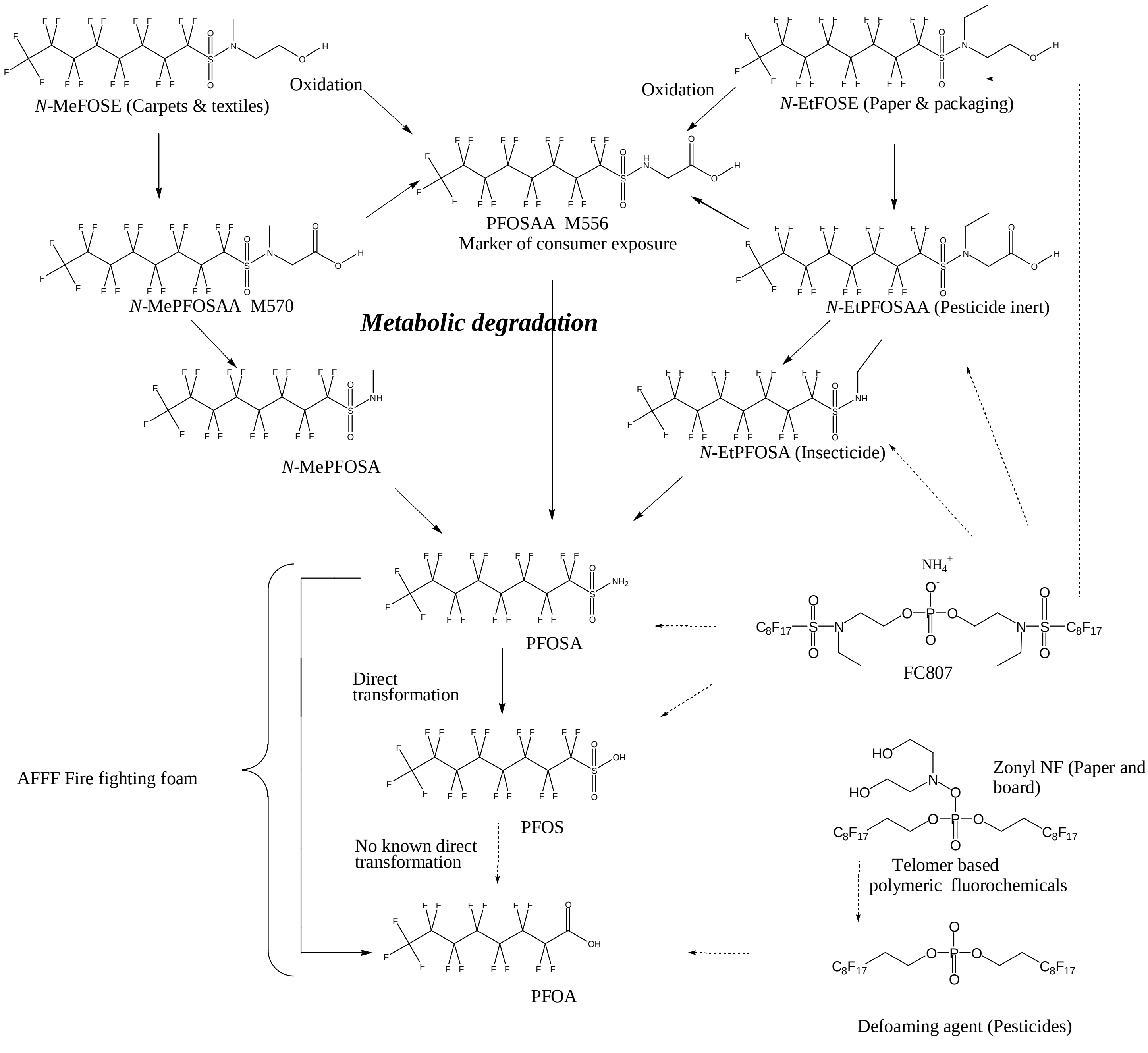
Table 9. Summary of concentrations of PFCs by food type

Class	Type	N	Range ΣPFCs µg/kg	N > LOQ	Mean	% Positive
Fish	Whitebait	7	3-62	7	**24**	100
	Eel	6	<1-63	3	**11**	50
	Carp	6	<1-8	5	**5**	83
	Sprats	2	1-7	3	**5**	100
	Sardines	6	2-7	6	**4**	100
	Cod	4	<0-5	2	**2**	50
	Mackerel	4	<1-3	1	<1	25
	Haddock	4	<1-3	3	<1	75
	Trout	4	<1-2	3	<1	50
	Herring	3	<1-2	1	<1	33
	Plaice	2	<1-1	1	<1	50
	Salmon	8	<1	0	<1	0
	Sole	2	<1	0	<1	0
Shellfish	Oysters	2	1-1	2	<1	100
Crustaceans	Crab	6	11-23	6	**15**	100
	Crayfish	1	2	1	**2**	100
	Prawns	2	<1-1	1	**1**	50
	Langoustine	1	<1	0	<1	0
Offal	Liver	23	<1-14	19	**3**	83
	Kidney	12	<1-5	8	**1**	67
	Other offal	9	<1	0	<1	0
Dairy	Milk	11	<1	0	<1	0
	Cheese	10	<1	0	<1	0
Eggs	Chicken	10	<1-1	1	<1	10
	Duck	2	<1	0	<1	0
Oils	Fish	4	<1	0	<1	0
	Vegetable	6	<1	0	<1	0
Plant produce	Grains/bread	12	<1-1	2	<1	17
	Vegetables	63	<1-2	2	<1	3
	Fruit/jam	6	<1	0	<1	0

Range ΣPFCs = lowest and highest values of the combined concentrations of all 11 individual fluorinated analytes.

