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# Dietary intake estimate for perfluorooctanesulphonic acid (PFOS) and other perfluorocompounds (PFCs) in English retail foods following determination using standard addition LC-MS/MS

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## Abstract

The analysis of 252 food samples (UK-produced and imported) purchased from a variety of retail outlets in England was undertaken for the presence of PFOS, PFOA and nine other PFCs. A limit of quantification (LOQ) of 1 µg/kg was achieved for all target analytes, in all samples. Standard addition was used for quantification of PFC levels. All eleven of the targeted PFCs were detected, in 75 of the individual foods. In 70% of the samples, including all meat other than offal, none of the analytes were present at above the LOD. The highest levels found were 59 µg/kg of perfluorooctanesulfonic acid (PFOS) and 63 µg/kg total PFCs (ΣPFCs) in an eel sample, and 40 µg/kg PFOS (62 µg/kg ΣPFCs) in a whitebait sample. The highest level in an offal sample was 10 µg/kg, in a wild roe deer liver. There were 6 samples with ΣPFCs >15 µg/kg (fish, shellfish, crustaceans), a further 7 samples with ΣPFCs 11-15 µg/kg (including a liver), nine with ΣPFCs 6-10 µg/kg (fish and livers), 31 with ΣPFCs 2-5 µg/kg (including kidneys, popcorn and processed peas) and a further 22 with ΣPFCs close to the LOD of 1 µg/kg (including eggs and potatoes). These concentrations indicate that English consumers are being exposed to a low level of PFC contamination from food. The estimated *upper bound* dietary intake of 10 ng/kg bodyweight/day of PFOS for average adult consumers is well below the 0.15 µg (150 ng)/kg bw Tolerable Daily Intake (TDI) set by the European Food Safety Authority.

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3 The *lower bound* adult dietary intake estimate of 1 ng/kg bodyweight/day is similar to  
4 estimates undertaken and reported in some other countries, such as Canada, Germany  
5 and Spain.  
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10 **Keywords:** perfluorooctanesulphonic acid, PFOS, perfluorocompounds, PFCs, food,  
11 fish, liver, TDI, dietary intake

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13 \*To whom correspondence should be addressed. e-mail [don.clarke@fera.gsi.gov.uk](mailto:don.clarke@fera.gsi.gov.uk)  
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## 16 17 18 19 **Introduction** 20

21  
22 PFOS is now the generally accepted term referring to the individual chemical  
23 perfluorooctanesulphonic acid and any closely related compounds that contain the  
24 PFOS moiety (C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>), including those that may potentially degrade to PFOS in  
25 the environment (Brooke 2004). This term is often used interchangeably with  
26 PerFluoro Compounds (PFCs), or PerFluoroAlkylated Substances (PFAS). The  
27 chemicals under consideration are best described as an homologous series of fully-  
28 fluorinated sulphonic acids, and these homologues can also be present as  
29 sulphonamide or carboxylic acid derivatives. The high-energy carbon-fluorine  
30 covalent bond makes the core perfluoroalkyl group resistant to hydrolysis, photolysis  
31 and microbial or mammalian metabolism. Standard metabolic processes can remove  
32 other constituents such as hydrocarbon groups. There are believed to be important  
33 introversions of larger to smaller molecular weight PFCs occurring in the  
34 environment. PFOS is therefore not readily degradable and can persist and  
35 bioaccumulate in the environment, probably by means of covalent protein binding.  
36 The US Environmental Protection Agency (EPA) reported in May 2000 that PFOS  
37 combines persistence, bioaccumulation and toxicological properties to an  
38 extraordinary degree. PFOS exhibits hepatotoxicity, neurotoxicity, carcinogenicity  
39 and reproductive toxicity. One of the most disturbing findings was its unusual ability  
40 to influence second-generation rodent reproduction at 0.4 mg/kg body weight per day  
41 (bw/day) (repeated daily dosing). PFCs are also known to be endocrine disruptors  
42 (Jensen 2008).  
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3 PFOS has global biospheric distribution, bioaccumulation and biomagnification  
4 patterns similar to other persistent organic pollutants (POPs). A recent review  
5 provides an up-to-date reference for sources, fate and transport of  
6 perfluorocarboxylates (Prevedouros 2006). The increases in global exposure levels,  
7 have led to elevated circulatory concentrations of PFOS in mammalian plasma.  
8 Retrospectively, this upward trend has been apparent for some decades. Aside from  
9 industrial exposure, it is not yet clear as to the exact mechanisms of exposure to  
10 specific fluorochemicals and their precursors, or their relative significance, e.g. via  
11 fire fighting foam, household and consumer products vs food and water, vs air and  
12 dust.  
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14 Historically the uses of PFOS have been widespread and include uses as; a metal  
15 surface treatment, as a fabric protector (stain repellents - carpets), impregnated in  
16 paper (grease proofing - pizza boxes), and leather, in waxes, polishes, paints,  
17 varnishes and cleaning products. In Europe the suggested scale of use is 80 tons of  
18 PFOS used between 1980 and 2005 by the North Sea oil industry (fire fighting) and  
19 an equivalent usage/emission as total European terrestrial pollution.  
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21 3M, the major PFC producer, had reduced PFOS production by 98% by the end of  
22 2000 (equivalent to an 88% reduction in world-wide production), with total cessation  
23 in 2002 (Olsen 2008, Spliethoff 2008). The global regulation of PFOS/PFOA,  
24 together with the voluntary change to alternative products that is already well  
25 underway in Westernised countries, should result in a decline in future environmental  
26 contamination and hence human exposure. The first declines in human exposure in  
27 localised areas have already been reported. The high human exposure to PFCs in  
28 North America led to this population and the blood samples collected by the  
29 American Red Cross, being the most highly contaminated in the world. However,  
30 their PFOS levels appear to have peaked, and are now declining in line with the  
31 previously reported half-life of 4-5 years in adult humans (Olsen 2008). A similar  
32 decline has very recently been observed in infants (Spliethoff 2008). While declines in  
33 US exposure to PFCs appear to have followed the fall in US production, this is not the  
34 case globally. PFOS levels appear to be continuing to increase in blood samples taken  
35 from Chinese citizens (Jin 2007).  
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As the estimated half-life of PFOS in the environment is 41 years, the legacy of environmental contamination cannot be expected to be solved rapidly. One of the clearest examples of a temporal trend in the food chain was seen in guillemot eggs obtained from a Baltic island, where the guillemots feed on fish from the Baltic Sea, thus reflecting the general level of contamination in the region. The concentration in eggs rose at an almost linear rate of 18 µg/kg/per year between 1968-2003, increasing from 17 µg/kg in 1968 to 623 µg/kg in 2003 (Holmstrom 2005). As these eggs are a human food source, the trend seen in these eggs can be directly correlated with the human food chain.

Various regulatory limits for acceptable levels of PFOS in the environment are being discussed. The European Food Safety Authority (EFSA) identified 0.03 mg/kg bw per day of PFOS as the lowest no-observed-adverse-effect level (NOAEL, liver pathology) for monkeys and considered this suitable for deriving a human Tolerable Daily Intake (TDI) for PFOS of 0.15 µg/kg bw. Similarly a ten-fold higher human TDI for PFOA of 1.5 µg/kg bw has also been agreed (EFSA 2008).

To date there have been very few studies that have determined PFCs in the human diet. The prevalence of PFOS and its impact on the wider human food chain only became apparent when the 3M Multi-City Study reported that four of the twelve positive food concentrations were from 'control' cities, i.e., those without a fluorochemical industry (3M Company, 2001). 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 (Berger 2007) focused on the four most likely food groups to be contaminated; meat products, dairy products, eggs and seafood. This survey did not positively identify any PFCs and reported less than the LOD (2.2, 3.2 µg/kg PFOS and PFOA, respectively) for all food composites surveyed. However, individual fish samples were found to contain up to 23 µg/kg PFOS (Berger 2007). A Spanish survey of composite foodstuffs found numerous trace levels 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

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freshwater fish (Tittlemier 2007). A large 7-day duplicate diet study in Germany reported average values from 214 separate daily diets collected from 31 adults as 0.06 and 0.69  $\mu\text{g}/\text{kg}$  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 123 and 270 ng of PFOS and PFOA, respectively, equivalent to 1.8 and 3.9 ng/kg bw/day. The duplicate diet collection model was therefore not dissimilar in outcome to the TDS model with regard to the intake estimates. Of interest in this study was the detailed analysis of each day's food in which just two PFOA values were unusually high. The higher of these was a concentration of 118  $\mu\text{g}/\text{kg}$  in the daily diet. This one-off high value was undoubtedly from smaller portions of a single discrete foodstuff containing at least an 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 heavily polluted industrialized areas.

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  $\mu\text{g}/\text{kg}$ , respectively, with the highest individual PFOS value at 92  $\mu\text{g}/\text{kg}$  in a chicken liver. Chinese chicken eggs were all found to contain PFOS in the range of 45-87  $\mu\text{g}/\text{kg}$  (Wang 2008). Oysters from Tokyo bay contained 3  $\mu\text{g}/\text{kg}$  of PFOS (So 2006).

The aim of the survey was to develop more robust analytical methods, in particular to lower the limit of detection, to enable improved estimates of dietary intakes of the chemicals and to provide data to inform negotiations regarding possible future limits for the chemicals in foods.

## Materials and methods

### *Collection and preparation of food samples*

Priority was given to foods in which the chemicals had been detected in the previous survey (potatoes and vegetables (FSA 2006), and foods in which it was anticipated that the chemicals would be present on the basis of literature reports (fish and offal).



