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Investigation into the Occurrence of Mixed Halogenated Dioxins, Furans and Biphenyls in Food

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SUMMARY

1. The dioxin-like biological effects observed for some mixed halogenated dioxins, furans and biphenyls (PXDD/Fs and PXBs) are reported to be at least equi-potent to the more widely studied chlorinated dioxins, and other effects such as hypothyroidism, thymic atrophy, wasting of body mass and lethality occur at doses that, on a molar concentration basis, are very similar to the chlorinated compounds. There is no information on the occurrence of these contaminants in food and very limited data on their occurrence in environmental compartments. The absence of food occurrence data prevents the estimation of human dietary intake and the assessment of risk arising from this exposure. This study aims to address this knowledge gap by characterising individual compounds from these contaminant groups on the basis of known toxicology and investigating the occurrence of a practical selection of these compounds in individual foods. The data obtained will provide the only available knowledge on occurrence levels of these compounds in food and allow estimation of the extent to which populations are exposed.

2. There are 4600 individual mixed halogenated (bromine and chlorine) dioxins and furans and 9180 mixed halogenated biphenyls, and like their chlorinated counterparts, only a small subset of these compounds are likely to show defined toxicities. In the first stage of this work criteria for the selection of individual compounds for analysis were set based on current toxicological knowledge, chemical configuration, type and degree of halogenation, and the limited knowledge on environmental occurrence levels. Practically, the final selection of compounds was also tempered by the availability of reliable standards and what could practically be synthesised in the project time frame. 19 compounds were chosen – 6 dioxins, 7 furans and 6 biphenyls.

3. Analytical methodology for the measurement of these compounds was developed, based on internal standardisation with $^{13}C_{12}$ labelled compounds and high resolution mass spectrometry (13.5-15K res). New extraction and purification methodology was also developed using dual activated carbon column fractionation. The methodology was validated and used to measure occurrence levels of these contaminants in ~ 100 foods. The limits of detection achieved by this methodology are similar to those used for chlorinated dioxin and biphenyl analysis and ranged from 0.005 to 0.02ng/kg fat depending on the congener and food type.

4. The data obtained from the analyses confirmed the presence of PXDD/Fs and PXBs in common items of retail food. The frequency and magnitude of detection varied depending on the foods, generally following the order – biphenyls > furans > dioxins. In general, the observed frequency of occurrence is lower than chlorinated dioxins, but greater than brominated dioxins. In a manner similar to the chlorinated and brominated dioxin occurrence, the compounds selected for analysis do not occur in isolation in some types of sample. Other congeners are also observed for certain food types – e.g. fish, eggs and particularly shellfish, which are less able to metabolise some of the non-planar congeners. Depending on the type of food, some of these congeners may also be other, non-targeted 2,3,7,8-substituted compounds.

5. A higher frequency of detection and relatively higher values of these contaminants were observed for samples of shellfish, fish, liver and eggs. Recent studies of brominated dioxins and furans (PBDD/Fs) have also shown that the frequency and magnitude of occurrence of these compounds is higher in these matrices.

6. It is difficult to accurately quantify the toxicity arising from the presence of these contaminants, as toxic equivalency factors have not been specified for these compounds. However, given the reported relative potency data, the observed frequency and levels of occurrence, and the limited number of targeted 2,3,7,8-substituted PXDD/Fs and planar PCBs, the combined toxicity arising from measured and unmeasured compounds is likely to make a significant contribution to total dioxin-like toxicity. This contribution will probably be greater than that arising from PBDD/Fs.

7. This report represents the first study of these contaminants in food and is unique. The patterns and levels of occurrence observed are consistent with the formation chemistry and levels of environmental occurrence of these compounds. The observed profiles were also in close agreement with the criteria set for selection of congeners. The data generated from this study provides information on the current baseline concentrations of these contaminants in food and may also be used to estimate levels of human dietary intake and thus the risk posed by these contaminants.

LIST OF CONTENTS

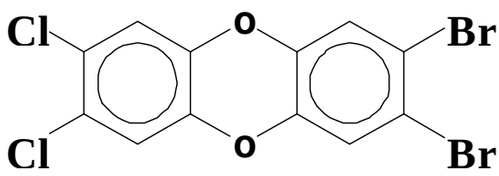
GLOSSARY

BDE	Brominated Diphenylether
BCR	Community Bureau of Reference
BFR	Brominated Flame Retardant
CRM	Certified Reference Material
EFSA	European Food Safety Authority
GC-HRMS	Gas chromatography - high resolution mass spectrometry
HPLC-MS/MS	LC-MS in multiple reaction monitoring mode
IUPAC	International Union of Pure and Applied Chemistry
LC-MS	High Pressure Liquid Chromatography - mass spectrometry
PCB/PBB	Polychlorinated biphenyl/ Polybrominated biphenyl
PBDE	Polybrominated Diphenylether
PBDD/F	Polybrominated dibenzo-*p*-dioxin/ furan
PCDD/F	Polychlorinated dibenzo-*p*-dioxin/ furan
PXDD/F	Polyhalogenated (Br/Cl) dibenzo-*p*-dioxin/ furan
PXB	Polyhalogenated (Br/Cl) biphenyl
PTV	Programmable temperature vaporisation
RM	Reference Material
SCF	EU Scientific Committee on Food
TDI	Tolerable Daily Intake
TDS	Total diet survey
TEF	Toxic Equivalence Factor
TEQ	Toxic equivalence
WHO	World Health Organisation
%U	Percentage Uncertainty

INTRODUCTION

Mixed bromo-chloro dibenzo-p-dioxins and dibenzofurans (PXDD/Fs) are inadvertent by-products of combustion and chemical processes. They show similar health effects in test animals as 2,3,7,8-TCDD (ie they are potent toxins). There is very little information on these compounds, but limited data on their occurrence in environmental compartments and toxicological effects have been documented. There are independent reports from toxicologists in the US and Europe (Behnisch et al, Birnbaum et al, Hornung et al, Mason et al, Olsman et al, Samara et al, Weber and Greim) that indicate that they are likely to be equi-potent or even exceed the potency of 2,3,7,8-TCDD.

2,3-Bromo 7,8-chloro dibenzo-p-dioxin



The theoretically possible substitution patterns of bromine (Br) and chlorine (Cl) on dibenzo-p-dioxin and dibenzofuran molecules, from one to eight substituents provide a total of 1550 PXDDs and 3050 PXDFs. Similarly, the theoretically possible substitution patterns for biphenyl (1-10 substituents) give a total of 9180 possible PXB congeners. Extrapolating from current knowledge on chlorinated dioxins and furans, it is likely that only the planar or laterally substituted (2,3,7,8) compounds are likely to be toxicologically significant, as far as Ah receptor activity is concerned. There are 337 theoretically possible 2,3,7,8-substituted PXDDs and 647 possible 2,3,7,8-substituted PXDFs. However existing studies on toxicology have focussed mainly on the tetra and penta-halogenated compounds with lateral (2,3,7,8) substitution. Of these two groups, there are theoretically, 13 tetra-halogenated compounds and 90 penta halogenated compounds that can assume a planar configuration. Additionally there are also some laterally substituted tri-halogenated compounds (eg 2,3,7- or 2,3,8-positions) that are likely to be toxicologically significant. (Mason et al, Birnbaum et al, WHO

1998). Applying the same rationale to the mixed bromo-chloro biphenyls (PXBs), the most toxicologically significant compounds are likely to be laterally substituted compounds with no (or at most, one) ortho substituents.