FIGURES

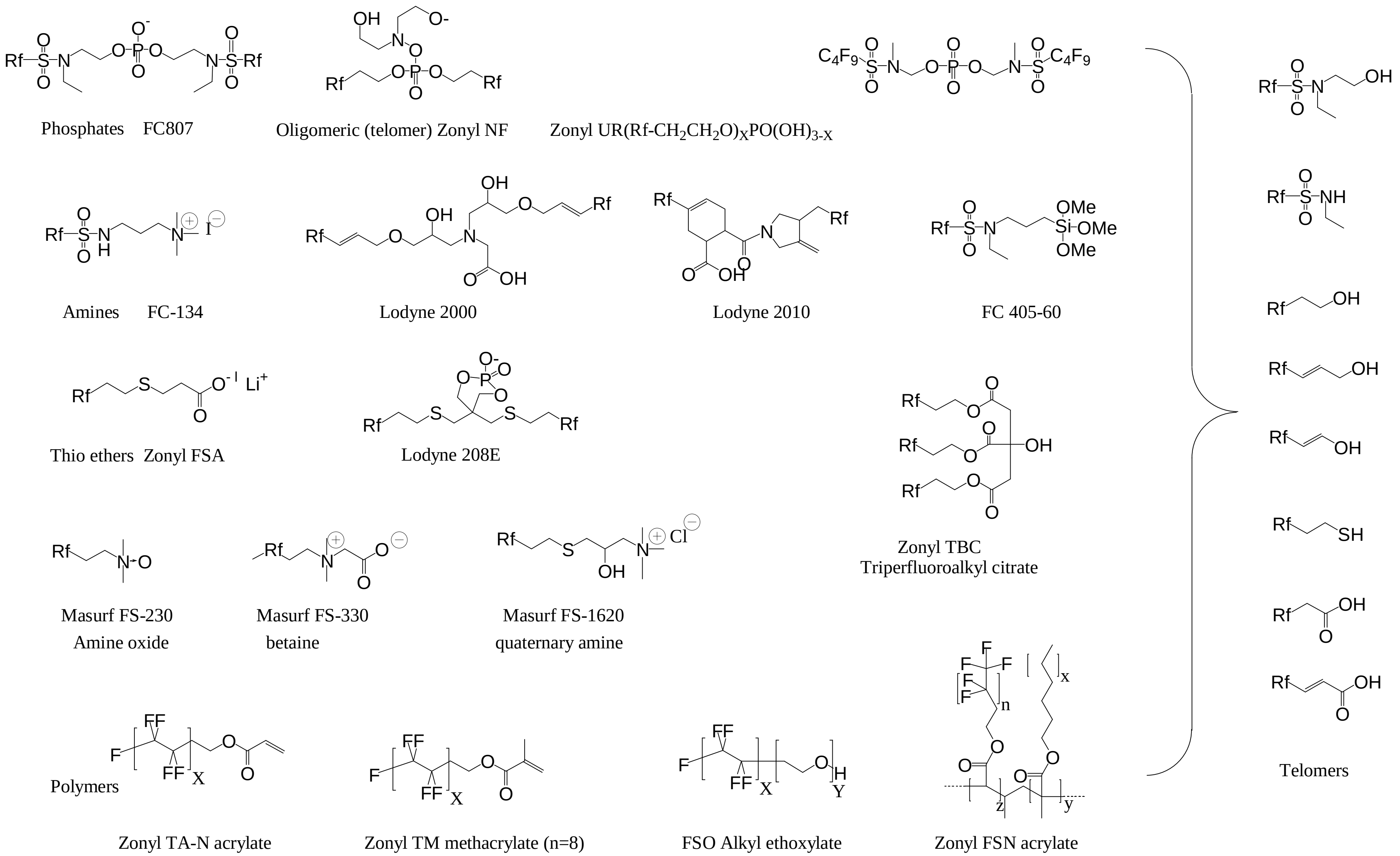
Figure 1. Possible interconversions and degradations of PFCs



Possible interconversions and degradations of PFCs and possible release from consumer products.

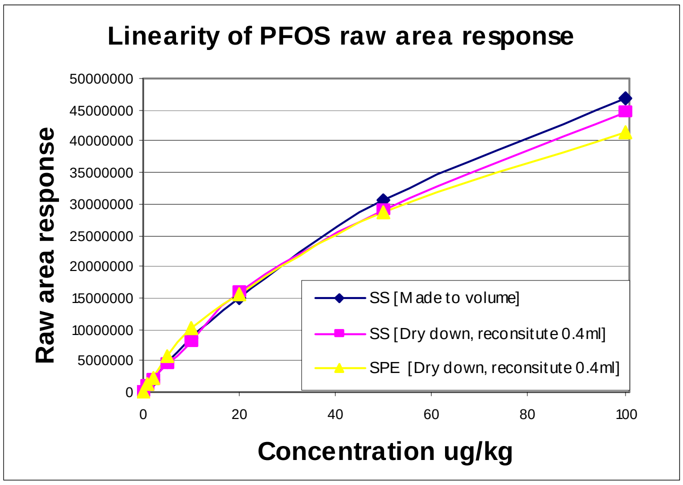
N-EtFOSE = *N*-Ethylperfluorooctanesulfonamidoethanol, *N*-EtPFOSAA = *N*-Ethylperfluorooctanesulfonamidoacetate, *N*-EtPFOSA = *N*-Ethylperfluorooctylsulfonamide, *N*-MeFOSE = *N*-Methylperfluorooctanesulfonamidoethanol, *N*-MePFOSA = *N*-Methylperfluorooctylsulfonamide, PFOSAA (M556) = Perfluorooctanesulfonamidoacetate, *N*-MePFOSAA (M570) =*N*-Methylperfluorooctanesulfonamidoacetate.

Figure 2. Representative PFC structures and putative telomers

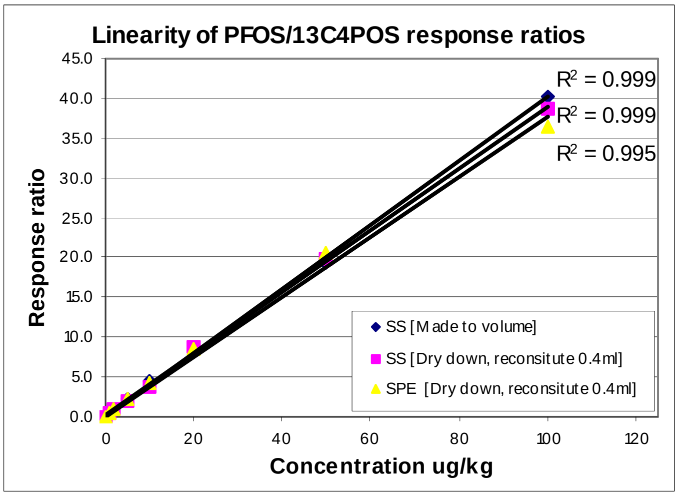


Rf = perfluoroalkyl chain $CF_3[CF_2]_n$, generally perfluorooctyl, $CF_3[CF_2]_7$