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3 A total of 252 samples of various foods (fish, liver, kidney, meat, cheese, milk, eggs,  
4 potatoes, vegetables, cereals and jam) were obtained by Ventress Technical Limited  
5 Ventress Technical Limited is an independent consultancy with specialist skills in the  
6 practice of food technology, food examinations and offers varied services to science  
7 and technology. Using trained sampling personnel and comprehensive field  
8 management information systems, it has many years experience of sampling a variety  
9 of food products, from bulk consignments on site to individual retail packs on retail  
10 sale. The samples for this survey were purchased from retail establishments in ten  
11 regions of the UK (covering all four countries but weighted towards England as the  
12 most populated of the countries), in two phases, the first in 2007. The second phase,  
13 used to follow up on foods in which higher concentrations of the chemicals had been  
14 found in phase 1, took place in 2008.  
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26 The retail establishments included major and smaller national supermarkets and  
27 independent retailers (including convenience stores, butchers, fishmongers, health  
28 food shops, farm shops, ethnic stores, licensed market stalls and mail order/internet  
29 sales). In selecting the retail establishments and numbers of samples obtained from  
30 each, a balance was struck between the relative market shares are supermarkets vs  
31 independent retailers and the need to cover a large number of establishments and  
32 locate some foods not widely available. All sampling was random. All samples were  
33 stored and transported to the Food and Environment Research Agency Laboratory,  
34 which carried out the analyses, mostly under similar conditions to those that prevailed  
35 when they were on sale. Approximately 400 g of each individual retail food was  
36 homogenised and extracted without any further processing. However certain meat and  
37 fish samples were frozen immediately after purchase and held in a frozen state  
38 throughout further storage and transfer stages to prevent microbial deterioration. The  
39 types of foods are described briefly in Table1. All other food samples and reference  
40 materials referred to in this report were obtained by the authors and were used for  
41 method development, method validation and quality assurance (QA) purposes only.  
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### 56 *Chemicals*

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All solvents were of HPLC grade. Ammonium acetate (99.99%), acetic acid (glacial), potassium hydroxide pellets were supplied by Sigma (Poole, UK). All other reagents,

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3 solvents and chemicals were of analytical grade, specific LC-MS grade or equivalent.  
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5 Strata XAW weak anion exchange SPE cartridges (6 cc/200 mg, 33  $\mu$ m) were  
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7 supplied by Phenomenex (Macclesfield, UK). All glassware was either washed three  
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9 times with methanol or heated to 600°C, and silyanised before use.

### 10 11 12 *Standards*

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15 The individual PFCs and internal standards are listed in Table 2. PFOS  
16 (perfluorooctanesulphonic acid), PFHxSK (potassium perfluorohexanesulphonic acid)  
17 (perfluorooctanesulphonic acid), PFHxSK (potassium perfluorohexanesulphonic acid)  
18 and PFHxA (perfluorohexanoic acid) were supplied by Fluka (Gillingham, UK),  
19 PFHpA (perfluoroheptanoic acid), PFOA (perfluorooctanoic acid), PFNA  
20 (perfluorononanoic acid), PFDeA (perfluorodecanoic acid), PFUnA  
21 (perfluoroundecanoic acid), PFDoA (perfluorododecanoic acid) and PFBSH  
22 (perfluorobutanesulphonic acid) and 3 $\alpha$ ,12 $\alpha$ -dihydroxy-5 $\beta$ -cholic acid-*N*-(2-  
23 sulfoethyl)-amide (taurodeoxycholic acid, TDCA) were supplied by Sigma (Poole,  
24 UK). PFOSA (perfluorooctanesulphonamide) and TH-PFOS (tetrahydro-PFOS) were  
25 supplied by ABCR GmbH (Karlsruhe, Germany), <sup>13</sup>C<sub>4</sub>-PFOA, <sup>13</sup>C<sub>2</sub>-PFDeA, D<sub>9</sub>-*n*-Et-  
26 FOSE (2-(*N*-D<sub>5</sub>-ethylperfluoro-1-octanesulfonamido)-D<sub>4</sub>-ethanol) and D<sub>3</sub>-*n*-Me-  
27 FOSA (*N*- D<sub>3</sub>-methylperfluoro-1-octanesulphonamide) were supplied by Greyhound  
28 Chromatography (Birkenhead, UK). Stock standards of those not already in solution  
29 were prepared at 1 mg/ml in methanol and stored at +4°C. Stock solution volumes  
30 were monitored by recording the weight before and after each aliquot was removed, to  
31 check for possible losses of solvent due to evaporation. Working solutions and  
32 mixtures were prepared fortnightly and also stored at +4°C. All fluorinated chemicals  
33 and reagents were assessed for purity and possible PFC cross contamination. For PFC  
34 analytical standards, the area responses of all multiple reaction monitoring (MRM)  
35 transitions in each separate 0.5  $\mu$ g/ml solution in methanol were measured and  
36 assessed as a percentage of the total ion response [assuming equal ionization].  
37 Chemical purities were all >90%, so no corrections were considered to be necessary.  
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### 56 *Sample extractions*

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59 Quadruple 10 g portions of each homogenised food were weighed out into Falcon  
60 tubes (50 ml). The appropriate volumes of internal standard (IS) and standard addition

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mixtures were added to prepare two unspiked portions; one overspiked at the reporting level (1 µg/kg) and one at 10-times the reporting level (10 µg/kg). The food portions were homogenised for 1-3 mins as required in 20 ml of methanol with an Ultra Turrax (T25 basic with S25N blade). Once homogenised, more methanol was added (*ca.* 40 ml in total) and mixed, while withdrawing the Ultra Turrax blade. Samples were shaken vigorously overnight (16 h), then centrifuged (15 min, 5000 rpm) (Tittlemier 2007). Eggs and milk samples required heating at 70°C for 2 hr to induce protein precipitation. The supernatant methanol extracts were evaporated under a nitrogen stream (80°C, in silanised glass vials) just to dryness, and the residues were re-dissolved in aqueous KOH (25 ml, 0.01 M, sonication 10 min). The aqueous solutions were then re-centrifuged (15 min, 5000 rpm). When required, the supernatants were poured in one continuous gentle movement, without breaking up the floating materials [fat] or disturbing the sediment, 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). The cartridges were loaded at a constant drip rate, by increasing from gravity feed to full vacuum as required. After loading, the 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 reduced under a stream of nitrogen gas (60°C), just to dryness and the residues taken up in methanol (400 µl, sonication 10 min). Extracts were transferred into silanised glass microvials (300 µl) for LC-MS/MS determination.

The analysis of cheeses was particularly problematic, due to the excessive amount of material (*ca.* 50 mg) left after the standard clean-up. The clean-up method was therefore extended. The residue was halved by elution of neutral amides off the SPE in methanol (4 ml, neutral pH), and then treating this fraction as a separate extract. Acids, both sulphonic and carboxylic were then eluted as before, using basic methanol (4 ml, 0.1% ammonia). Each fraction still contained *ca.* 25 mg of coextractives. A fluoruous solvent mixture was then used to partition fluorinated from non-fluorinated compounds by liquid-liquid extraction (F-LLE). SPE eluates (neutral or basic) were dried 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)

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3 were added, the mixture was shaken (1 min), and then sonicated for 10 min. When the  
4 residues were in solution, the resulting triphasic system was heated to 80°C for one  
5 hour to achieve a monophasic mixture. The mixtures were then cooled to -70°C for  
6 one hour and the upper 10 ml of DCM was pipetted out and discarded as the non-  
7 fluorinated fraction. The lower two fluorinated layers were pipetted out together and  
8 dried under a stream of nitrogen gas (30°C) until just dry, and the residues taken up in  
9 methanol (400 µl, sonicated for 10 min). Extracts were transferred into silanised glass  
10 microvials (300 µl) for determination by LC-MS/MS.  
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### 18 19 *Chromatography and quantification* 20

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23 Analysis was undertaken by LC-MS/MS. A CTC Pal autosampler (Presearch, UK)  
24 and an HP1100 HPLC system with column oven (Agilent, UK) were coupled to an  
25 API4000 triple quadrupole mass spectrometer (MDS Sciex Instruments, UK). The  
26 guard cartridge was C<sub>8</sub>. The HPLC column (5 µm, 60 Å, 2.1 x 150 mm) was  
27 Fluorosep RP Octyl phase, thermostatically held at 30°C in the column oven. The  
28 injection volume was generally 10 µl. The gradient programme (methanol: aqueous  
29 ammonium formate, 5 mM, pH 4) was: 10% methanol increasing to 30% at 0.1 min  
30 (linear gradient), to 75% at 7 min and 100% methanol at 10 min, this was held for 5  
31 min (column washing), then decreased to 10% methanol at 15.1 min, this was held 4.9  
32 min at 10% methanol (column re-conditioning). The eluate was diverted to the mass  
33 spectrometer between 7 and 19.5 min, whereas from 0-7 and 19.5-20 min it was  
34 discarded by valve switching to waste, in order to protect the ion source. A summary  
35 of MRM transitions, retention times and solvent-based LODs of the PFC analytical  
36 standards are given in Table 2. Analyst 1.4.2 software was used for instrument  
37 control, file acquisition and peak integration. The MS detector in MRM mode with a  
38 Turbo Ion Spray source was used for quantitative analysis. Data acquisition was  
39 conducted in one simultaneous acquisition schedule. Instrumental parameters were  
40 optimised by infusion of standard solutions directly into the MS detector (1 µg/ml in  
41 1:1 methanol: aqueous ammonium formate (5 mM, pH 4). The Turbo Ion Spray (TIS)  
42 conditions were; turbo-gas 50 psi, curtain-gas 12 psi, nebuliser-gas 50 psi, desolvation  
43 temperature 450°C. An Excel spreadsheet was used to calculate PFC concentrations  
44 from the standard additions. The standard addition calculation approach is illustrated  
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3 in Figure 1, with representative chromatograms demonstrating the response of the less  
4 sensitive but highly selective secondary qualifying ion for PFOS in Figure 2.  
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#### 8 9 *Analytical quality assurance*