Literature on these contaminants is scarce. A limited amount of historical data on occurrence is recorded, the vast majority of which is qualitative information that confirms the occurrence of the compounds in incinerator emissions (Chatkittikunwong and Creaser, Harless et al, Huang et al, Nakao et al, Soderstrom and Marklund, Tong et al). This data deals with the occurrence of unspeciated homologue groups relating to the different variants of chlorine and bromine on the parent dibenzo-p-dioxin or dibenzofuran molecule and reflects the analytical difficulties in chromatographically and spectrometrically separating the individual compounds either from other congeners or from potential interferants. The latter difficulty arises due to the molecular similarity of a number of different trace environmental contaminants which are essentially aromatic combinations of carbon, hydrogen (and oxygen in some cases) with halogenated substituents. Thus for example, monobromo-trichloro dibenzofuran with a target mass of 349.8487 daltons, requires a resolution of at least 11000 to separate the potential pentachloro phenanthrene interferant with a mass of 349.8806 daltons. However, the few reports on toxicology have concentrated on individual compounds, the majority of which are laterally substituted.

Key studies from the literature, on the formation chemistry of these compounds, toxicology and occurrence have been reviewed and the information obtained from these has been used to discuss and inform the prioritisation of specific compounds for investigation. A brief overview of the review is given in the discussion section (Prioritisation of compounds) together with the list of compounds selected for measurement.

The major obstacle to the assessment of risk from these compounds arising from human dietary exposure is the absence of occurrence data for food. The complexity of the analytical methodology required for the measurement of these contaminants far exceeds that used for chlorinated dioxins and PCBs and at best, only a handful of laboratories world-wide have the capability to measure these contaminants in environmental matrices. The difficulties are compounded where food matrices are concerned, as these are analytically more challenging than environmental matrices and additionally, require measurements at greater sensitivities in order to make the risk assessments meaningful. Consequently, there is no data available on

food occurrence levels of these contaminants. This study addresses these issues. In addition to allowing the assessment of risk, the data it will generate will provide knowledge on the occurrence of these contaminants in food.

EXPERIMENTAL

Samples

Most samples were generally taken from recent studies where sampling was carried out according to structured sampling plans. The foods covered the range of commonly consumed dietary items and included milk and dairy products, eggs and poultry, meat and meat products, fish, shellfish, offal, fruit and vegetables. The majority of the samples were individual foods, but a few such as green vegetables, bread and fruit were composites made up of up to 5 sub-samples. Samples were ground and homogenised and most samples were freeze-dried (except for lipid rich materials such as oils). The resulting powders were thoroughly mixed before taking aliquots for the analysis. A description of the samples is given in Table 2.

Fat Determinations

Fat determinations were performed by a UKAS (ISO 17025) accredited laboratory on sub-samples of the freeze-dried and homogenised samples using a standard method (British Standards Institute).

Analytes

The mixed halogenated compounds analysed in this work include 6 dioxins, 7 furans and 6 biphenyls as detailed in Table 1. The table also includes information on the $^{13}C_{12}$ labelled compounds which were used either as internal or sensitivity standards.

Materials

Reference standards for the above analytes, native as well as ^{13}Carbon labeled for the individual analyte groups, were prepared by the dilution and/or combination of standards that were produced by laboratories specializing in the synthesis of these compounds. Some of the standards were synthesized especially for this project. The standards originated either from Wellington Laboratories Inc. Ontario, Canada or from Cambridge Isotope Labs, Mass. USA.

Solvents such as hexane, dichloromethane (dcm), nonane and toluene were all obtained as doubly distilled grade from Rathburns Chemicals Ltd, Walkerburn, Scotland, UK.

Other reagents included:

Alumina – WB5-Basic, Sigma Aldrich, Germany

Silica- YMC Gel, Kyoto, Japan

Sulphuric acid –Reagent Grade, Fisher Scientific

Deionised water was generated within the laboratory

Sodium sulphate anhydrous – Laboratory reagent grade, Fisher Scientific

Extraction and purification

An aliquot of the dry, homogenized sample was fortified with a known amount (typically 50 µL) of the $^{13}C_{12}$ labeled internal standards for each of the analyte groups. The size of the aliquot was dependent on the proportion of lipid present and the equivalent of 4-7 g of lipid weight was typically taken. The fortified sample was left to equilibrate for an hour and then blended with 200 ml hexane and 75 g acid modified silica gel (YMC Gel, Kyoto, Japan; prepared by roller mixing in the ratio of 1:1, 37N,H_2SO_4: Silica, for min. 6 hours). The mixture was quantitatively transferred to the top of a multi-layer column (70 x 600 mm) packed from top to bottom with; 30 g of anhydrous sodium sulphate, 10 g of acid modified silica gel, 50 g of base modified silica gel (YMC Gel, Kyoto, Japan; prepared by mixing in the ratio 3:1, 5M KOH in methanol:silica and allowing evaporation of methanol and stabilization for 24 hours), 10 g of sodium sulphate and silanised glass wool. The column was plugged with 2 glass fibre frits and connected in series to a carbon column (20 x 95 mm containing 0.1 g of activated carbon dispersed on 1 g of glass fibre) and an outflow reservoir. The columns were eluted with hexane (100 mL) and hexane:dichloromethane (95:5 v/v, 75 mL). This forward eluate represented the fraction containing mass-interferants such as di-ortho-substituted PCBs/PXBs/PBBs, PBDEs etc. and was discarded. The columns were further eluted with 275 mL of hexane:dichloromethane (80:20 v/v) to yield the mono-ortho halogen substituted biphenyls. This fraction was concentrated using a TurboVap II^{TM} (Zymark Corporation) apparatus and treated with 37N sulphuric acid (5 drops) and mixed by rotary shaking. The mixture was allowed to stand for 15 minutes to allow the aqueous acid and organic layers to separate. The bottom aqueous layer was discarded and the process was repeated. The organic fractions were combined (Fraction A) and set aside for further purification. The carbon column was disconnected from the multi-layer column and reverse-eluted with 200 ml of 75:25 dichloromethane:toluene, followed by 25 ml of toluene, to yield

a fraction containing the non-ortho substituted halogenated biphenyls and the mixed halogenated dibenzo-p-dioxins and dibenzofurans.

This reverse eluted fraction was concentrated using a TurboVap II^{TM} (Zymark Corporation) apparatus at ~ 35^{0}C and solvent exchanged to ~0.5 ml of hexane to exclude all traces of toluene. The concentrated fraction was re-chromatographed on a carbon column. The column was forward eluted with 400 ml of dichloromethane:hexane which was discarded and then reverse eluted with 200 ml of 75:25 dichloromethane:toluene followed by 25 ml of toluene, which was concentrated to ~0.5ml (Fraction B) and treated with 37N sulphuric acid (5 drops) as described above. The organic layer was purified on two micro-columns (6mm x 100mm) in series, the upper column packed with acid modified silica gel (~3.5 cm) eluting directly onto the lower column containing ~7 cm activated alumina (WB5-Basic, Sigma Aldrich, Germany; activated by baking for min. 16h in a muffle furnace at 450^{0}C). The columns were eluted with 15 ml of hexane to waste followed by disposal of the silica column and elution of the alumina column with 30 ml of dcm:hexane (30:70 v/v). This eluate was concentrated with the addition of the $^{13}C_{12}$ labelled internal sensitivity standard contained in the keeper solvent to approximately 25 µL. Fraction A (mono-ortho substituted biphenyls) was purified in exactly the same manner as Fraction B, except for the elution through the two micro-columns, which was 10 mlL to waste followed by 20 ml of dichloromethane:hexane (30:70 v/v).