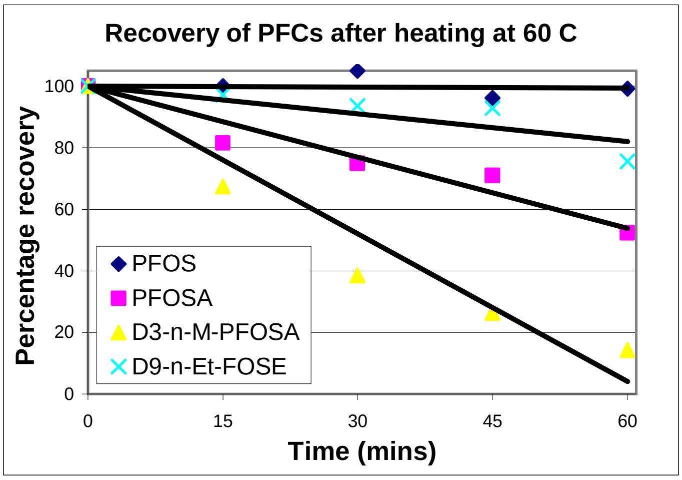
Figure 3. Basic performance characteristics (evaporation/concentration)



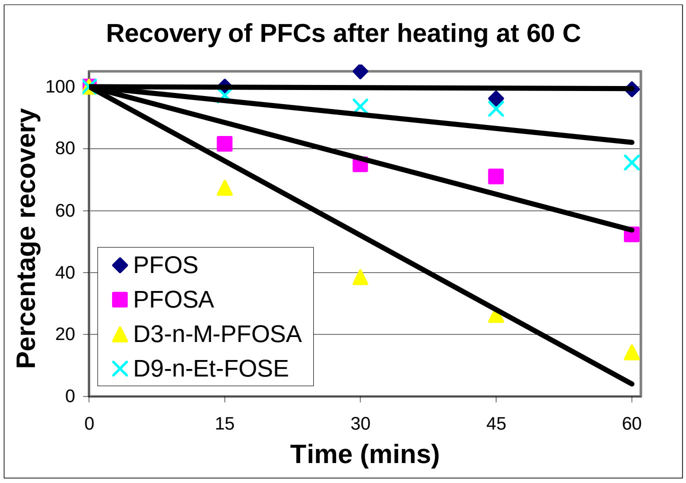
A)



B)



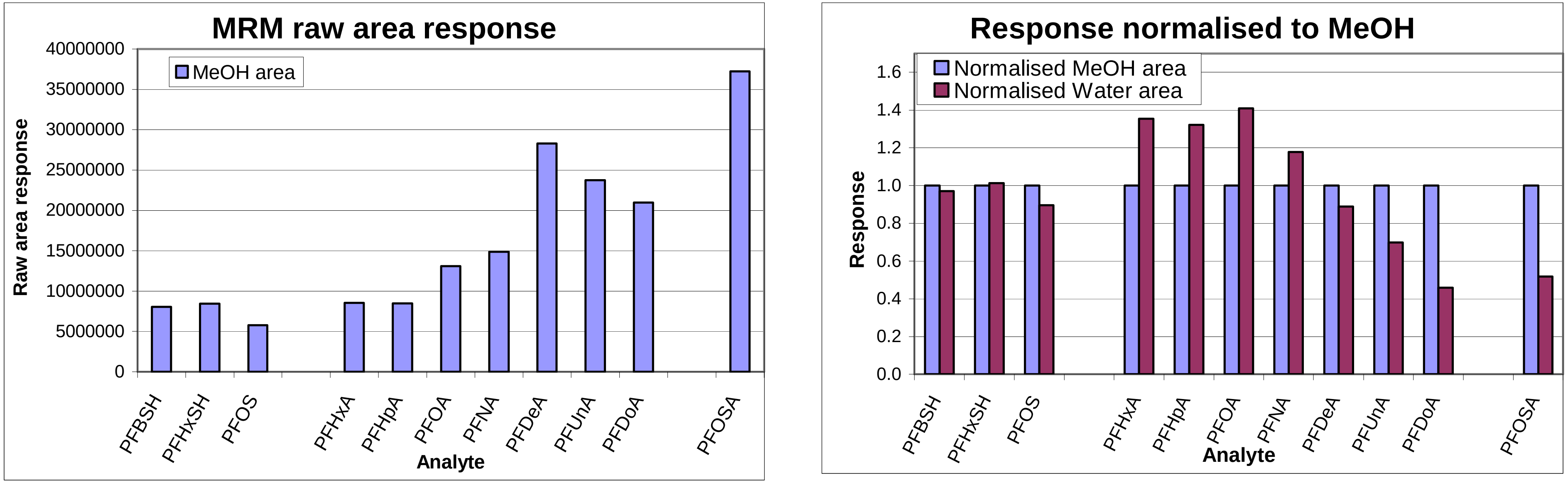
C)



D)