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12 Stock standard solutions were prepared at 1 mg/ml in methanol and stored at 4°C.  
13 Dilutions of these were prepared bi-weekly to minimise surface binding or  
14 evaporation losses. Dispensing of stock solutions was monitored for any possible  
15 losses, due to evaporation, by weighing. Working solutions of mixed standards were  
16 prepared at 5 and 0.5 µg/ml in methanol for spiking. Foods (10 g) were overspiked at  
17 1 and 10 µg/kg by addition of 20 µl @ 0.5 or 5 µg/ml of a mixed standards solution.  
18 Tetrahydro-PFOS (TH-PFOS), <sup>13</sup>C<sub>4</sub>-PFOA, <sup>13</sup>C<sub>4</sub>-PFOS, <sup>13</sup>C<sub>2</sub>-PFDeA, D<sub>9</sub>-*n*-Et-FOSE  
19 and D<sub>3</sub>-*n*-Me-FOSEA were used as internal standards (IS) by addition of 200 µl @ 0.5  
20 µg/ml of a mixed solution, giving a 10 µg/kg IS addition level. Each food sample was  
21 analysed in duplicate throughout the entire extraction method to ensure that  
22 advantageous point contamination was not mistaken for the presence of any native  
23 PFC. Each sample was also overspiked at a minimum of two concentrations (1 & 10  
24 µg/kg). For a specific analyte to be considered present in a sample extract the  
25 following criteria had to be met: i) the relative retention times of the analyte had to be  
26 comparable to those of a retention time marker, an internal standard, and to authentic  
27 analytical standards of each analyte; ii) the peak had to have the correct mass  
28 transition, maximising at the correct retention time; iii) the signal to noise ratio of any  
29 peak had to be greater than 3:1. In order to prove the absence of a given PFC, the  
30 internal standard had to be present in all extracts, the blank extract had to show no  
31 signal at the retention time of the target PFC, whilst the overspiked extracts had to  
32 show a peak for the target PFC at the required retention time. As many of the foods  
33 behave differently with respect to extraction, recovery of analytes through the SPE  
34 stages and matrix induced suppression of ionisation, a single LOD (reporting level)  
35 for all foods or all target PFCs was not possible. In the absence of any suitable  
36 certified reference material (CRM), a number of samples from previous surveys that  
37 had been found to contain measurable levels of specific PFCs were re-analysed to  
38 demonstrate inter-batch reproducibility (Table 3).  
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#### *Dietary intakes*

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Calculations were performed by the UK Food Standards Agency using the Intake2 programme. Intake2 is the FSA in-house system supplied by Dietica for assessing exposure to chemicals in the food we eat and conducting nutrition and consumption assessments using NDNS (National Diet and Nutrition Survey) data. Intake2 is comprised of a bespoke VB front end and a Sagent back end database containing the NDNS consumption surveys, Nutrient information on all foods, and recipe composition data. Users set up a food group containing foods of interest and, if required, the system identifies recipes containing these foods and the percentage within the recipe. For intake assessments, users apply levels of chemicals to the foods selected. Intake2 essentially identifies which consumers have eaten the foods of interest, the amount eaten, and the level of or contaminants within the foods, and provides summary distributional analyses across consumers or the survey population.

All calculations are consumer-based, i.e. where only those who eat a particular food item are included in the calculations, rather than the data being averaged over the whole population. Average and individual age group estimates are calculated based on the most recent UK consumption data for the elderly (65 years and over) (Finch 1998) adults (19- 64 years) (Henderson 2002), school children (4-18 years) (Gregory 2000) and toddlers (1½ - 4½ years)(Gregory 1995)) surveys. (Table 7). High level consumer based estimates are taken as the 97.5% percentile (Table 8). Other calculations are illustrative and based on multiple consumption of single analytes contained in individual samples from Table 4 (Table 9).

## Results

In almost three quarters of the samples, including all those of meat other than offal, none of the chemicals was observed above the limit of detection. PFOS was the chemical detected most often, especially in fish, shellfish, liver and kidney, and usually at the highest concentrations. 75 of the food samples contained trace levels of PFOS and other PFCs just above the reporting level of 1 µg/kg. All of the listed eleven perfluoro analytes were found to be present across these food samples. All of the foods found to contain concentrations exceeding the limit of detection have been reported individually, by analyte in descending order of the summed concentration of the individual PFCs (ΣPFCs) of 1-63 µg/kg (Tables 4-6). The highest concentrations

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3 were found in samples of smoked eel and whitebait. PFOSA was the next most  
4 frequently detected chemical, but only in certain fish species and crab. PFOA was  
5 detected at low concentrations in some samples of whitebait, crab and liver. The  
6 other chemicals analysed were detected only occasionally and at low concentrations,  
7 but no chemical was absent from and totally undetected in all of the samples. A  
8 summary table of the results for all 252 samples, arranged by sample type, illustrates  
9 the frequency, range and mean levels of contamination (Table 1). The highest  
10 individual concentrations were of 59 µg/kg of perfluorooctanesulphonic acid (PFOS)  
11 and 63 µg/kg total PFCs (ΣPFCs) in an eel sample, and 40 µg/kg PFOS (62 ΣPFCs) in  
12 a whitebait sample. There were 6 samples with ΣPFCs >15 µg/kg (fish &  
13 crustaceans), a further 7 samples with ΣPFCs in the range 11-15 µg/kg (including a  
14 liver), nine with ΣPFCs in the range 6-10 µg/kg (fish and livers), 31 with ΣPFCs  
15 in the range 2-5 µg/kg (including kidneys, popcorn and processed peas) and 22 with  
16 ΣPFCs at the reporting level of 1 µg/kg (including eggs and potatoes).  
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30 A set of representative chromatograms for one of the PFOS determinations is given  
31 (Figure 2). It was noted in separate LC-TOF experiments that PFOS [M-H]<sup>-</sup> *m/z*  
32 498.927 can be readily distinguished from the isobaric interferences. These have a  
33 profile *m/z* 498.289, 499.289 and 500.289 which, within the constraint of containing a  
34 sulphonate grouping (MRM 499>80), gave a single fit [M-H]<sup>-</sup> formulae of  
35 C<sub>26</sub>H<sub>44</sub>NO<sub>6</sub>S, taurodeoxycholic acid, with the first natural abundance isotope peak  
36 [M+1,-H]<sup>-</sup> *m/z* 499.289 being the actual interfering ion. As there is a set of largely  
37 indistinguishable di-hydroxycholate epimers about the C<sub>3</sub>, C<sub>6</sub>, C<sub>7</sub>, C<sub>12</sub> positions, the  
38 actual interferences in the various foods differ between samples as do bile salts  
39 between the various mammalian, fish and avian sources. As the di-hydroxycholate  
40 epimers in foods are secondary metabolites, there is as yet no clear relationship  
41 between the primary bile salts in a species and the observed interferences.  
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53 The highest positive results were all in the fish and offal food groups, as anticipated.  
54 Other primary produce foods, such as shellfish, meat, milk, butter, cheese, cereals and  
55 vegetables, were essentially free from contamination (Table 1). There was no  
56 observable trend in farming and husbandry practices; free range, organic, farmed and  
57 wild foods were all indistinguishable by PFC content.  
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## Discussion

### *Analytical methods*

The analytical method has been validated previously (Lloyd 2009) and performed satisfactorily, with all samples being analysed to meet the required reporting level (RL) (Tables 1-2). The method proved reproducible and accurate over the course of this survey as determined by repeat analysis of in-house reference food samples (Table 3).

### *Intake estimates*

Making the assumptions that these retail food samples reflect the general diet in the UK, it can be assumed that the latter is low in PFC. Dietary intakes of PFOS, PFOA and PFOSA were estimated from the results of this survey using food consumption data from various dietary surveys, in which the food eaten by each of up to 1,724 individual consumers was recorded over a 4- or 7-day period (Gregory 1995, Gregory 2000, Finch 1998, Henderson 2002). Average concentrations of the chemicals found in the oily fish, white fish, shellfish, liver, kidney, meat, milk and milk products, cereals, popcorn, jams, potatoes and vegetables samples were applied to all samples of the relevant food type. These dietary intakes do not take account of food types that were not included in the survey, nor of carp for which there were no recorded consumers in any of the dietary surveys. Adults were assumed to have a body weight of 60 kg. For the other age groups the individual bodyweights of each recorded consumer were used.

The dietary intakes so estimated are presented in Table 7 for consumers in different age groups. These intakes are consumer rather than population intakes, as non-consumers of a given food type are ignored in calculating the average figures. The numbers of recorded consumers of the oily fish species containing the highest concentrations, and of offal are relatively low in all age groups which, when combined with the relatively high concentrations in these food types, inflate the consumer intakes from those food types. However, because foods bread, milk and potatoes, all of which are consumed by nearly all the UK population were also



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3 included, the overall intakes shown in Table 7 also apply to the whole population.  
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5 The estimated *upper bound* average adult dietary intakes of PFOS and PFOA 0.01 and  
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7 0.01 µg/kg bodyweight/day respectively (Table 7) are within the Tolerable Daily  
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9 Intakes for these chemicals (0.15 and 1.5 µg/kg bodyweight/day respectively) set by  
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11 the European Food Safety Authority (European Food Safety Authority, 2008), as are  
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13 the corresponding high level (97.5 percentile) adult intakes of 0.02 and 0.02 µg/kg  
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15 body weight/day respectively (Table 8).