Measurement

The extracts resulting from both fractions were analysed by HRGC-HRMS (high resolution gas chromatography- high resolution mass spectrometry). The measurements were performed on a Micromass Autospec Ultima high resolution mass spectrometer coupled to a Hewlett Packard 6890N gas chromatograph fitted with a 60m x 0.25mm i.d. J&W DB-5 MS fused silica capillary column (0.25µm film thickness) and a programmable temperature vaporisation (PTV) injector operated in constant flow (~1ml/min helium) mode.

The mass spectrometer was operated in electron ionisation (EI) mode at a mass resolution of 13000 – 15000 (at 10% peak height) with the mass axis calibrated within a window of 250ppm$_{mass}$ prior to measurement. For the PXDD/Fs, the two most intense ions that did not suffer from chemical interference, in the molecular ion cluster for each homologue group were targeted and were separated into 4 discrete groups based on the molecular mass range and chromatographic retention. These 4 groups of ions were monitored in the selected ion

monitoring (SIM) mode to record ion chromatograms for each of the monitored masses. The same GC-MS programme was used for the mono-ortho PXBs (fraction A) which were monitored in 2 of the ion groups used for PXDD/Fs. An acceleration voltage of 7kV was used in conjunction with an electron energy of 32-37eV and a trap current of 450 µA. The GC-MS interface was set to 280°C.

Standard solutions and sample extracts were introduced by 10 µl injections into the PTV injector at 50°C using a CTC Analytics PAL GC autosampler. Analyte transfer to the GC column was effected using a PTV injector programme which consisted of a 3 minute isothermal period at 50°C followed by heating at 12°C/sec to 320°C, for 3 min, then at 12°C/sec to 350°C to the end of the run.

Chromatographic separation was achieved using a GC oven temperature programme consisting of a 5 minute isothermal period at 50°C followed by heating at 120°C/min to 140°C and then at 15°C/min to 210°C followed by 3°C/min to 270°C for 10 min., then 30°C/min to 310°C for ~4min, then 10°C/min to 320°C for 3 min.

Data handling

Data reduction for the GC-MS analyses, and processing to calculate the mass of each compound present was performed using Masslynx 3.5 software supplied by Waters. These data were transcribed to Microsoft Excel for collation and quantitation of concentration data.

RESULTS AND DISCUSSION

Prioritisation of compounds

The first stage of this work involved the prioritisation of individual compounds for analysis, based on current toxicological knowledge, formation chemistry, chemical configuration, type and degree of halogenation, and the limited knowledge on environmental occurrence levels. The reported formation of PXDD/Fs during incineration processes, and their detection in environmental compartments confirm the environmental occurrence of these compounds, and coupled with the known properties of environmental persistence, there is little doubt that these compounds are available for human bio-accumulation through food-chains – this could either be through atmospheric fallout mechanisms where leaf and root vegetables, fruits, cereal crops etc are consumed, or through the consumption of marine and animal products.

Toxicological data on the more studied chlorinated dioxins and furans show that the Ah receptor mediated effects are primarily due to the lateral substitution of the halogen on the dioxin molecule (Mason et al, Birnbaum et al). Similar studies on brominated dioxins and a small number of PXDD/Fs carried out mainly on laterally halogenated compounds, also provide strong indications that this structural feature should be targeted (Behnisch et al, Hornung et al, Olsman et al, Samara et al, Weber and Griem). However, this still leaves hundreds of laterally substituted compounds, which although desirable to measure, would present very real and difficult analytical hurdles to overcome. There are two observations that could help refine the choice – the first of these concerns the degree of halogenation and hence molecular size. The toxicity of the chlorinated dioxins (referring to Ah receptor mediated toxicity only) as represented by WHO-TEF values, decreases markedly with increasing halogenation. Whilst some laterally substituted tetra- and penta- chlorinated compounds show TEF values of 1.0 and 0.5, the hepta- and octa-chlorinated compounds are far less potent, showing values of 0.01 and 0.0001. At the other end of the scale, the tri-chlorinated compounds are only poorly responsive, but the tri-brominated compounds show more appreciable effects. This is likely associated with the relative size of the halogen atoms as noted by other workers (Birnbaum et al).

The other observation is on the formation chemistry of these compounds, and supporting occurrence data. Under *de novo* synthesis conditions, the formation of furans from carbon is more likely than dioxins. Formation proceeds through preformed biphenyl structures and the dominance of furans over dioxins has been recorded in other combustion/incineration studies (Soderstrom, Soderstrom and Marklund, Nakao et al,). The type and degree of halogenation of the compounds formed during combustion processes, is also governed by the relative proportions of the different atomic species present. Except for specific cases, i.e. the incineration of BFR containing waste or incinerator feed with a high proportion of bromine (Weber and Kuch, Luijk et al), the higher usage of chlorine is likely to favour the formation of molecules with a relatively lower proportion of bromine. This is supported by occurrence data (Soderstrom, Hayakawa et al, Terauchi et al) as well as human exposure data (Ohta et al, B) which shows the occurrence of monobromo-polychlorinated dioxins/furans/biphenyls.

Data on the relative occurrence of laterally substituted congeners within a halogenated group may also provide indications. Such data exists only for the chlorinated dioxins/biphenyls and

for some brominated dioxins/furans. For food matrices, for example, the congener with the 2,3,4,7,8-substitution pattern for penta furans generally shows a much greater level of occurrence than the 1,2,3,7,8 pattern and this is observed for chlorinated as well as brominated furans (Fernandes et al 2008, 2009C, Liem and Theelen, Tsutsumi et al). Similarly, for hexa chlorinated furans, the congener with the 1,2,3,7,8,9-substitution pattern is rarely detected in foods relative to the other hexa-chlorinated congeners. In emission and environmental samples the relative occurrence of this congener is generally always lower, relative to the other laterally substituted hexa- congeners.

On the basis of these observations it is not unreasonable to condense the available information into the following proposed criteria:

- Initially target tetra- to penta-halogenated compounds as these are likely to elicit the greatest toxicity. Tri-halogenated compounds may also be important.

- Apply a greater emphasis to the furans as the available information shows that occurrence levels are likely to be higher

- Target compounds with a lower proportion of bromine e.g. mono- and di-bromo polychloro compounds – occurrence of some of these has been confirmed

- Target specific substitution patterns based on empirical observations for chlorinated and brominated dioxins/furans.

This process considerably reduces the number of compounds that could potentially be targeted and in the absence of other information, form the basis of an initial proposed list. In practice however, the quantitative analytical determination of these compounds will be determined by two further criteria.

- The first of these is the availability of reliable analytical standards. There are only a few of these that have recently become available and some were especially synthesised for this investigation. Fortunately, the majority of the available standards appear to fulfil the criteria listed above. It is important to note that if further compounds that fulfil the criteria become available in time for future investigations, the design of the methodology that has been developed will be able to accommodate the additions.

- The second consideration has been briefly discussed before and relates to the mass spectral properties of some of the homologue groups of these compounds. Although high

resolution mass spectrometry will be used to measure these compounds, some of the targeted masses (particularly for some furans) are prone to interferences from other similar halogenated compounds such as diphenyl ethers and PCBs. Despite the fact that new and rigorous purification procedures were developed, the interfering compounds are generally present at much higher concentrations. The use of higher mass resolution, (in excess of 10000) is only practical to the point where detection limits start to become compromised.