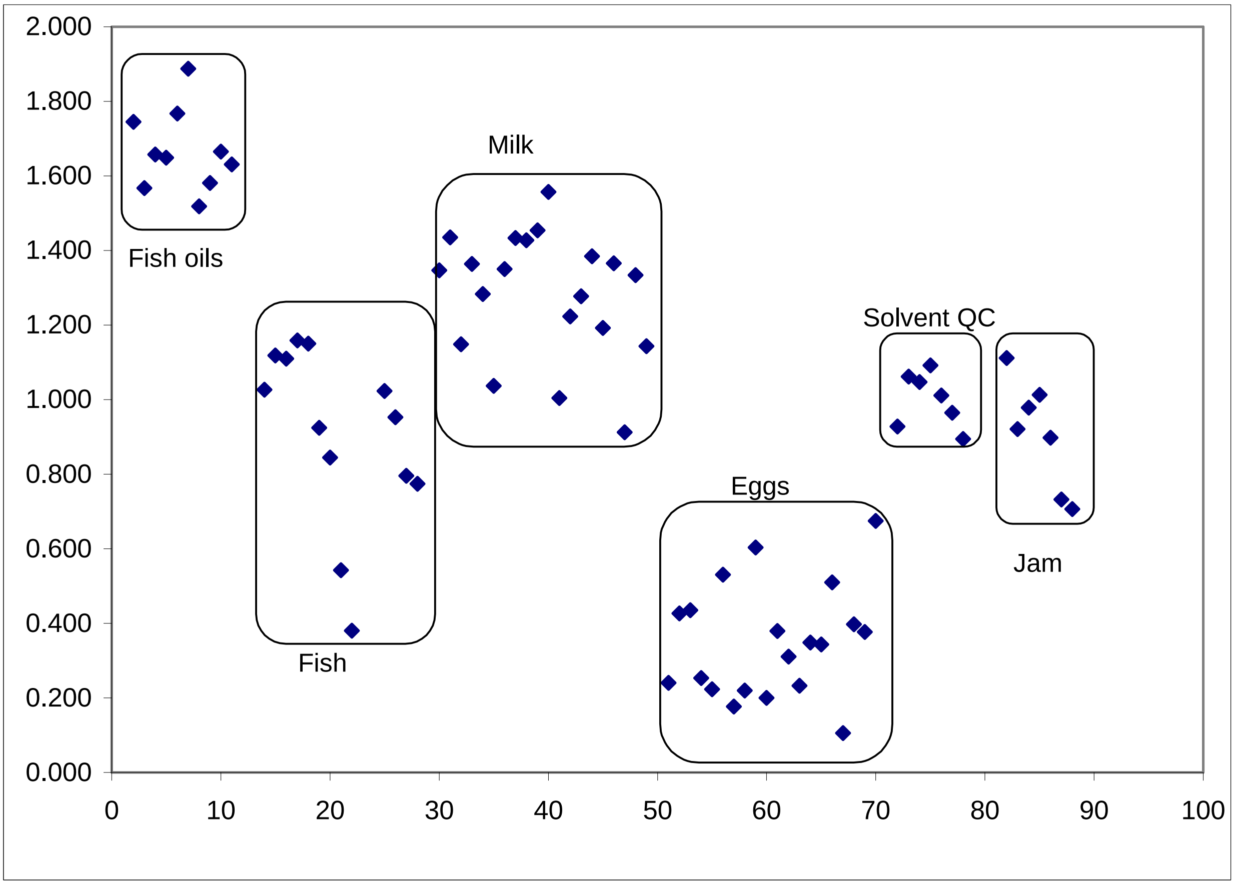
Basic performance characteristics. A) Raw area response curve of PFOS in methanol (solvent standards) compared to the response before and after drying (reconstitued in methanol) and with drying and reconstitution in methanol after SPE. B) Linearity of native/labelled PFOS response ratio, in this example. C) PFOS in methanol (solvent standards) compared to response before and after drying (reconstitued in methanol) and with drying and reconstitution in methanol after SPE. D) Stability/volatility losses af PFOS, PFOSA and larger labelled amides on heating in a nitrogen stream.

Figure 4. LC-MS/MS relative responses in methanol and water



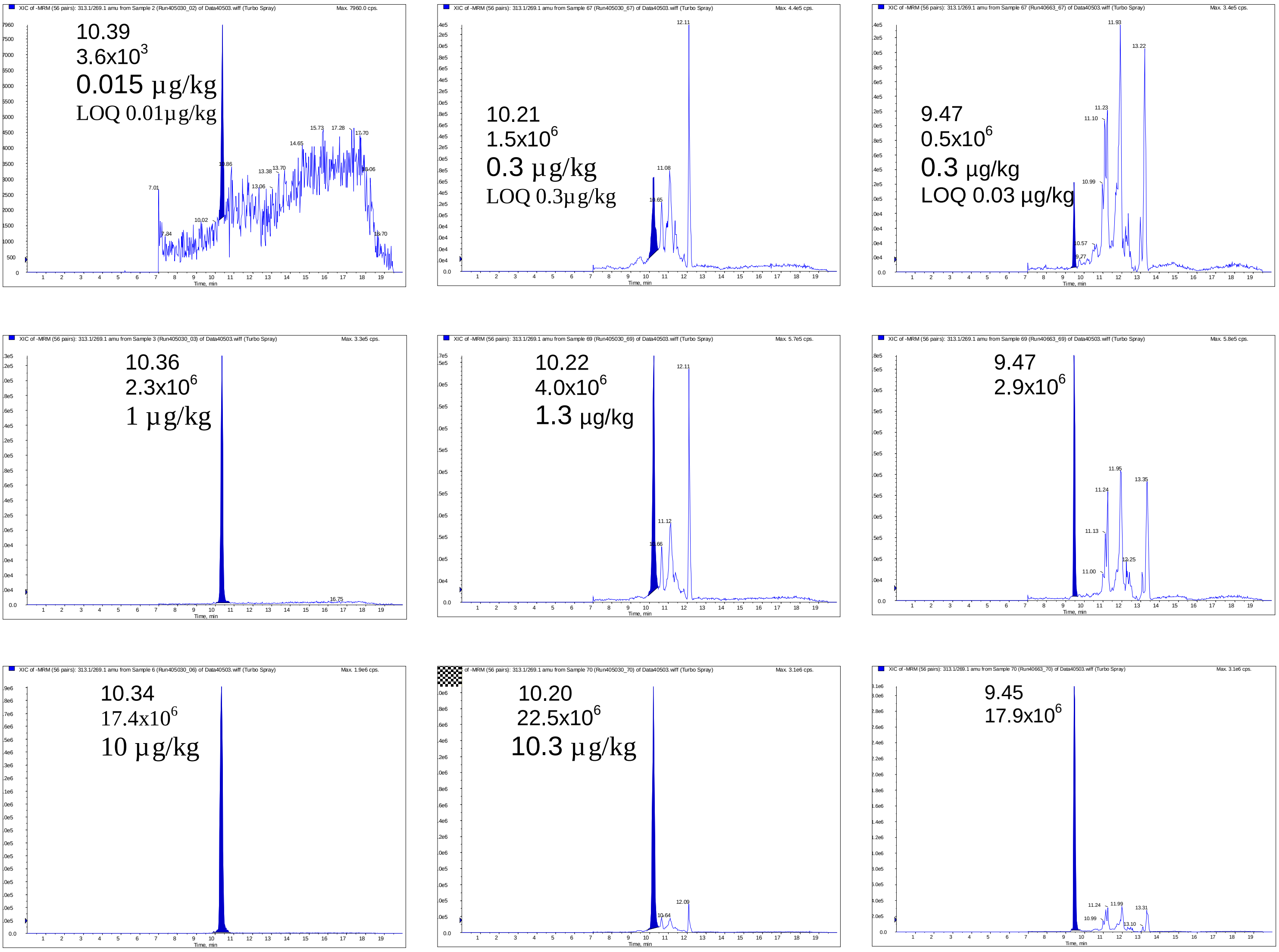
Both enhancement [x1/2] and suppression [x1/2] were observed in water injections relative to those conducted those in methanol.