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18 An alternative method of estimating the dietary intakes of consumers of oily fish is to  
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20 add the dietary intakes from typical portions of this food to that for the rest of the diet.  
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22 This method allows for more robust intake estimates from oily fish species for which  
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24 there were very few or no recorded consumers, e.g. eel, whitebait and carp. The  
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26 Agency advises that all consumers should eat two portions of fish, one of which  
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28 should be oily, as part of a balanced diet; that girls and women who may have  
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30 children should not eat more than two portions of oily fish per week; and that boys,  
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32 men and women who will not have children should not eat more than four portions of  
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34 oily fish per week (Scientific Advisory Committee on Nutrition and Committee on  
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36 Toxicity of Chemicals in Food, Consumer Products and the Environment 2004, Food  
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38 Standards Agency 2004). A man who ate four 70 g portions of consistently the most  
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40 contaminated oily fish in the survey (i.e. smoked eel, 59 µg/kg) per week combined  
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42 with average consumption of the rest of the diet (i.e. excluding the normal  
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44 contribution from fish) would have a PFOS intake of 0.050 µg/kg bodyweight/day,  
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46 which is again within the TDI (Table 9).

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48 The concentrations of PFOS and PFOA in fish were consistent with those reported by  
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50 other countries (Senthilkumar 2007, de Voogt 2008, Nania 2009). The predominance  
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52 of PFOS accords with evidence that pefluoroalkyl sulphonates such as PFOS are more  
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54 bioaccumulative than perfluoroalkanoic acids, such as PFOA, with the same  
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56 fluorinated carbon chain length (Condor 2008). The concentrations found suggest  
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58 that, if regulatory limits were to be considered, these might be appropriate only for  
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60 PFOS in fish and animal liver, Limits are not likely to be needed in other foods, or at  
all for PFOA. However, the results of this survey do not indicate a need for increased  
consumer protection.

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3 Accurate quantification of PFCs at concentrations below 1 µg/kg in food, while  
4 feasible, is complex and costly (Lloyd 2009). It is clear from the results and the  
5 intake estimates, that it was possible to demonstrate that exposure to PFOS and PFOA  
6 would be considerably below the respective TDIs even for the highest consumers  
7 working to an LOD of 1 µg/kg. On this basis, the analytical method described and  
8 used in this paper to generate the intake estimates was fit-for-purpose. The *lower*  
9 *bound* estimate for PFOS dietary intake in the UK of 1 ng/kg/day as estimated from  
10 the results of this study, was calculated as a consumer rather than population based  
11 estimate, which gave a higher result, but this is still comparable to estimates  
12 calculated for Spain 1 ng/kg/day (Ericson 2008), Ireland 1 ng/kg/day (Clarke in  
13 press), Germany 2 ng/kg bw/day (Fromme), and Canada (4 ng/kg bw/day Tittlemier  
14 2007).

## 25 26 **Conclusions**

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30 The results from this study indicate an extremely low level of contamination in the  
31 English food chain, and they are directly comparable to the findings in other countries  
32 that have conducted similar studies. It would therefore be unlikely for any consumer,  
33 even an extreme consumer of the more contaminated foods, to exceed the TDI for  
34 PFOS or PFOA.

## 35 36 37 38 39 40 **Acknowledgments**

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46 the UK Food Standards Agency.  
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Table 1. Summary of the levels of PFCs by food type.

| Class         | Type         | N       | Range<br>ΣPFCs µg/kg | N ≥ LOQ | Mean      | % Positive |     |
|---------------|--------------|---------|----------------------|---------|-----------|------------|-----|
| Fish          | Whitebait    | 6       | 8-62                 | 6       | <b>28</b> | 100        |     |
|               | Eel          | 6       | <1-63                | 3       | <b>11</b> | 50         |     |
|               | Carp         | 6       | <1-8                 | 5       | <b>5</b>  | 83         |     |
|               | Sprats       | 3       | 3-8                  | 3       | <b>5</b>  | 100        |     |
|               | Sardines     | 6       | 1-7                  | 6       | <b>4</b>  | 100        |     |
|               | Cod          | 4       | <0-4                 | 2       | <b>2</b>  | 50         |     |
|               | Mackerel     | 4       | <1-3                 | 2       | <b>2</b>  | 50         |     |
|               | Haddock      | 4       | <1-3                 | 3       | <b>1</b>  | 75         |     |
|               | Trout        | 4       | <1-1                 | 2       | <1        | 50         |     |
|               | Herring      | 4       | <1-2                 | 1       | <1        | 25         |     |
|               | Plaice       | 2       | <1-1                 | 1       | <1        | 50         |     |
|               | Salmon       | 8       | <1                   | 0       | <1        | 0          |     |
|               | Sole         | 2       | <1                   | 0       | <1        | 0          |     |
|               | Shellfish    | Oysters | 2                    | 1-1     | 1         | <1         | 50  |
|               | Crustaceans  | Crab    | 6                    | 11-20   | 6         | <b>16</b>  | 100 |
| Crayfish      |              | 1       | 2                    | 1       | <b>2</b>  | 100        |     |
| Prawns        |              | 2       | <1-1                 | 1       | <b>1</b>  | 50         |     |
| Langoustine   |              | 1       | <1                   | 0       | <1        | 0          |     |
| Offal         | Liver        | 25      | <1-14                | 19      | <b>2</b>  | 76         |     |
|               | Kidney       | 12      | <1-3                 | 8       | <b>1</b>  | 75         |     |
|               | Other offal  | 4       | <1                   | 0       | <1        | 0          |     |
| Meat          | Carcass meat | 16      | <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 = the lowest and highest values of the combined concentration of all 11 Individual fluorinated analytes. Mean = lower bound, <LOD = 0

N = The number of samples analysed in each group.

N ≥ LOQ = The number of samples where residues were measured.

Meat = pork, lamb, beef, venison, chicken, turkey.

Table 2. Summary of MRM transitions, retention time, solvent based and matrix based LODs

| Test analyte                     | Primary Ions |   | Qualifier Ions |                               | MeOH LODs |                                    | Matrix based LODs $\mu\text{g}/\text{kg}^{\text{b}}$ |      |         |        |
|----------------------------------|--------------|---|----------------|-------------------------------|-----------|------------------------------------|--|------|---------|--------|
|                                  | Transition   | Product ion                                       | Transition     | Product ion                   | Rt        | $\mu\text{g}/\text{kg}^{\text{a}}$ | Milk   | Jam  | Veg Oil | Salmon |
| PFHxA                            | 313.1>269.1  | $[\text{C}_5\text{F}_{11}]^-$                     | 313.1>119.1    | $[\text{C}_2\text{F}_5]^-$    | 11.25     | 0.01                               | 0.025  | 0.1  | 0.05    | 0.3    |
| PFHpA                            | 363.1>319.1  | $[\text{C}_6\text{F}_{13}]^-$                     | 363.1>169.1    | $[\text{C}_3\text{F}_7]^-$    | 11.92     | 0.005                              | 0.01   | 0.05 | 0.02    | 0.01   |
| PFOA                             | 413.1>369.1  | $[\text{C}_7\text{F}_{15}]^-$                     | 413.1>169.1    | $[\text{C}_3\text{F}_7]^-$    | 12.43     | 0.005                              | 0.025  | 0.01 | 0.05    | 0.01   |
| PFNA                             | 463.1>419.1  | $[\text{C}_8\text{F}_{17}]^-$                     | 463.1>219.1    | $[\text{C}_4\text{F}_9]^-$    | 12.86     | 0.001                              | 0.05   | 0.02 | 0.05    | 0.02   |
| PFDeA                            | 513.1>469.1  | $[\text{C}_9\text{F}_{19}]^-$                     | 513.1>219.1    | $[\text{C}_4\text{F}_9]^-$    | 13.26     | 0.001                              | 0.025  | 0.02 | 0.02    | 0.05   |
| PFUnA                            | 563.1>519.1  | $[\text{C}_{10}\text{F}_{21}]^-$                  | 563.1>319.1    | $[\text{C}_6\text{F}_{13}]^-$ | 13.66     | 0.001                              | 0.025  | 0.02 | 0.01    | 0.02   |
| PFDoA                            | 613.1>569.1  | $[\text{C}_{12}\text{F}_{23}]^-$                  | 613.1>269.1    | $[\text{C}_5\text{F}_{11}]^-$ | 14.02     | 0.001                              | 0.025  | 0.02 | 0.02    | 0.05   |
| PFBSH                            | 299.1>80.1   | $[\text{SO}_3]^-$                                 | 299.1>99.1     | $[\text{SO}_3\text{F}]^-$     | 10.05     | 0.01                               | 0.05   | 0.05 | 0.01    | 0.05   |
| PFHxS                            | 399.1>80.1   | $[\text{SO}_3]^-$                                 | 399.1>99.1     | $[\text{SO}_3\text{F}]^-$     | 11.64     | 0.01                               | 0.05   | 0.02 | 0.05    | 0.1    |
| PFOS                             | 499.1>80.1   | $[\text{SO}_3]^-$                                 | 499.1>99.1     | $[\text{SO}_3\text{F}]^-$     | 12.59     | 0.01                               | 0.1  | 0.1  | 0.05    | 0.1    |
| PFOSA                            | 498.1>78.0   | $[\text{SNO}_2]^-$                                | 498.1>169.1    | $[\text{C}_3\text{F}_7]^-$    | 13.96     | 0.002                              | 0.025  | 0.02 | 0.1     | 1      |
| THPFOS                           | 427.1>407.1  | $[\text{M-HF}]^-$                                 | -              | -                             | 12.34     | -                                  | -  | -    | -       | -      |
| $^{13}\text{C}_2$ -PFDeA         | 515.1>470.1  | $[\text{C}_8^{12}\text{C}_2^{13}\text{F}_{19}]^-$ | -              | -                             | 13.26     | -                                  | -  | -    | -       | -      |
| $^{13}\text{C}_4$ -PFOA          | 417.1>372.1  | $[\text{C}_4^{12}\text{C}_4^{13}\text{F}_{15}]^-$ | -              | -                             | 12.42     | -                                  | -  | -    | -       | -      |
| $^{13}\text{C}_4$ -PFOS          | 503.1>80.1   | $[\text{SO}_3]^-$                                 | -              | -                             | 12.57     | -                                  | -  | -    | -       | -      |
| $\text{D}_9$ - <i>n</i> -Et-FOSE | 639.1>45.0   | $[\text{HCO}_2]^-$                                | -              | -                             | 14.81     | -                                  | -  | -    | -       | -      |
| $\text{D}_3$ - <i>n</i> -Me-FOSA | 515.1>169.1  | $[\text{C}_3\text{F}_7]^-$                        | -              | -                             | 14.68     | -                                  | -  | -    | -       | -      |

Summary of MRM transitions, retention times and solvent based Limits of Determination LODs of PFC analytical standards.