It is on the basis of these considerations that the current list of compounds has been selected (Table 1). Similar criteria have been applied to the selection of the mixed bromo-chlorobiphenyls that are included in this list, with some minor modifications. Higher levels of Ah receptor mediated toxicity are observed for tetra- to hexa–substituted chlorinated biphenyls with the laterally substituted penta CB (PCB 126) showing the most potent effects. However, some mono-ortho substituted biphenyls e.g. PCB118 (2,3',4, 4',5-CB), although less potent, occur at levels that are a few orders of magnitude higher than PCB 126 (Fernandes et al 2009 B), and can thus make a significant contribution to the halogenated biphenyl toxicity. This is reflected in the PXB selection shown in Table 1.

Method Development and Validation

Fractionation

As far as extraction and exclusion of bulk interferences such as lipids go, the procedures used for PXDD/Fs and PXBs are not expected to be vastly dissimilar to chlorinated dioxin and PCB analysis. This is evident from the fact that the procedures for brominated dioxins are the same as those for chlorinated dioxins and procedures for PXDD/Fs used by other workers in the analysis of emission related samples are the same as those used for chlorinated dioxins. The most important methodological considerations are the fractionation of the PXDD/Fs away from the other similar co-extractives such as the PCBs, PBDEs, etc that have the potential to produce mass spectrometric interference, and the measurement by GC-MS at higher resolution (in excess of 10K).

The most effective fractionations that have been used to separate planar molecules such as dioxins from non-planar molecules have used carbon, either as different types of activated carbon or as re-formed particles such as porous graphitic carbon. These methodologies when finely adjusted can produce separation efficiencies of 99% or better, for compounds such as

the PCBs and PBDEs. However there is potential for the unfractionated 1% to provide interference during the following GC-MS measurement not simply due to the similarity in mass spectral characteristics, but also because the interferants are commonly present at much higher concentrations i.e. a PCB congener occurring at typically nanogram levels, would still leave 10s of picograms co-eluting with the dioxins (which typically occur at picogram or sub-picogram levels), even after a 99% efficient extraction. Thus a more complete fractionation is required. This was achieved by carrying out a second fractionation on carbon, but using a much lower boiling polar/aromatic elution system consisting of dichloromethane and toluene. Using a less polar solvent such as a hexane/toluene mix is also possible, but requires a much larger elution volume. Reduction of these large volumes is time consuming and more importantly, can result in analyte losses during the evaporation stages. Thus the dichloromethane: toluene elution system was used. Final purification was carried out on activated basic alumina and the elution scheme here – rejection of the initial non-polar fraction - extends the fractionation process, by excluding traces of any non-polar compounds that still persist. This approach provides a practical means of excluding in excess of 99.99% of non-polar interferants such as PCBs and PBDEs. These are generally the most significant interferants because of the much greater concentrations in which they occur.

Mass Spectrometry

The very low detection limits required for the measurement of PXDD/Fs and PXBs makes the use of high resolution GC - high resolution MS essential. The use of 60m narrow bore capillary columns is well established for the analysis of chlorinated dioxins and provides a good measure of chromatographic resolution. Fully brominated dioxins/furans suffer adsorption when higher chromatographic phase loading (0.25 micron coating) are used but the mixed halogenated compounds investigated here did not show this effect. However this problem may manifest itself if higher halogenated compounds (with a greater proportion of bromine) are investigated in future and should be kept in consideration. Similarly, the chromatographic programme used here provides an adequate separation for the homologue groups currently under investigation, but may need to be revised if other groups hitherto uninvestigated, are introduced.

The use of mass resolution in excess of 10000 to exclude interferences has been mentioned earlier. A comparison of masses illustrates this issue: The most intense ion in the molecular ion cluster for monobromo-trichloro-dioxin is m/z 363.8460 compared to 363.8536 for the

M+6 hexachloro biphenyl ion. If these ions were of equal intensity then an impractical resolution of ~100000 would be required. A resolution of >20000 is practically feasible by excluding a proportionately greater part of the ion beam, but results in a simultaneous loss in sensitivity. The most practical solution in such a case is the use of alternative ions if this is feasible. Here for e.g. it is possible to use m/z 365.8431 for the PXDD which shows a relative intensity of 97.2%. The corresponding ion for the PCB would be the M+8 which would only have a relative intensity of ~4%. In addition the differences in gas chromatographic retention – particularly with the greater resolution of a 60m column can also be used to avoid interferences. Thus, four different approaches have been combined to exclude interferences and positively identify PXDD/Fs and PXBs:

- Intensive extract fractionation
- Practical higher mass resolution (13500-15000 res)
- Differences in chromatographic retention
- Judicious choice of ions for measurement coupled with relative ion ratios.

The result in most cases and certainly for the analytes selected in this study, are relatively interference-free traces, and demonstrate a practical way of excluding interfering compounds. More specificity and a greater degree of certainty can of course be incorporated if more standards for specific PXDD/F and PXB compounds become available, because the additional criteria of exact retention time and ion ratio can be incorporated to achieve positive identification.

Validation and quality control

In very general terms, the purification and measurement methodology described here is an extension and a refinement of the methodology used at FERA for chlorinated and brominated dioxin and biphenyl measurement (Fernandes et al 2004, Fernandes et al 2008) and exploits the common physical and chemical properties of chlorinated and brominated dioxins/PCBs and PXDD/Fs and PXBs. The use of these techniques has been accredited and peer-reviewed, and the methodology has been used successfully over many years for the measurement of brominated and chlorinated dioxins, PCBs and PBDEs, as evidenced by the excellent results returned in international inter-comparison trials (Quasimeme, Norwegian Institute of Public Health 2005, 2007-2009). As there are no formal acceptance criteria for data quality for PXDD/Fs and PXBs, the quality control for the accompanying data has followed the criteria currently used for chlorinated dioxins and PCBs (Ambidge et al, European Commission Directive 2002/69/EC).

The use of HRGC-HRMS at a resolution of 13.5-15K confers a higher degree of measurement specificity than that used for PCDD/Fs or PBDD/Fs, with only minor compromises to the sensitivity. In practical terms the instrument limit of detection (ILOD) ranges from 20 femtograms (fg) for 3-Br, 7,8-ClDF (most sensitive) to 50fg for 1,3-Br2,7,8-ClDF (least sensitive). This corresponds to an average method limit of detection (MLOD) of the order of ~0.007 picograms/g fat which is similar to sensitivities for the chlorinated and brominated dioxins. It is anticipated that sensitivity would be lower for the higher halogenated compounds as is observed for both chlorinated as well as brominated dioxins and furans. These MLODs allow measurement of PXDD/Fs and PXBs at a level at which they are reported to be toxicologically significant. Method blanks have been investigated over the course of this work and have been shown to be free from any significant presence of the analytes. In keeping with conventional practice, method blank levels are used to compute MLODs.

Despite a relatively high degree of sample and extract handling as is evident from the description of the procedure above, the recovery of the analytes is still within an acceptable range for this type of analysis – typically 50-90%, with generally lower recoveries (typically 40-70%) for the more volatile tri-halogenated compounds. These recovery values are based on experiments using fortified matrices, as well as the use of ^{13}C labelled internal standards used for the analysis of the food samples. The exclusion of water from the samples was found to be critical to obtaining good recoveries. Samples that were analysed wet, returned considerably lower recovery on average (27 and 37%) compared to freeze-dried samples and hence, all samples (except for oils) were analysed after freeze-drying.