Figure 5. LC-MS/MS - Variability in the raw area response



Variability in the raw area response of the 13C_4-PFOS isotope dilution internal standard within a single analytical batch. Data are scaled to the reagent blank QC aliquots as 1.00. Deviations from this value are a combination of procedural recovery and ionisation enhancement or suppression. Sample identification fish oils [n=4 replicates of; cod liver oil, salmon oil, tuna oil], fish [n=9 carp roe, n=4 plaice fillets], milk [n=4 replicates of 5 bovine milks], eggs [n=4 replicates of 5 hen eggs].

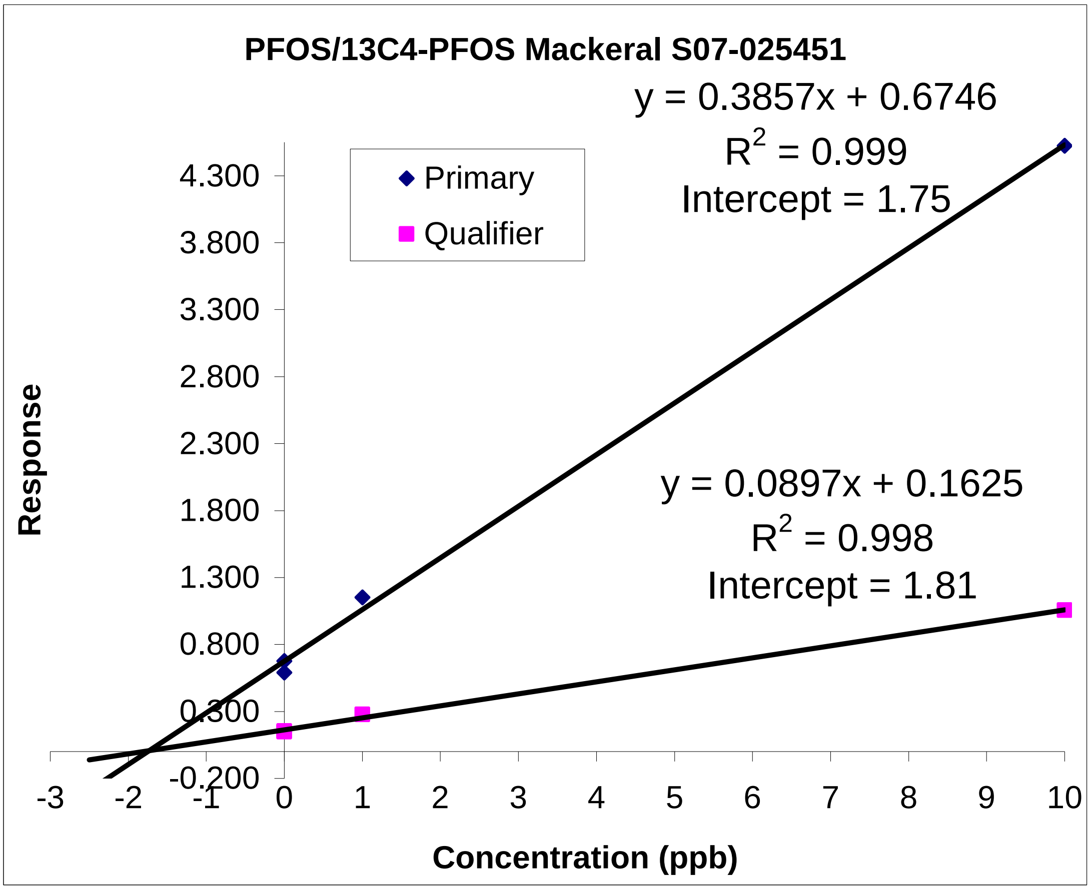
Figure 6. Chromatograms of trout extracts



A) Column-1 $SiO-C_8F_{17}$ B) Column-1 $SiO-C_8F_{17}$ C) Column-2 $SiO-(CH_2)_3-C_5F_5$

Chromatograms of A) standard solutions of PFHxA (MRM 313.1>269.1) at 0, 1, 10 µg/kg (equivalents i.e 0, 25 and 250 ng/ml), and B) trout extracts overspikes at 0,1,10 µg/kg. Trout extracts re-run on second column C). The trout extracts contain various coeluting coextractants at 1/3 of the S/N of the 1 µg/kg overspike when coeluting.

Figure 7. Standard addition calculation procedure



Standard addition calculation procedure for a fish sample. Both sets of ion responses are normalised to the $^{13}C_4$-PFOS isotope dilution internal standard . Qualifying ion is 24% of the primary ion response. Ion ratios 1.81/1.75, are within 4%. Rounded to 1 significant figure and reported as a PFOS concentration of 2 µg/kg.