<sup>a</sup>Methanol based LODs (3x S/N) were all <10 ng/kg (0.25 ng/ml).

<sup>b</sup>Concentrations expressed as  $\mu\text{g}/\text{kg}$  food equivalent, matrix matched. 10 g food matrix concentrated in the extract 25-fold.

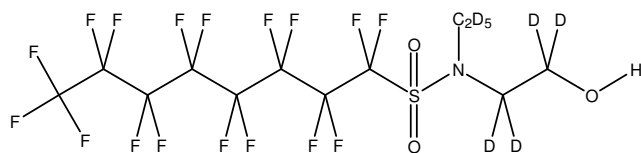
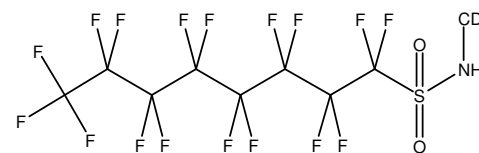
D<sub>9</sub>-*n*-Et-FOSE2-(*N*-D<sub>5</sub>-ethylperfluoro-1-octanesulfonamido)-D<sub>4</sub>-ethanolD<sub>3</sub>-*n*-Me-FOSA*N*-D<sub>3</sub>-methylperfluoro-1-octanesulfonamide



Table 3. Interbatch reproducibility data for repeat analysis of food sample contaminated with PFCs.

| Sample              | Measured PFC concentration $\mu\text{g}/\text{kg}$ |       |          |       |       |      |      |       |       |       |        |
|---------------------|--|-------|----------|-------|-------|------|------|-------|-------|-------|--------|
|                     | PFBS   | PFHxS | PFOS     | PFHxA | PFHpA | PFOA | PFNA | PFDeA | PFUnA | PFDoA | PFOSA  |
| Mackerel            |  |       | 1[2]     |       |       |      |      |       |       |       | 1[1]   |
| Dressed crab        |  |       | 6[4]     |       |       | 9[8] | 1[2] |       |       |       | 1[1]   |
| Whitebait           |  |       | 11[15]   |       |       |      |      |       |       |       | 10[27] |
| Whitebait           |  |       | 12[9]    |       |       |      |      |       |       |       | 6[4]   |
| Whitebait           |  |       | 48[40]   |       |       | 4[5] |      |       | 1[2]  |       |        |
| Cromer crab         |  | 1[1]  | 14[12]   |       |       | 4[4] | 2[1] | 1[1]  |       |       | 1[2]   |
| Spider crab         |  | 2[1]  | 13[9]    |       |       | 5[6] |      |       |       |       |        |
| Wild roe deer liver |  |       | 10[11]   |       |       | 3[6] | 1[2] |       |       |       |        |
| Carp roe            |  |       | 765[757] |       |       |      |      |       |       |       |        |

Interbatch reproducibility data for repeat analysis of naturally incurred PFC containing food sample.  
Results for the second determination are presented in parenthesis.

1 *Table 4. Individual concentrations of PFCs in each food sample.*

|        |                       | Measured PFC concentration $\mu\text{g}/\text{kg}$ |       |          |          |          |          |          |      |          |           |           |                     |
|--------|-----------------------|--|-------|----------|----------|----------|----------|----------|------|----------|-----------|-----------|---------------------|
| Sample |                       | PFHxA  | PFHpA | PFOA     | PFNA     | PFDeA    | PFUnA    | PFDoA    | PFBS | PFHxS    | PFOS      | PFOSA     | $\Sigma\text{PFCs}$ |
| 1      | Smoked Eel            | <1   | <1    | <1       | <1       | <b>2</b> | <b>2</b> | <1       | <1   | <1       | <b>59</b> | <1        | 63                  |
| 2      | Whitebait             | <1   | <1    | <b>5</b> | <1       | <1       | <b>2</b> | <1       | <1   | <b>1</b> | <b>40</b> | <b>14</b> | 62                  |
| 3      | Whitebait             | <b>7</b>   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>15</b> | <b>27</b> | 49                  |
| 4      | Cromer crab (dressed) | <1   | <1    | <b>4</b> | <b>1</b> | <1       | <b>1</b> | <1       | <1   | <b>2</b> | <b>12</b> | <1        | 20                  |
| 5      | Spider crab (whole)   | <1   | <1    | <b>6</b> | <b>1</b> | <1       | <1       | <1       | <1   | <1       | <b>13</b> | <1        | 20                  |
| 6      | Whitebait             | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>9</b>  | <b>7</b>  | 16                  |
| 7      | Whitebait             | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>9</b>  | <b>6</b>  | 15                  |
| 8      | Dressed Crab          | <1   | <1    | <b>8</b> | <b>2</b> | <1       | <1       | <1       | <1   | <1       | <b>4</b>  | <b>1</b>  | 15                  |
| 9      | Brown crab (whole)    | <1   | <1    | <b>6</b> | <b>3</b> | <1       | <1       | <1       | <1   | <1       | <b>3</b>  | <b>2</b>  | 14                  |
| 10     | Wild roe deer liver   | <1   | <1    | <b>3</b> | <b>1</b> | <1       | <1       | <1       | <1   | <1       | <b>10</b> | <1        | 14                  |
| 11     | Whitebait             | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>9</b>  | <b>4</b>  | 13                  |
| 12     | Crab (whole)          | <1   | <1    | <b>5</b> | <b>1</b> | <1       | <b>1</b> | <b>1</b> | <1   | <1       | <b>2</b>  | <b>3</b>  | 13                  |
| 13     | Dressed Crab          | <1   | <1    | <b>4</b> | <b>1</b> | <1       | <1       | <1       | <1   | <1       | <b>4</b>  | <b>2</b>  | 11                  |
| 14     | Mirror carp           | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>8</b>  | <1        | 8                   |
| 15     | Frozen sprats         | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>4</b>  | <b>4</b>  | 8                   |
| 16     | Whitebait             | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>5</b>  | <b>3</b>  | 8                   |
| 17     | Carp                  | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>8</b>  | <1        | 8                   |
| 18     | Sardines              | <1   | <1    | <1       | <1       | <1       | <b>2</b> | <1       | <1   | <1       | <b>3</b>  | <b>2</b>  | 7                   |
| 19     | Venison Liver         | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>7</b>  | <1        | 7                   |
| 20     | Fresh carp            | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>6</b>  | <1        | 6                   |
| 21     | Common carp           | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>6</b>  | <1        | 6                   |
| 22     | Pigs liver            | <1   | <1    | <b>2</b> | <1       | <1       | <1       | <1       | <1   | <1       | <b>4</b>  | <1        | 6                   |
| 23     | Sliced lamb liver     | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>5</b>  | <1        | 5                   |
| 24     | Pigs kidney           | <1   | <1    | <b>1</b> | <1       | <1       | <1       | <1       | <1   | <1       | <b>4</b>  | <1        | 5                   |
| 25     | Sprats                | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>1</b>  | <b>4</b>  | 5                   |
| 26     | Cornish Sardines      | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>2</b>  | <b>3</b>  | 5                   |
| 27     | Ox Liver              | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>5</b>  | <1        | 5                   |
| 28     | Carp                  | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>4</b>  | <1        | 4                   |
| 29     | Bideford cod          | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>2</b>  | <b>2</b>  | 4                   |
| 30     | Sardines              | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>3</b>  | <b>1</b>  | 4                   |
| 31     | Pork Liver            | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>4</b>  | <1        | 4                   |
| 32     | Lambs Liver           | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>4</b>  | <1        | 4                   |
| 33     | Sardines              | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>2</b>  | <b>1</b>  | 3                   |
| 34     | Beef liver            | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>3</b>  | <1        | 3                   |
| 35     | Halal beef liver      | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>3</b>  | <1        | 3                   |
| 36     | Lambs liver           | <1   | <1    | <1       | <1       | <1       | <1       | <1       | <1   | <1       | <b>3</b>  | <1        | 3                   |

|    |                |                            |     |     |     |     |     |     |     |     |     |     |     |   |
|----|----------------|----------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|---|
| 37 | English Sprats | < 1                        | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | 2   | 3 |
| 38 | Whole Herring  | 3                          | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 3 |
| 1  | 39             | Mackerel                   | 2   | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 3 |
| 2  | 40             | Whole Mackerel             | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 2   | 1   | 3 |
| 3  | 41             | Cornish Sardines           | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | 2   | 3 |
| 4  | 42             | Ox Kidney                  | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 3   | < 1 | 3 |
| 5  | 43             | Farmed red deer liver      | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 2   | < 1 | 2 |
| 6  | 44             | Lambs kidney               | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 2   | < 1 | 2 |
| 7  | 45             | Wild English Eels          | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 2   | < 1 | 2 |
| 8  | 46             | Cod                        | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 2   | < 1 | 2 |
| 9  | 47             | Crayfish                   | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 2   | < 1 | 2 |
| 10 | 48             | Lambs Liver                | < 1 | < 1 | 1   | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 2 |
| 11 | 49             | Lambs Liver                | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 2   | < 1 | 2 |
| 12 | 50             | Lambs Liver                | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 2   | < 1 | 2 |
| 13 | 51             | Ox Kidney                  | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 2   | < 1 | 2 |
| 14 | 52             | Marrowfat Peas             | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 2   | < 1 | < 1 | < 1 | 2 |
| 15 | 53             | Toffee Popcorn             | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 2   | < 1 | < 1 | < 1 | 2 |
| 16 | 54             | Haddock fillet             | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 17 | 55             | Haddock portions           | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 18 | 56             | Smoked eel                 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 19 | 57             | Herring                    | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 20 | 58             | Cornish sardines           | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 21 | 59             | Ox liver                   | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 22 | 60             | Wild venison liver         | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 23 | 61             | Beef kidney                | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 24 | 62             | Lambs kidney               | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 25 | 63             | R. Trout                   | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 26 | 64             | Whole R. Trout             | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 27 | 65             | Plaice fillets             | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 28 | 66             | Haddock Fillets            | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 29 | 67             | N. Atlantic Prawns         | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 30 | 68             | Pacific Oysters            | < 1 | 1   | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1 |
| 31 | 69             | Pork Sliced Liver          | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 32 | 70             | Ox Liver                   | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 33 | 71             | Organic pig kidney         | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 34 | 72             | Pig Kidney                 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 35 | 73             | Organic Free Range Eggs    | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | 1 |
| 36 | 74             | Baby Potatoes [Maris Peer] | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1   | < 1 | < 1 | < 1 | 1 |
| 37 | 75             | Sweet Pop Corn             | < 1 | 1   | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 | 1 |

1 ΣPFCs = combined total concentration of all individual PFCs = PFAS.