The applicability of the methodology to different types of food matrices was investigated prior to the analysis of the samples. Fish, meat, liver, eggs, milk and shellfish were all investigated using the method and good recoveries and interference-free traces were observed for all these foods. This result for liver, in particular, is encouraging as it is known to be a difficult matrix to analyse for dioxins.

The precision of the methodology has been investigated using replicate analyses of a fish tissue matrix. The measurement is considerably aided by the use of ^{13}Carbon labelled congeners and this is evidenced by average precision of around 10% (range, 3-16%) over 16 of the compounds included in this study. There are no available reference materials (RMs) for

these compounds, but an in-house reference material (fortified fish oil) investigated during the course of this work yielded data that was consistent with the fortified levels. This data is given in Table 4. Measurement uncertainty has been estimated and average % uncertainty for the different food types is given in Table 5. A summary of the method validation data is given in the table below:

Analyte	Method Precision	Typical Recovery	Method Limit of Detection/ Quantitation (per congener)	Linearity of Measurement	Measurement Uncertainty
	%	%	ng/kg fat weight		% (at ng/kg)
PXDD/Fs	10	50-80	0.005 – 0.02	0.0001 - 2.0 ng	40(0.05) -250 (<0.005)
PXBs	9	50-90	0.005–0.05	0.0001 - 4.0 ng	20(0.1) - 250(<0.005)

Results of the analysis of Food samples

The results of the analysis of just over 100 samples are given in Table 3. The concentrations are given in ng/kg fat. These data confirm the presence of PXDD/Fs and PXBs in common items of retail food. Most of the foods analysed showed the presence of at least some of these contaminants, but a higher frequency of detection and relatively higher values of these contaminants were observed for samples of shellfish, fish and liver. Recent studies of brominated dioxins and furans (PBDD/Fs) have also shown that the frequency and magnitude of occurrence of these compounds is higher in these matrices (Fernandes et al 2008, 2009, 2009C).

All of the selected congeners were detected, but the frequency and magnitude of detection varied, generally following the order – biphenyls > furans > dioxins. The most frequently detected congeners were mono-brominated - PXB 126, PXB 118, 2-Br-7,8-CDF, PXB 105, 4-Br-2,3,7,8-CDF, 2-Br-7,8-CDD. The di-brominated congeners were detected in about a quarter to a third of the samples. The single tri-brominated biphenyl occurred less frequently – in just over a 10^{th} of the sample set – mostly in shellfish and liver. In the single instance where two configurations from a homologue group were measured – 1,2,3,7,8- and 2,3,4,7,8-penta furans, the occurrence of the latter far exceeded that of the former which was only

present in around a tenth of the samples. This pattern has been seen before for chlorinated and brominated dioxins (Fernandes et al 2008, 2009). These observations support the criteria that were set for selection of congeners, described earlier.

A notable observation was made from the high resolution ion chromatograms – in a manner similar to the chlorinated and brominated dioxin occurrence in some types of sample, the compounds selected for analysis do not occur in isolation. The identity of these signals is not currently known, but given the highly specific purification procedures used, and the very selective measurement technique, it is very likely that these are other non-targeted PXDD/F and PXB congeners. These are observed for some sample types – eggs, fish, game birds (mallard), and in particular, shellfish, which are less able to metabolise some of the non-planar congeners. It is also however possible, given that some of the higher order animals metabolise non-planar compounds, that some of the observed signals may arise from other, non-targeted 2,3,7,8-substituted compounds. It would be difficult to identify these compounds in the absence of analytical standards. It is important to note at this stage that unlike chlorinated and brominated dioxins and biphenyls, where the number of congeners accessible to measurement usually represent all, or the majority of toxic compounds within the group, the 19 compounds selected here, only form a small minority (e.g. two out of five tetra-XDD congeners, three out of eight tetra-XDF congeners and five out of 90 penta-XDD/F congeners) of the several hundred possible laterally substituted and hence potentially toxic PXDD/F congeners (plus a similar number of PXB congeners). If the cumulative toxicity from the measured compounds is estimated, it will therefore only be a small proportion of the total PXDD/F and PXB toxicity.

It is difficult to accurately quantify the toxicity arising from the presence of these contaminants, as toxic equivalency factors have not been specified for these compounds. However, given the reported relative potency data, the observed frequency and levels of occurrence, and the limited number of targeted 2,3,7,8-substituted PXDD/Fs and planar PCBs, the combined toxicity arising from measured and unmeasured compounds is likely to make a significant contribution to total dioxin-like toxicity. This contribution will probably be greater than that arising from PBDD/Fs.

The absence of other data, particularly PXDD/F concentrations in food, does not allow comparison or observations on the trend in occurrence for these compounds. Recently there

has been a report (Ohta et al 2008) on the occurrence of some PXB congeners in fish from Japan. The concentrations reported, ranged from n.d. (0.1) - 23 pg/g wet weight. The concentrations of PXB congeners reported in the fish and shellfish in this study ranged from <0.005 (not detected) to 924 pg/g fat which corresponds to 104 pg/g on a wet weight basis.

This data will allow the estimation of dietary intake for different population sub-groups and the assessment of risk through this mode of exposure. The data also provides an essential measure of the baseline from which data from future studies can be gauged. The ongoing use of incineration for waste disposal, uncontrolled fires, recycling of flame retarded plastics, continued BFR usage and the resulting potential of PXDD/F and PXB formation from the disposal of these materials make it prudent to continue surveillance on the occurrence of these contaminants.

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Table 1. PXDD/F and PXB analytes selected for measurement (including labelled internal and sensitivity standards)

Analyte	Configuration	Halogenation Level	Ion 1	Ion 2
DIOXINS				
	2-Br-7,8-Cl-DD	Tri	329.8850	331.8830
	2-Br-3,7,8-Cl-DD	Tetra	365.8431	367.8410
	2,3-Br-7,8-Cl-DD	Tetra	409.7935	411.7914
	1-Br-2,3,7,8-Cl-DD	Penta	399.8041	401.8021
	2-Br-1,3,7,8-Cl-DD	Penta	399.8041	401.8021
	2-Br-3,6,7,8,9-Cl-DD	Hexa	433.7652	435.7631
^{13}C LABELLED				
	8-Br-2,3-Cl-DF	Mixed Br/Cl	**325.9304**	**327.9283**
	2,3,7,8-TCDD	Cl dioxin	**331.9368**	**333.9339**
	3-Br-2,7,8-Cl-DF	Mixed Br/Cl	**361.8893**	**363.8864**
	2,3-Br-7,8-Cl-DD (IS)	Mixed Br/Cl	**421.8337**	**423.8308**
	1-Br-2,3,7,8-Cl-DD (IS)	Mixed Br/Cl	**411.8444**	**413.8423**
	4-Br-2,3,7,8-Cl-DF	Mixed Br/Cl	**393.8504**	**397.8474**
FURANS				
	2-Br-7,8-Cl-DF	Tri	313.8901	315.8881
	2-Br-6,7,8-Cl-DF	Tetra	349.8491	351.8461
	3-Br-2,7,8-Cl-DF	Tetra	349.8491	351.8461
	2,3-Br-7,8-Cl-DF	Tetra	393.7986	395.7956
	1-Br-2,3,7,8-Cl-DF	Penta	381.8122	385.8072
	4-Br-2,3,7,8-Cl-DF	Penta	381.8122	385.8072
	1,3-Br-2,7,8-Cl-DF	Penta	427.7596	429.7566
BIPHENYLS				
	4'-Br-3,3',4,5-Cl-B	PCB 126 Ana	369.8299	371.8279
	3,4-Br-3',4',5'-Cl-B	PCB 126 Ana	413.7793	415.7783
	3',4',5-Br-3,4-Cl-B	PCB 126 Ana	457.7297	459.7277
	4'-Br-2,3',4,5-Cl-B	PCB 118 Ana	369.8299	371.8279
	4'-Br-2,3,3',4,-ClB	PCB 105 Ana	369.8299	371.8279
	4'-Br-2,3,3',4,5-Cl-B	PCB 156 Ana	403.7909	405.7889
^{13}C LABELLED				
	4'-Br-3,3',4,5-Cl-B (IS)	**PCB 126 Ana**	**381.8701**	**383.8681**
	4'-Br-2,3',4,5-Cl-B (IS)	**PCB 118 Ana**	**381.8701**	**383.8681**
	4'-Br-2,3,3',4,5-Cl-B (IS)	**PCB 156 Ana**	**415.8312**	**417.8292**
SENSITIVITY STANDARDS		**^{13}C LABELLED**		
	1,2,3,4 –TCDD (SS)	Tetra	**331.9368**	**333.9339**
	1,2,3,7,8,9-HxCDD (SS)	Hexa	**401.8559**	**403.8530**