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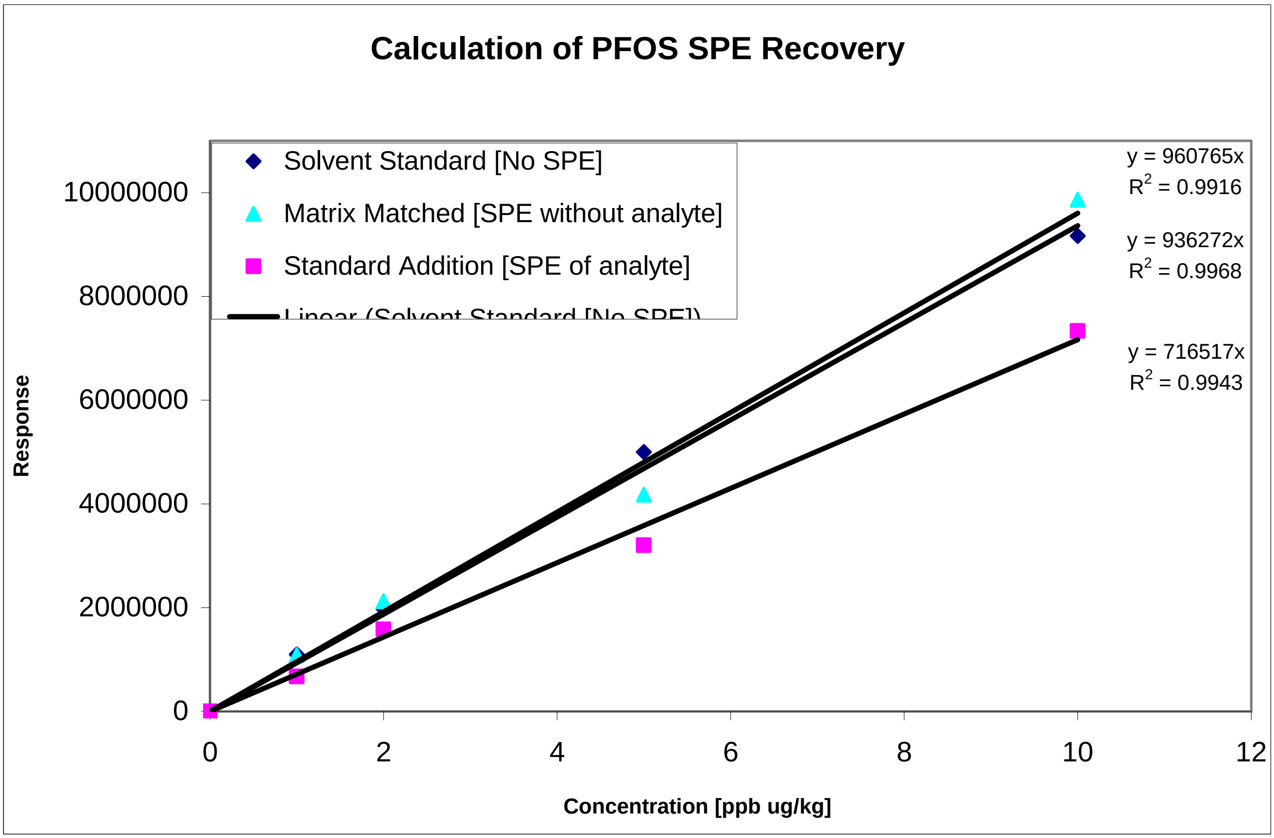
Figure 8. Calculation of analytical recovery



Calculation of analytical recovery. Linearity of the raw area responses of PFOS are compared between (i) methanol based solvent standards, which have not gone through any process, with matrix matched standards where only the matrix has been through the extraction and (ii) analyte is added immediately prior to analysis, and (iii) standard addition where the analyte is added to the matrix before the extraction process. Recovery is the ratio of the slopes of the calibration lines. In this instance 716517/96065 = 75% analytical recovery of PFOS from matrix. Recovery was linear over the range 1-10 µg/kg.

Figure 9. Analytical recovery by food type

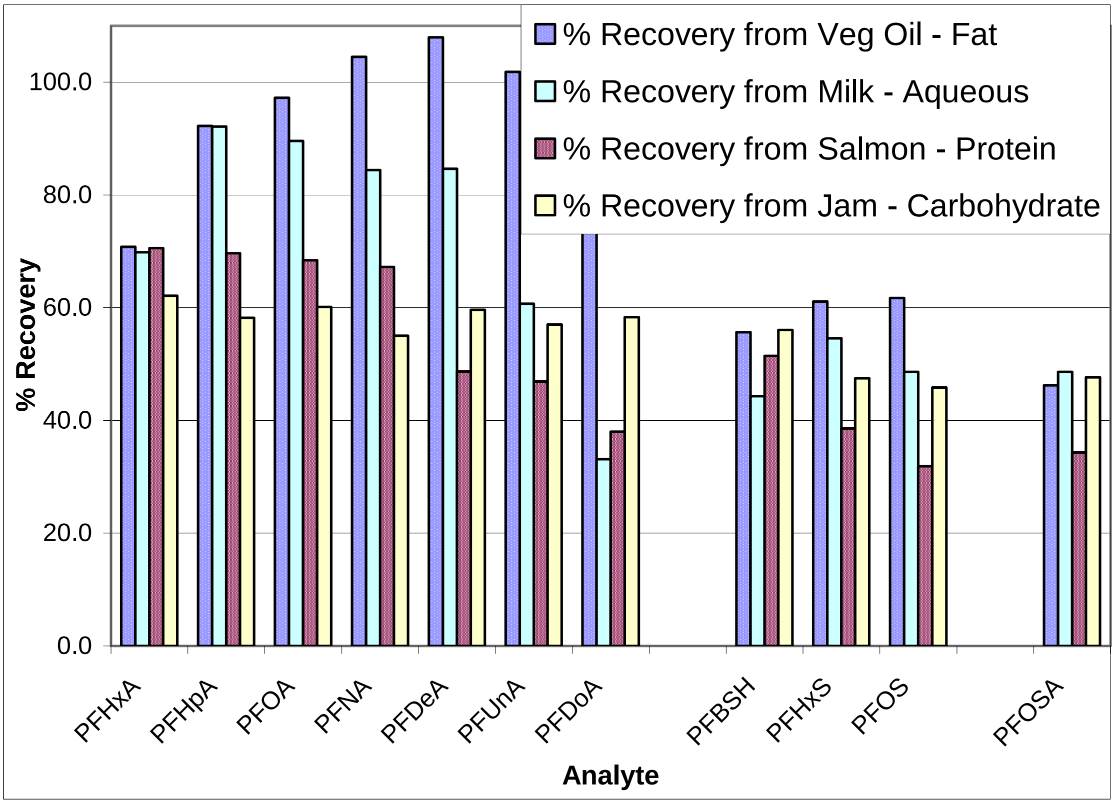
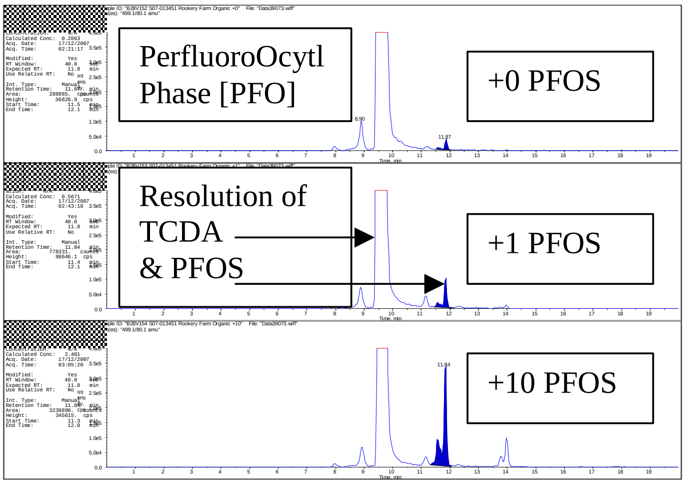
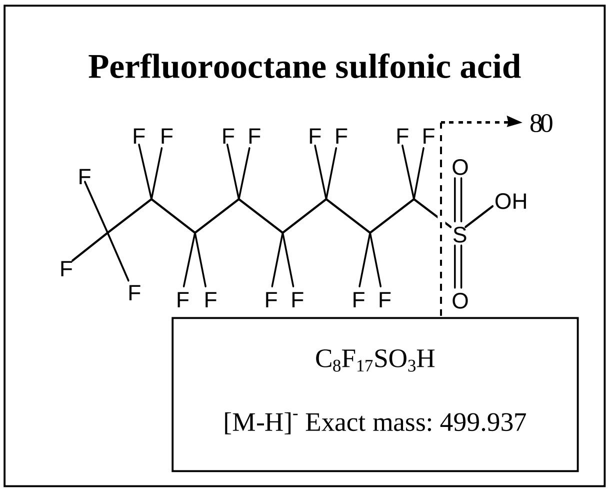