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Table 5. Concentrations ( $\mu\text{g}/\text{kg}$  fresh weight) of PFOS, PFOA, PFAS and PFOSA in fish and shellfish

| Species<br>(No of samples)   | PFOS       |                 | PFOA         |            | PFAS (lower bound) |             | PFAS (upper bound) |              | PFOSA      |             |
|------------------------------|------------|-----------------|--------------|------------|--------------------|-------------|--------------------|--------------|------------|-------------|
|                              | Mean       | Range           | Mean         | Range      | Mean               | Range       | Mean               | Range        | Mean       | Range       |
| Eel (fresh) (3)              | 1.3        | <1-2            | <1           | -          | 0.7                | 0-2         | 11                 | 11-12        | <1         | -           |
| Eel (smoked) (3)             | 20         | <1-59           | <1           | -          | 21                 | 0-63        | 31                 | 11-71        | <1         | -           |
| Herring (4)                  | 1.0        | <1-1            | <1           | -          | 1.0                | 0-3         | 12                 | 11-13        | <1         | -           |
| Mackerel (4)                 | 1.2        | <1-2            | <1           | -          | 1.5                | 0-3         | 11                 | 11-12        | <1         | -           |
| Atlantic salmon (farmed) (5) | <1         | -               | <1           | -          | 0                  | -           | 11                 | -            | <1         | -           |
| Atlantic salmon (wild) (2)   | <1         | -               | <1           | -          | 0                  | -           | 11                 | -            | <1         | -           |
| Alaskan salmon (wild) (1)    | <1         | -               | <1           | -          | 0                  | -           | 11                 | -            | <1         | -           |
| Sardines (6)                 | 2.0        | 1-3             | <1           | -          | 5.5                | 1-7         | 13                 | 11-15        | 2.2        | 1-3         |
| Sprats (3)                   | 3.0        | 1-4             | <1           | -          | 5.3                | 3-8         | 14                 | 12-17        | 3.3        | 2-4         |
| Trout (farmed) (4)           | 1.0        | <1-1            | <1           | -          | 0.50               | 0-1         | 11                 | -            | <1         | -           |
| Whitebait (6)                | 15         | <1-40           | 1.3          | <1-5       | 28                 | 8-62        | 36                 | 17-68        | 10         | 1-27        |
| Carp (6)                     | 5.5        | <1-8            | <1           | -          | 5.3                | 0-8         | 16                 | 11-18        | <1         | -           |
| <b>All oily fish (47)</b>    | <b>4.8</b> | <b>&lt;1-59</b> | <b>1.1</b>   | <b>-</b>   | <b>6.7</b>         | <b>0-63</b> | <b>17</b>          | <b>11-71</b> | <b>2.5</b> | <b>1-27</b> |
| Cod (4)                      | 1.5        | <1-2            | <1           | -          | 1.5                | 0-4         | 12                 | 11-13        | <1         | -           |
| Haddock (4)                  | 1.0        | <1-1            | <1           | -          | 1.3                | 1-2         | 11                 | -            | <1         | -           |
| Plaice(2)                    | 1.0        | <1-1            | <1           | -          | 0.5                | 0-1         | 11                 | -            | <1         | -           |
| Sole (2)                     | <1         | <1-1            | <1           | -          | 0                  | -           | 11                 | -            | <1         | -           |
| <b>All whitefish (12)</b>    | <b>1.2</b> | <b>&lt;1-2</b>  | <b>&lt;1</b> | <b>-</b>   | <b>0.8</b>         | <b>0-4</b>  | <b>11</b>          | <b>11-13</b> | <b>1.1</b> | <b>1-2</b>  |
| Crab (6)                     | 6.3        | 2-13            | 5.5          | 4-8        | 16                 | 11-20       | 22                 | 18-28        | 1.7        | 1-3         |
| Crayfish (1)                 | <1         | -               | <1           | -          | 2.0                | -           | 12                 | 12           | <1         | -           |
| Langoustine (1)              | <1         | -               | <1           | -          | 1.0                | -           | 11                 | 11           | <1         | -           |
| Pacific oysters (2)          | 2.5*       | 1-10*           | <1           | -          | 0                  | -           | 17*                | 11-47*       | <1         | -           |
| Prawns (2)                   | <1         | <1-1            | <1           | -          | 0.5                | 0-1         | 11                 | 11           | <1         | -           |
| <b>All shellfish (12)</b>    | <b>4.4</b> | <b>1-13</b>     | <b>3.3</b>   | <b>1-8</b> | <b>8.2</b>         | <b>0-20</b> | <b>20</b>          | <b>11-47</b> | <b>1.3</b> | <b>1-3</b>  |

Note: \* Means and ranges affected by one or more higher than usual LODs. PFAS =  $\Sigma$ PFCS.

Table 6. Concentrations ( $\mu\text{g}/\text{kg}$  fresh weight) of PFOS, PFOA, PFAS and PFOSA in other foods

| Food<br>(No of samples)  | PFOS              |             | PFOA              |            | PFAS (lower bound) |             | PFAS (upper bound) |              | PFOSA             |          |
|--------------------------|-------------------|-------------|-------------------|------------|--------------------|-------------|--------------------|--------------|-------------------|----------|
|                          | Mean <sup>†</sup> | Range       | Mean <sup>†</sup> | Range      | Mean               | Range       | Mean               | Range        | Mean <sup>†</sup> | Range    |
| Chicken liver (2)        | <1                | -           | <1                | -          | 0                  | -           | 16                 | 11,20        | <1                | -        |
| Chicken liver pate (1)   | <1                | -           | <1                | -          | 0                  | -           | 11                 | -            | <1                | -        |
| Duck liver pate (1)      | <1                | -           | <1                | -          | 0                  | -           |                    |              | <1                | -        |
| Lambs' liver (7)         | 2.6               | <1-5        | <1                | -          | 2.6                | 0-5         | 13                 | 11-15        | <1                | -        |
| Ox liver (5)             | 1.8               | <1-5        | <1                | -          | 1.4                | 0-5         | 12                 | 11-15        | <1                | -        |
| Pigs' liver (5)          | 2.2               | <1-4        | 1.2               | 1-2        | 2.2                | 0-6         | 12                 | 11-15        | <1                | -        |
| Venison liver (4)        | 5.0               | 1-10        | 1.5               | 1-3        | 6.0                | 1-14        | 16                 | 11-22        | <1                | -        |
| <b>All liver (25)</b>    | <b>2.5</b>        | <b>1-10</b> | <b>1.1</b>        | <b>1-3</b> | <b>2.4</b>         | <b>0-14</b> | <b>13</b>          | <b>11-22</b> | <b>&lt;1</b>      | <b>-</b> |
| Lambs' kidney (4)        | 1.3               | 1-2         | <1                | -          | 0.8                | 0-2         | 11                 | 11-12        | <1                | -        |
| Ox kidney (4)            | 1.8               | <1-3        | <1                | -          | 1.5                | 0-3         | 12                 | 11-13        | <1                | -        |
| Pigs' kidney (4)         | 1.6               | <1-4        | <1                | -          | 0.7                | 0-1         | 11                 | -            | <1                | -        |
| <b>All kidney (12)</b>   | <b>1.4</b>        | <b>1-3</b>  | <b>&lt;1</b>      | <b>-</b>   | <b>1.3</b>         | <b>0-5</b>  | <b>12</b>          | <b>11-14</b> | <b>&lt;1</b>      | <b>-</b> |
| Lambs' heart (2)         | <1                | -           | <1                | -          | 0                  | -           | 11                 | -            | <1                | -        |
| Black pudding (2)        | <1                | -           | <1                | -          | 0                  | -           | 11                 | -            | <1                | -        |
| Bread (4)                | <1                | -           | <1                | -          | 0                  | -           | 11                 | -            | <1                | -        |
| Cereals (4)              | <1                | -           | <1                | -          | 0                  | -           | 11                 | -            | <1                | -        |
| Popcorn (4)              | <1                | -           | <1                | -          | 0.8                | 0-2         | 11                 | 11-12        | <1                | -        |
| Cheese (10)              | <1.9*             | <1-<10*     | <1                | -          | 0                  | -           | 15*                | 11-47*       | <1                | -        |
| Milk (11)                | <1                | -           | <1                | -          | 0                  | -           | 11                 | 11-12        | <1                | -        |
| Eggs (12)                | <1                | <1-1        | <1                | -          | 0.1                | 0-2         | 11                 | -            | <1                | -        |
| Fish oil supplements (4) | <1                | -           | <1                | -          | 0                  | -           | 11                 | -            | <1                | -        |
| Vegetable oils (6)       | <1                | -           | <1                | -          | 0                  | -           | 11                 | -            | <1                | -        |
| Jams (6)                 | <1                | -           | <1                | -          | 0                  | -           | 11                 | -            | <1                | -        |
| Meat (not offal) (16)    | <1                | -           | <1                | -          | 0                  | -           | 11                 | -            | <1                | -        |
| Potatoes & products (21) | <1                | -           | <1                | -          | 0.1                | 0-1         | 11                 | -            | <1                | -        |
| Vegetables (42)          | <1                | -           | <1                | -          | 0.1                | 0-2         | 11                 | 11-12        | <1                | -        |

Note: † Upper bound values (where the value of the LOD is used in place of <LOD)

Means and ranges affected by one or more higher than usual LODs. PFAS =  $\Sigma$ PFCS.