Table 2: Description of Food Samples

	Sample ID.	Description	fat %W
List 1		**Fish**	
	10965	Sprats composite	9.5
	12478	Fresh Whole Sprats	12.4
	12494	Eels, UK	24.0
	18626	Whole mackerel (NE Atlantic)	20.7
	18627	Whole mackerel (fishmonger cleaned)	14.2
	13699	Smoked mackerel	21.0
	14000	Smoked peppered wild mackerel	20.4
	13962	Kippers	17.3
	18624	Farmed Salmon side fillet	17.4
	18625	Fresh Scottish Salmon	24.6
	14092	Traditional oak-smoked Scottish salmon	12.5
	11076	Wild dogfish composite	7.2
	11064	Seabass composite	6.3
		Shellfish	
	14903	Cockles Composite	0.9
	12044	Cooked shelled mussels	2.8
	12184	Cooked shelled mussels	1.6
	18629	Native Oysters, Loch Ryan, Scotland	0.7
	18630	Rock Oysters, Grouville, Jersey East coast	0.5
	15957	Mitten crab, Holland Diep , Holland	11.2
	15952	Mitten crab, Thames	10.6
		Offal	
	13314	Red Deer Liver, Durris, Kincardine	3.7
	11374	Lambs liver	5.8
	11443	Halal lambs liver	5.4
	11468	Ox liver	3.4
	11420	Pigs Liver	3.5
		Meat	
	11868	Fresh boneless ribjoint Beef	18.8
	12410	Beef burgers	14.3
	11896	Fresh British Lamb	10.8
	12434	Lamb Mince	19.9
	11867	Organic whole chicken	7.4
		Eggs	
	11829	Yorkshire Farmhouse Eggs	9.8
	12407	Organic Eggs, Ayrshire	10.4
	11719	Duck Eggs	13.4
	12539	Gulls Eggs	8.4
		Milk	
	12500	Whole Milk with Omega 3	2.8
	12501	Omega3 Enriched Whole Milk	2.4
	11854	Pasturised goats milk	3.9

Table 2 (cont'd): Description of Food Samples

	Sample ID.	Description	fat %W
		Dairy products	
	11830	Coloured Cheshire	31.7
	12533	Grated mozzarella	18.3
	12525	Organic cream, fresh, pasteurised, Oaks in Charnwood	46.4
List 2		**Fish**	
	12477	Butterfish fillet portions	28.8
	12479	Fresh whole sprats	9.6
	12493	Freshwater Eel -whole	27.0
	12495	Whole Eel	23.6
	12473	Conger Eel Steaks	3.3
	13426	Hot smoked trout fillets, Scotland	5.7
	15369	Whole mackerel	12.2
	16166	Whole Cornish mackerel	24.8
	13670	Smoked mackerel	28.0
	13675	Hot smoked Scottish mackerel fillets	20.7
	15450	Whole herring	24.1
	16189	Herring (filleted by fishmonger)	9.7
	13752	Kipper Fillets	18.3
	15315	Organic boned Scottish salmon fillets	13.8
	16159	Lochmuir Scottish salmon portions	16.5
	13895	Arran salmon	10.7
	11655	Salmon pate	11.5
	15564	Wild Atlantic salmon	7.8
	15555	Whitebait	9.1
	15565	Whitebait	2.1
	15516	Whole Cornish sardines	5.5
	11582	Blanchbait (smelt)	2.1
		Shellfish	
	14039	Mussels in shell	1.4
	12332	Oysters, Scottish	1.9
	14040	Native Oysters in shell	0.7

Table 2 (cont'd): Description of Food Samples

Sample ID.	Description	fat %W
	Offal	
13317	Red Deer Liver, Millden, Glenesk	3.7
11522	Roe venison liver	3.7
11372	Lambs Liver	5.7
11389	Lambs Liver	6.1
11424	Ox Liver	3.5
11449	British pork liver	2.7
11520	Pigs liver	3.9
11529	Chicken livers	3.6
11444	Halal lamb kidney	4.8
11440	Ox Kidney	7.0
11422	Chicken liver	3.2
	Meat	
12200	British Beef Topside/Top Rump	10.0
12412	Beef Sausages	22.4
12414	Corned beef slices	13.6
12198	British Lamb Half Bone In Shoulder	13.4
12327	Lamb	9.8
12433	Welsh Lamb Mince	21.6
12191	Mutton	13.9
12330	Organic chicken	11.2
12441	Fresh Mallard	22.0
12445	Oven Ready Pigeon	3.5
	Eggs	
11717	Organic Free Range Eggs	9.0
12535	Omega 3 free range eggs	8.5
	Dairy products	
11849	English goats cheese	31.5
	Other foods	
12030	Bread composite - brown, sunflower multigrain, wholemeal, granary, white	2.7
11334	VEG composite - Kale, Leek, spring greens , green cabbage , brocoli	1.0
11339	Potato Composite -King Edwards, Maris Piper, Juliettes, Charlottes, Estima	0.2
12325	Uk Apple Composite - Bramley, George Cave, James Grieve, Discovery, Grenadier	0.3
11836	Salmon Oil	100
12480	Fresh Sprats	8.4
16151	Smoked Eel	35.7
16169	Farmed Salmon fillets	15.5
13698	Manx Kippers	15.9
13692	Hot smoked mackerel	19.5
12081	North Atlantic cooked cockles	0.8
13869	Smoked scallops	1.9
15529	Chicken livers	4.6
11442	Pigs Kidney	3.5

Table 3: Concentrations of PXDDs, PXDFs and PXBs in foods.