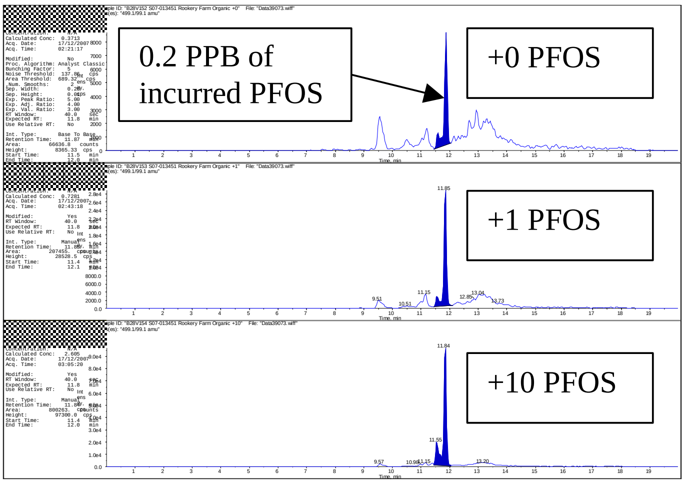
Figure 10. Misreporting of PFOS in eggs

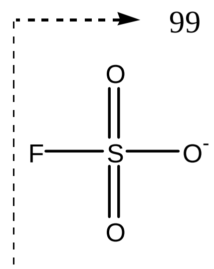
A) Ion channel 499/80 PFOS 11.85 min [alkyl sulfate]





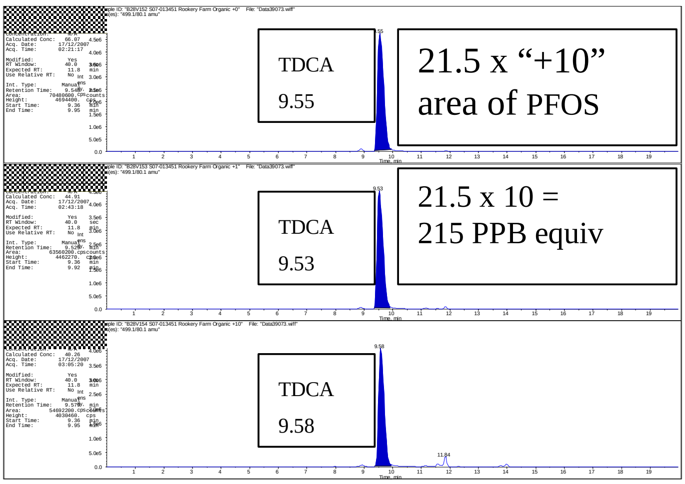
B) Ion channel 499/99 PFOS 11.85 min [fluoro sulfate]





Unique $[SO_3F]^-$ fluorinated fragment

C) Ion channel 499/80 TDCA 9.6 min [alkyl sulfate]