1 Table 7. Estimated average UK dietary intakes ( $\mu\text{g}/\text{kg}$  bodyweight/day) of fluorinated chemicals by consumers of different age ranges  
 2 from the diet in 2007-08  
 3

| Food group              | Estimated average dietary exposure ( $\mu\text{g}/\text{kg}$ bodyweight/day) |              |              |              |              |              |              |              |
|-------------------------|--|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
|                         | PFOS   |              | PFOA         |              | PFOSA        |              | PFAS         |              |
|                         | <i>Upper</i>   | <i>Lower</i> | <i>Upper</i> | <i>Lower</i> | <i>Upper</i> | <i>Lower</i> | <i>Upper</i> | <i>Lower</i> |
| <i>Senior citizens</i>  |  |              |              |              |              |              |              |              |
| - living at home        | 0.009  | 0.0009       | 0.008        | <0.00005     | 0.008        | 0.0003       | 0.09         | 0.001        |
| - in old peoples' homes | 0.008  | 0.0004       | 0.007        | <0.00005     | 0.007        | 0.0001       | 0.08         | 0.0007       |
| <i>Adults</i>           | 0.01   | 0.0001       | 0.01         | <0.00005     | 0.01         | 0.0004       | 0.1          | 0.002        |
| <i>Schoolchildren</i>   |  |              |              |              |              |              |              |              |
| -age 4-6 years          | 0.02   | 0.001        | 0.02         | <0.00005     | 0.02         | 0.0003       | 0.3          | 0.002        |
| -age 7-10 years         | 0.02   | 0.0008       | 0.02         | <0.00005     | 0.02         | 0.0003       | 0.2          | 0.001        |
| -age 11-14 years        | 0.01   | 0.0005       | 0.01         | <0.00005     | 0.01         | 0.0002       | 0.1          | 0.001        |
| -age 15-18 years        | 0.01   | 0.0005       | 0.009        | <0.00005     | 0.009        | 0.0002       | 0.1          | 0.001        |
| <i>Toddlers</i>         |  |              |              |              |              |              |              |              |
| - age 1.5-2.5 years     | 0.04   | 0.0008       | 0.04         | <0.00005     | 0.04         | 0.0002       | 0.4          | 0.001        |
| - age 2.5-3.5 years     | 0.03   | 0.001        | 0.03         | <0.00005     | 0.03         | 0.0003       | 0.4          | 0.002        |
| - age 3.5-4.5 years     | 0.03   | 0.0009       | 0.03         | <0.00005     | 0.03         | 0.0003       | 0.3          | 0.002        |

4 PFAS =  $\Sigma$ PFCS The estimates for PFAS are both *upper* and *lower bound*. Intake estimates are consumer rather than population based,  
 5 where the non-consumers of a given food type are excluded, resulting in higher values.  
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Table 8. Estimated high-level 97.5 percentile UK dietary intakes ( $\mu\text{g}/\text{kg}$  bodyweight/day) of fluorinated chemicals by consumers of different age ranges from the diet in 2007-08

| Food group              | Estimated average dietary exposure ( $\mu\text{g}/\text{kg}$ bodyweight/day) |              |              |              |              |              |              |              |  |
|-------------------------|--|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--|
|                         | PFOS   |              | PFOA         |              | PFOSA        |              | PFAS         |              |  |
|                         | <i>Upper</i>   | <i>Lower</i> | <i>Upper</i> | <i>Lower</i> | <i>Upper</i> | <i>Lower</i> | <i>Upper</i> | <i>Lower</i> |  |
| <i>Senior citizens</i>  |  |              |              |              |              |              |              |              |  |
| - living at home        | 0.02   | 0.004        | 0.02         | 0.0002       | 0.02         | 0.002        | 0.2          | 0.007        |  |
| - in old peoples' homes | 0.02   | 0.003        | 0.02         | 0.0001       | 0.02         | 0.001        | 0.2          | 0.004        |  |
| <i>Adults</i>           | 0.02   | 0.006        | 0.02         | 0.0002       | 0.02         | 0.002        | 0.2          | 0.009        |  |
| <i>Schoolchildren</i>   |  |              |              |              |              |              |              |              |  |
| -age 4-6 years          | 0.05   | 0.006        | 0.04         | 0.0002       | 0.05         | 0.002        | 0.5          | 0.01         |  |
| -age 7-10 years         | 0.05   | 0.004        | 0.03         | 0.0001       | 0.03         | 0.002        | 0.3          | 0.006        |  |
| -age 11-14 years        | 0.02   | 0.003        | 0.02         | 0.0001       | 0.02         | 0.001        | 0.2          | 0.004        |  |
| -age 15-18 years        | 0.02   | 0.003        | 0.02         | 0.0001       | 0.02         | 0.001        | 0.2          | 0.006        |  |
| <i>Toddlers</i>         |  |              |              |              |              |              |              |              |  |
| - age 1.5-2.5 years     | 0.08   | 0.005        | 0.08         | 0.0001       | 0.08         | 0.001        | 0.9          | 0.007        |  |
| - age 2.5-3.5 years     | 0.08   | 0.007        | 0.08         | 0.0002       | 0.08         | 0.002        | 0.8          | 0.01         |  |
| - age 3.5-4.5 years     | 0.06   | 0.005        | 0.06         | 0.0002       | 0.06         | 0.002        | 0.6          | 0.008        |  |

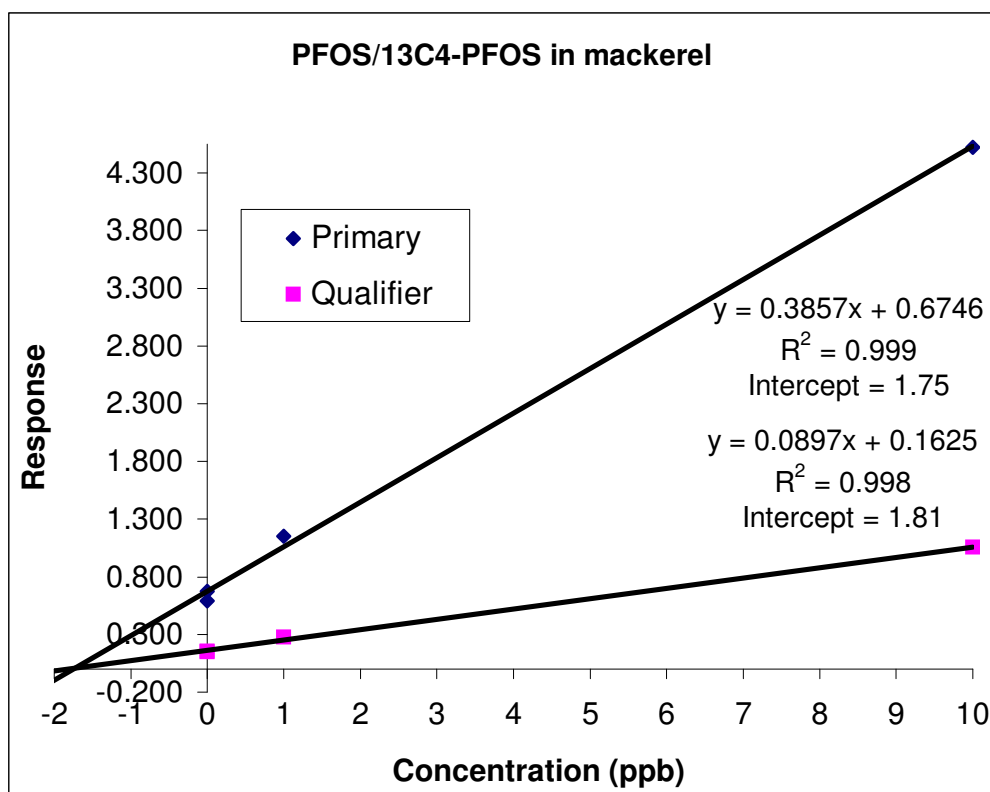
PFAS =  $\Sigma$ PFCS

Table 9. Illustrative intakes ( $\mu\text{g}/\text{kg}$  bodyweight/day) of PFOS and PFOSA from selected fish compared to remainder of diet.

| Intake from non-fish part of the diet           | PFOS       |           |            | PFOSA        |            |           |
|---|------------|-----------|------------|--------------|------------|-----------|
|   | 0.010      | 0.010     | 0.010      | 0.010        | 0.010      | 0.010     |
| Species of fish                                 | Smoked eel | Whitebait | Smoked eel | Dressed crab | Whole crab | Whitebait |
| Concentration in fish (mg/kg fresh weight)      | 0.001      | 0.04      | 0.059      | 0.001        | 0.003      | 0.03      |
| Fish portion (gram)                             | 70         | 70        | 70         | 70           | 70         | 70        |
| Daily intake from one weekly portion of fish    | 0.000      | 0.007     | 0.010      | 0.0002       | 0.0005     | 0.0045    |
| Total daily intake fish + non-fish intake       | 0.011      | 0.017     | 0.020      | 0.010        | 0.011      | 0.015     |
| Daily intake from two weekly portions of fish   | 0.000      | 0.013     | 0.020      | 0.0003       | 0.001      | 0.009     |
| Total daily intake fish + non-fish intake       | 0.011      | 0.024     | 0.030      | 0.010        | 0.011      | 0.019     |
| Daily intake from three weekly portions of fish | 0.001      | 0.020     | 0.030      | 0.0005       | 0.002      | 0.014     |
| Total daily intake fish + non-fish intake       | 0.011      | 0.030     | 0.040      | 0.011        | 0.012      | 0.024     |
| Daily intake from four weekly portions of fish  | 0.001      | 0.027     | 0.039      | 0.0007       | 0.002      | 0.018     |
| Total daily intake fish + non-fish intake       | 0.011      | 0.037     | 0.050      | 0.011        | 0.012      | 0.028     |

Based on representative fish in this survey from Table 4.