OPHA Sample No.	10965	12478	12494	18626	18627	13699	14000	13962	18624
Sample Details:	Sprats composite	Fresh Whole Sprats	Eels, UK	Whole mackerel (NE Atlantic)	Whole mackerel (fishmonger cleaned)	Smoked mackerel	Smoked peppered wild mackerel	Kippers	Farmed Salmon, side fillet
Fat content (% of whole)	9.5	12.4	24	20.7	14.2	21	20.4	17.3	17.4
ng/kg fat									
PXDD/Fs									
2-B-7,8-CDD	<0.011	0.031	0.048	0.059	0.268	<0.006	<0.005	<0.005	0.267
2-B-3,7,8-CDD	<0.005	<0.009	<0.006	<0.005	<0.005	<0.006	<0.005	<0.005	<0.007
2,3-B-7,8-CDD	0.010	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
1-B-2,3,7,8-CDD	0.010	<0.005	<0.005	<0.005	<0.007	<0.006	<0.005	<0.005	<0.005
2-B-1,3,7,8-CDD	0.010	<0.01	<0.006	<0.007	<0.008	<0.005	<0.005	<0.005	<0.007
2-B-3,6,7,8,9-CDD	0.013	<0.005	<0.005	<0.009	<0.011	<0.009	<0.006	<0.007	0.007
2-B-7,8-CDF	0.020	<0.008	0.011	0.008	0.01i	0.012	0.011	<0.007	0.056
3-B-2,7,8-CDF	<0.005	<0.005	<0.005	<0.005	0.009	0.012	0.017	0.011	0.035
2-B-6,7,8-CDF	<0.012	<0.01	<0.006	<0.008	0.018	<0.011	<0.008	0.017	0.039
2,3-B-7,8-CDF	<0.009	<0.005	0.011	<0.007	0.009	0.016	0.167	<0.005	<0.005
1-B-2,3,7,8-CDF	<0.007	<0.005	<0.005	<0.009	<0.011	<0.01	<0.007	<0.008	<0.005
4-B-2,3,7,8-CDF	0.025	<0.005	<0.005	<0.006	0.014	<0.011	<0.008	0.012	0.102
1,3-B-2,7,8-CDF	<0.01	<0.011	<0.007	<0.007	<0.009	<0.006	<0.005	<0.005	<0.008
PXBs									
4'-B-3,3',4,5-CB (PXB126)	0.134	0.046	0.022	0.029	0.036	0.083	0.061	0.110	0.024i
3,4-B-3',4',5'-CB (PXB126 di-Br)	<0.005	<0.006	<0.005	<0.005	0.007	<0.005	<0.005	<0.005	0.007
3',4',5'-B-3,4-CB (PXB126 tri-Br)	<0.005	<0.008	<0.005	<0.008	<0.009	<0.005	<0.005	<0.005	<0.006
4'-B-2,3',4,5-CB (PXB 118)	3.676	0.616	0.429	0.254	0.395	0.256	0.367	0.861	0.363
4'-B-2,3,3',4-CB (PXB 105)	1.205	0.255i	0.163	0.495i	0.78i	0.345i	0.318i	1.005i	0.264
4'-B-2,3,3',4,5-CB (PXB 156)	0.312	0.101	0.057	0.032	0.060	0.080	<0.055	0.107	0.054

i – indicative value

Table 3 (cont'd): Concentrations of PXDDs, PXDFs and PXBs in foods.

OPHA Sample No.	18625	14092	11076	11064	14903	12044	12184	18629	18630
Sample Details:	Fresh Scottish Salmon	Traditional oak-smoked Scottish salmon	Wild dogfish composite	Seabass composite	Cockles Composite	Cooked shelled mussels	Cooked, shelled mussels	Native Oysters, Loch Ryan, Scotland	Rock Oysters, Grouville, Jersey East coast
Fat content (% of whole)	24.6	12.5	7.2	6.3	0.9	2.8	1.6	0.7	0.5
ng/kg fat									
PXDD/Fs									
2-B-7,8-CDD	0.088	<0.006	0.013	0.032	6.089	1.639	1.418	810.8i	92.673
2-B-3,7,8-CDD	0.007	<0.006	<0.005	<0.005	<0.058	<0.027	0.043	0.245i	0.161
2,3-B-7,8-CDD	<0.005	<0.005	0.006	0.007	<0.033	0.018	<0.019	1.119	0.359
1-B-2,3,7,8-CDD	<0.005	<0.007	<0.005	0.012	<0.033	<0.016	<0.019	<0.058	<0.021
2-B-1,3,7,8-CDD	<0.006	<0.005	<0.006	<0.007	<0.064	<0.03	<0.037	<0.069	<0.029
2-B-3,6,7,8,9-CDD	<0.005	<0.009	<0.007	<0.008	<0.03	0.047	<0.017	<0.098	<0.033
2-B-7,8-CDF	0.006	<0.01	0.008	0.015	<0.052	0.278	0.304	0.633	2.902
3-B-2,7,8-CDF	0.006	<0.009	<0.005	0.014	<0.024	0.096	0.070	0.404	0.689
2-B-6,7,8-CDF	<0.006	<0.012	<0.011	0.017	<0.063	0.098	0.189	0.724	0.591
2,3-B-7,8-CDF	<0.005	<0.006	<0.008	<0.009	0.053	<0.011	0.215i	0.269	<0.038
1-B-2,3,7,8-CDF	<0.005	<0.01	<0.007	<0.008	<0.018	<0.008	<0.01	<0.091	<0.033
4-B-2,3,7,8-CDF	0.005	<0.012	<0.006	<0.007	<0.027	0.062	0.072	0.362	0.428
1,3-B-2,7,8-CDF	<0.007	<0.006	<0.01	<0.011	<0.073	<0.034	<0.042	<0.079	<0.045
PXBs									
4'-B-3,3',4,5-CB (PXB126)	0.017	0.094	0.035	0.025	0.053	0.094	0.088	0.202	0.104
3,4-B-3',4',5'-CB (PXB126 di-Br)	<0.005	0.006	0.015	<0.005	<0.038	<0.018	<0.022	0.059	<0.017
3',4',5'-B-3,4-CB (PXB126 tri-Br)	<0.005	<0.005	<0.005	<0.005	<0.055	<0.025	<0.031	<0.081	<0.017
4'-B-2,3',4,5-CB (PXB 118)	0.204	0.968	10.137	4.416	4.497i	1.129	1.766	10.260	1.152
4'-B-2,3,3',4-CB (PXB 105)	0.135	0.437	2.098	1.567	0.637i	0.501	0.802	2.749	0.877i
4'-B-2,3,3',4,5-CB (PXB 156)	0.058	0.154	1.182	0.841	<0.082	<0.037	<0.044	0.731	0.555

i – indicative value

Table 3 (cont'd): Concentrations of PXDDs, PXDFs and PXBs in foods.