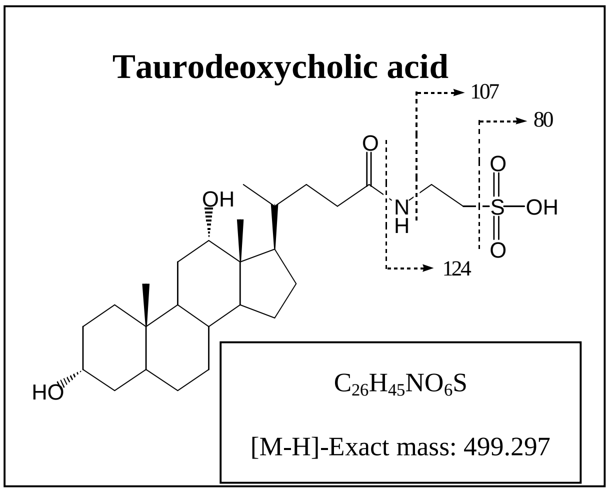
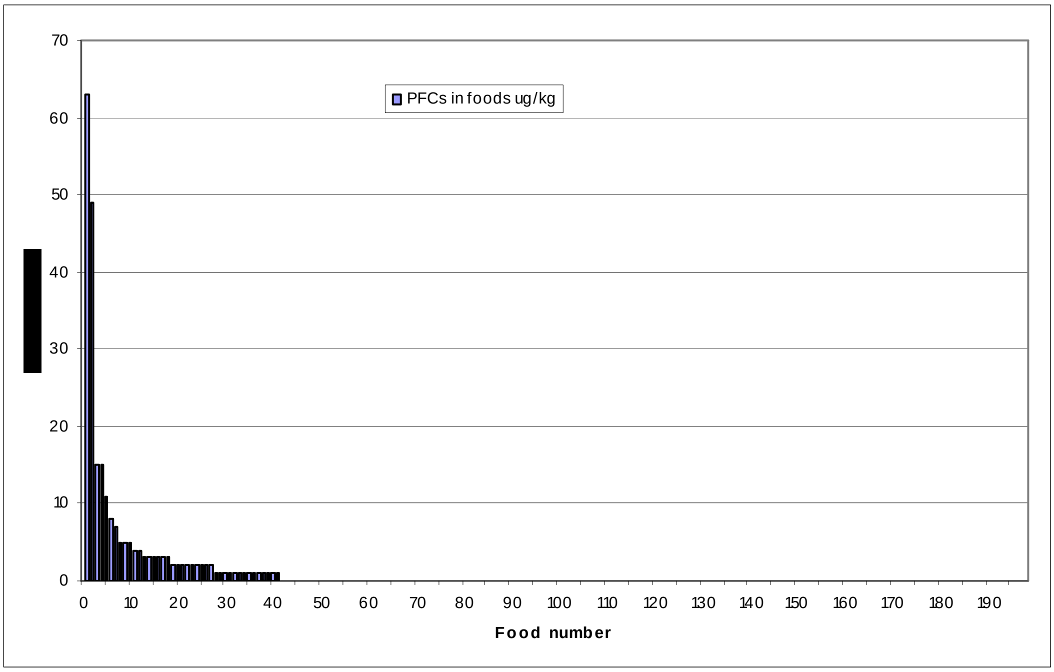
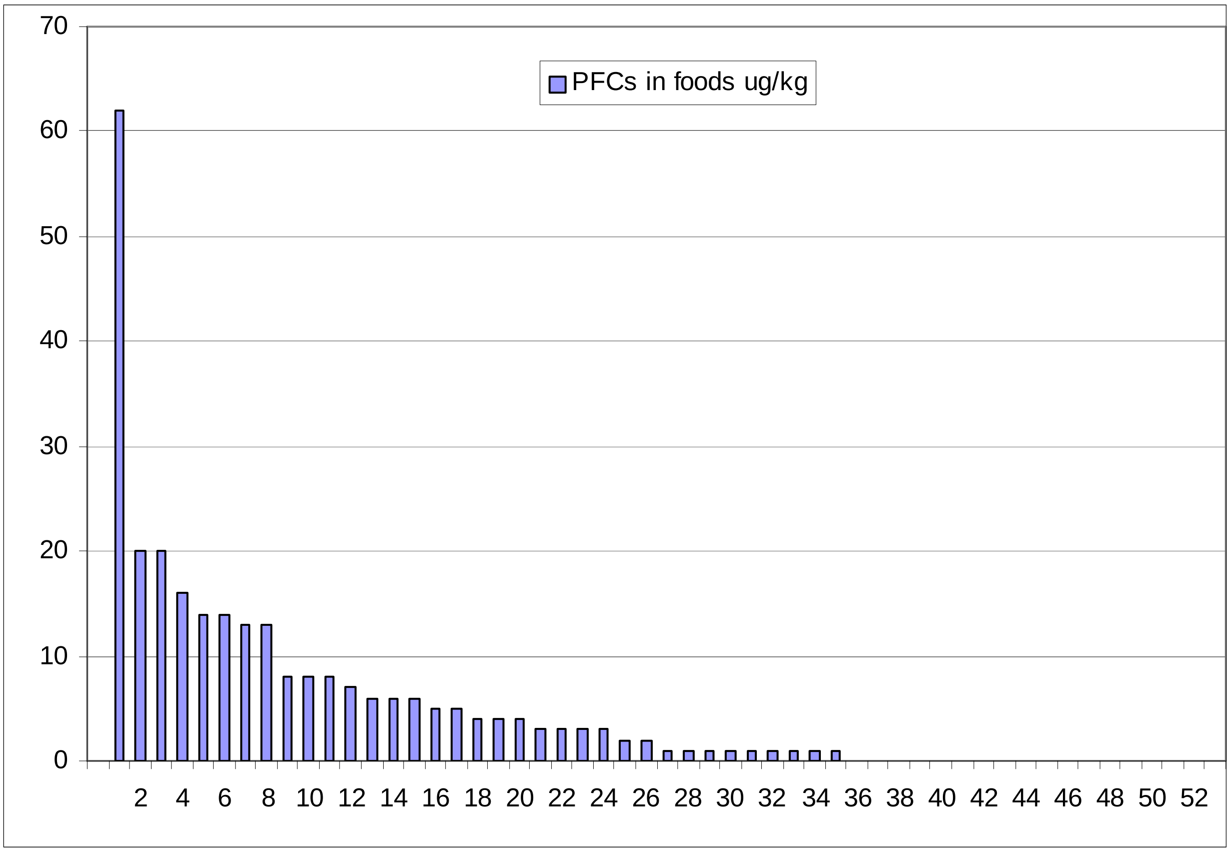


Figure 11. Concentrations of PFCs in Phase-1 individual foods



Concentrations of summed PFCs concentrations in 199 individual foods. 41 individual foods of 199 contained PFCs at > 1 µg/kg. Highest values were for fish, shellfish, crustaceans and offal based foods.

Figure 12. Concentrations of PFCs in Phase-2 individual foods



A further 53 samples of fish, shellfish, crustaceans and offal were collected as Phase-2 35 of the individual foods of 53 contained PFCs at > 1 µg/kg.

Figure 13. Distribution of PFCs in combined Phase-1 & 2 foods