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*Figure 1. Standard addition calculation procedure for an English mackerel fish sample. Both sets of ion responses are first normalised to the <sup>13</sup>C<sub>4</sub>-PFOS isotope dilution internal standard. The result is calculated where the line crosses the x-axis. Data are rounded to 1 significant figure, this sample was reported as PFOS contamination of 2 µg/g (primary 1.75, qualifier 1.81). The qualifying ion has a constant 24% of the response of the primary ion response (0.0897/0.3857). The average ion ratio for native and overspiked PFOS is equivalent to the precision ratio, 1.81/1.75 4%.*

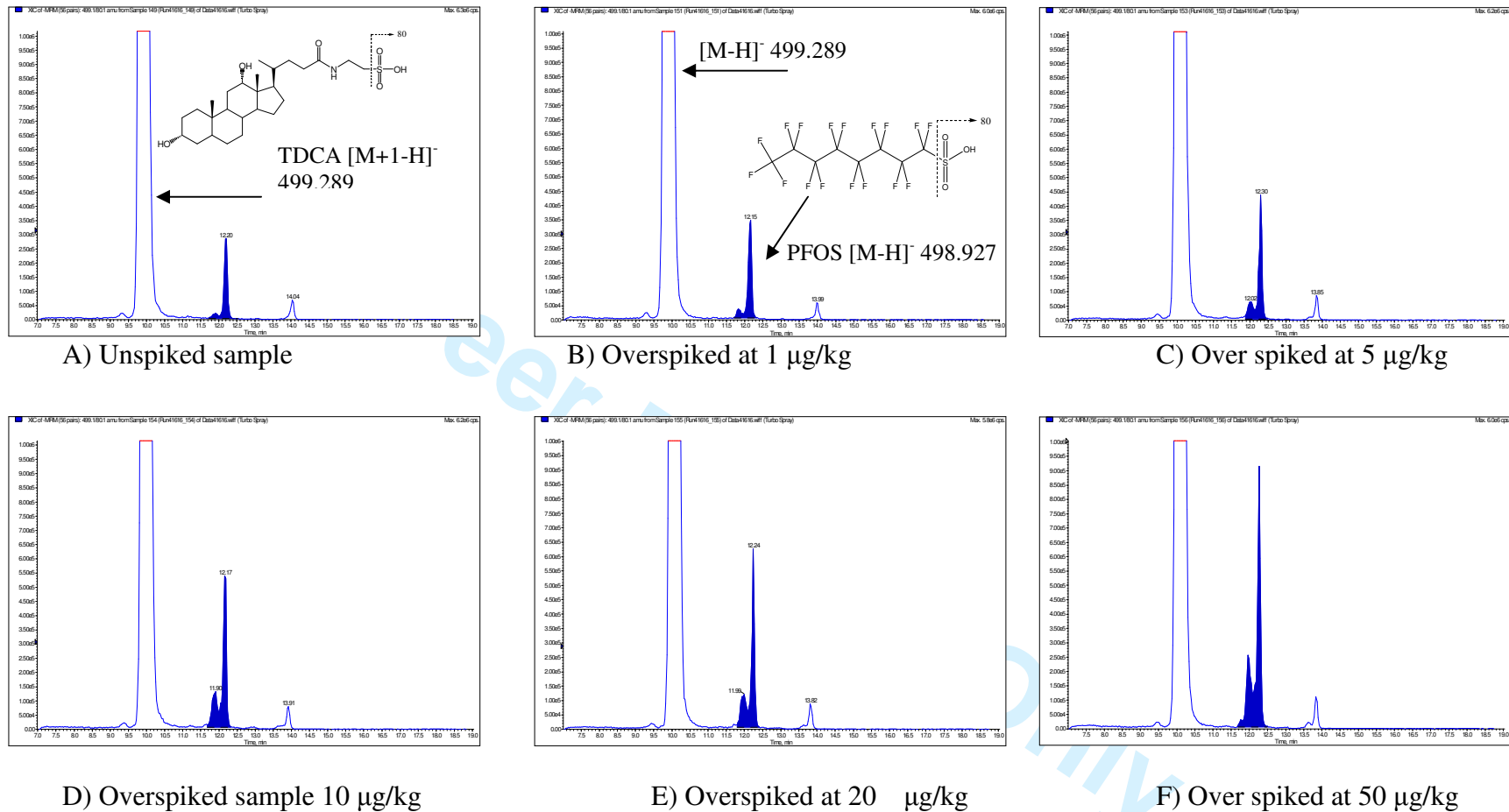


Figure 2. A) Chromatogram of the primary ion  $499.1 > 80.1 [M > SO_3]^-$  for PFOS in a sample of whitebait (sample 3 in Table 1, containing 15 µg/kg naturally incurred PFOS) using; A) unspiked sample, B) overspiked at 1 µg/kg, C) overspiked at 5 µg/kg, D) overspiked at 10 µg/kg, E) overspiked at 20 µg/kg and F) overspiked at 50 µg/kg. Other peaks in this MRM are most likely due to epimers of taurodeoxycholic acid, specifically the  $^{13}C_1$  native abundance M+1 isotope.

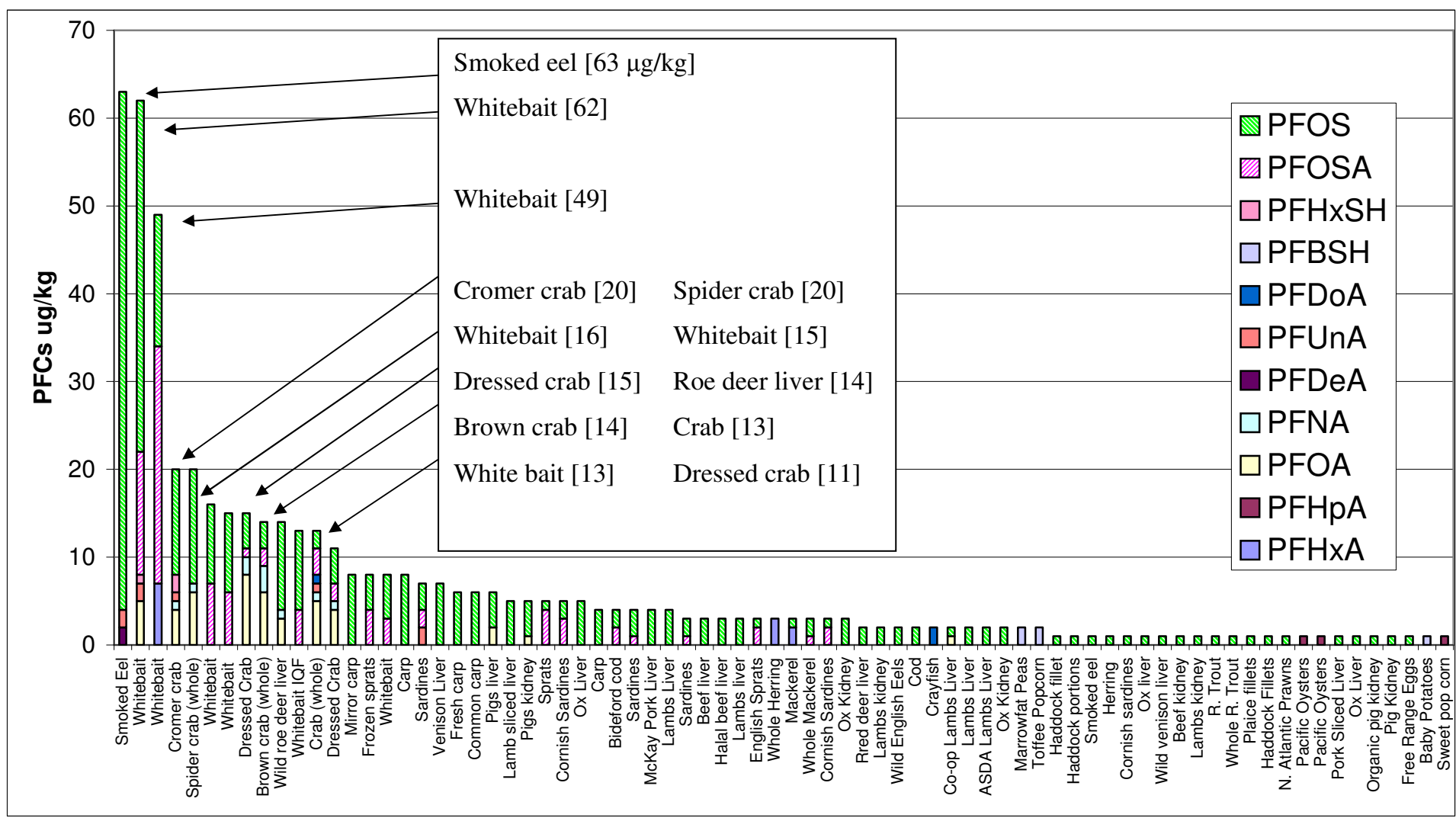


Figure 3. Distribution of individual PFCs (µg/kg) in 75 contaminated foods. The majority of these, 68 foods, contained PFOS, 20 contained PFOSA and 11 contained PFOA.