OPHA Sample No.	15957	15952	13314	11374	11443	11468	11420	11868	12410
Sample Details:	Mitten crab, Hollands Diep , Holland	Mitten crab, Thames	Red Deer Liver, Durris, Kincardine	Lambs liver	lambs liver, Halal	Ox liver	Pigs Liver	Fresh boneless ribjoint, Beef	Beef burgers
Fat content (% of whole)	11.2	10.6	3.7	5.8	5.4	3.4	3.5	18.8	14.3
ng/kg fat									
PXDD/Fs									
2-B-7,8-CDD	175.8	200.8	0.012	<0.010	0.044	0.029	<0.015	<0.005	0.016
2-B-3,7,8-CDD	0.459	0.233	0.141	0.014	<0.007	0.025	<0.008	<0.005	<0.005
2,3-B-7,8-CDD	0.199	3.648	0.061	0.007i	<0.007	<0.01	<0.009	<0.005	0.005
1-B-2,3,7,8-CDD	0.042	0.027	0.044	<0.008	<0.006	<0.013	<0.013	<0.005	<0.005
2-B-1,3,7,8-CDD	0.021	0.051	0.039	<0.007	<0.009	<0.005	<0.011	<0.005	0.007
2-B-3,6,7,8,9-CDD	0.109	0.111	0.057	0.021	0.056	0.027	<0.013	0.005	0.013
2-B-7,8-CDF	2.424	1.131	0.030	<0.005	<0.008	0.043	<0.006	<0.005	<0.005
3-B-2,7,8-CDF	1.846	1.403	0.066	0.013	<0.006	<0.018	<0.01	<0.005	<0.005
2-B-6,7,8-CDF	2.139i	0.555	<0.02	<0.005	<0.016	<0.023	<0.005	<0.005	<0.009
2,3-B-7,8-CDF	2.641	1.048	0.101	0.020	0.011	<0.013	<0.015	<0.005	<0.006
1-B-2,3,7,8-CDF	0.108i	0.116i	<0.018	<0.018	<0.01	<0.021	<0.027	<0.005	<0.006
4-B-2,3,7,8-CDF	0.666	0.45i	2.365	0.360	0.186	0.060	0.118	<0.005	0.016
1,3-B-2,7,8-CDF	0.450	0.433	0.036	<0.009	<0.013	<0.013	<0.014	<0.005	<0.008
PXBs									
4'-B-3,3',4,5-CB (PXB126)	1.712	0.502	1.289	0.334	0.444	0.244	0.145	0.045	0.034
3,4-B-3',4',5'-CB (PXB126 di-Br)	0.228	0.311	0.492	0.091	0.091	0.034	0.013	<0.005	0.008
3',4',5'-B-3,4-CB (PXB126 tri-Br)	0.079	0.144	0.09i	0.026	0.067	0.011	<0.015	<0.005	<0.005
4'-B-2,3',4,5-CB (PXB 118)	924	43.2	0.248i	0.039	0.037	0.449	0.052	0.198	0.104i
4'-B-2,3,3',4-CB (PXB 105)	844	33.0	0.123	<0.005	0.04i	0.050	<0.03	0.023	0.014i
4'-B-2,3,3',4,5-CB (PXB 156)	75	6.14	0.117i	0.029	<0.005	<0.161	<0.018	0.063	0.068

i – indicative value

Table 3 (cont'd): Concentrations of PXDDs, PXDFs and PXBs in foods.

OPHA Sample No.	11896	12434	11867	11829	12407	11719	12539	12500	12501
Sample Details:	Fresh British Lamb	Lamb Mince	Organic whole chicken	Yorkshire Farmhouse Eggs	Organic Eggs, Ayrshire	Duck Eggs	Gulls Eggs	Whole Milk with Omega 3	Omega3 Enriched Whole Milk
Fat content (% of whole)	10.8	19.9	7.4	9.8	10.4	13.4	8.4	2.8	2.4
ng/kg fat									
PXDD/Fs									
2-B-7,8-CDD	0.017	0.007	<0.005	<0.007	<0.007	<0.006	<0.009	<0.006	<0.007
2-B-3,7,8-CDD	0.022	0.011	<0.005	0.008	0.028	<0.005	0.186	<0.005	0.007
2,3-B-7,8-CDD	<0.007	<0.005	<0.005	<0.005	0.009	<0.005	0.077	<0.005	<0.005
1-B-2,3,7,8-CDD	0.009	<0.005	<0.005	<0.006	<0.006	0.009	0.021	<0.005	<0.006
2-B-1,3,7,8-CDD	0.009	<0.005	<0.005	0.008	<0.005	<0.005	0.096i	<0.005	<0.005
2-B-3,6,7,8,9-CDD	0.017i	<0.006	<0.007	<0.006	0.020	0.033	0.342	<0.006	<0.006
2-B-7,8-CDF	0.011	0.014	<0.007	<0.005	0.021	0.008	0.024	<0.005	<0.005
3-B-2,7,8-CDF	<0.005	<0.005	<0.007	0.015	0.073	0.017	0.030	<0.005	<0.005
2-B-6,7,8-CDF	<0.009	<0.007	0.016	<0.005	0.127	0.026	<0.005	<0.005	<0.005
2,3-B-7,8-CDF	0.012	0.013	0.017	<0.007	0.066	0.022	<0.009	<0.006	<0.007
1-B-2,3,7,8-CDF	0.007	<0.006	<0.008	<0.012	<0.013	0.016	0.060	<0.011	<0.013
4-B-2,3,7,8-CDF	0.020	0.013	<0.009	<0.011	<0.013	<0.011	0.261	<0.011	0.014
1,3-B-2,7,8-CDF	<0.008	<0.005	<0.005	<0.006	<0.007	<0.006	<0.008	<0.006	<0.007
PXBs									
4'-B-3,3',4,5-CB (PXB126)	0.06i	0.056	0.060	0.051	0.091	0.053	0.544	<0.043	0.056
3,4-B-3',4',5'-CB (PXB126 di-Br)	0.013	<0.005	<0.005	<0.005	0.020	<0.005	0.218	0.006	<0.005
3',4',5'-B-3,4-CB (PXB126 tri-Br)	0.007	<0.005	<0.005	<0.006	0.017	<0.006	0.078	<0.006	<0.007
4'-B-2,3',4,5-CB (PXB 118)	0.096i	0.249	0.121	0.030	0.324	0.165	11.280	0.113	0.170
4'-B-2,3,3',4-CB (PXB 105)	0.043i	0.048	0.099i	0.017	0.113	0.076	6.107i	0.063	0.071i
4'-B-2,3,3',4,5-CB (PXB 156)	0.115	0.091	<0.059	<0.007	<0.007	0.091i	2.735	<0.006	<0.005

i – indicative value

Table 3 (cont'd): Concentrations of PXDDs, PXDFs and PXBs in foods.

OPHA Sample No.	11854	11830	12533	12525
Sample Details:	Pasturised goats milk	Coloured Cheshire	Grated mozzarella	Organic cream, fresh, pasteurised. Oaks in Charnwood
Fat content (% of whole)	3.9	31.7	18.3	46.4
ng/kg fat				
PXDD/Fs				
2-B-7,8-CDD	<0.007	<0.005	<0.021	<0.005
2-B-3,7,8-CDD	<0.005	0.015	<0.008	0.009
2,3-B-7,8-CDD	<0.005	<0.005	<0.005	<0.005
1-B-2,3,7,8-CDD	<0.005	<0.005	<0.005	<0.005
2-B-1,3,7,8-CDD	<0.005	<0.005	<0.009	<0.005
2-B-3,6,7,8,9-CDD	<0.006	0.021	<0.005	<0.005
2-B-7,8-CDF	<0.005	<0.008	0.012	<0.005
3-B-2,7,8-CDF	<0.005	<0.007	0.007	<0.005
2-B-6,7,8-CDF	<0.005	<0.009	<0.009	<0.005
2,3-B-7,8-CDF	<0.007	<0.005	0.009	<0.005
1-B-2,3,7,8-CDF	<0.012	<0.008	<0.005	<0.009
4-B-2,3,7,8-CDF	<0.011	0.021i	0.012	0.014
1,3-B-2,7,8-CDF	<0.006	<0.005	<0.011	<0.005
PXBs				
4'-B-3,3',4,5-CB (PXB126)	0.047	0.066	0.016	0.064
3,4-B-3',4',5'-CB (PXB126 di-Br)	<0.005	<0.005	<0.006	0.007i
3',4',5'-B-3,4-CB (PXB126 tri-Br)	<0.006	<0.005	<0.008	0.005
4'-B-2,3',4,5-CB (PXB 118)	0.075	0.083	0.131	0.138
4'-B-2,3,3',4-CB (PXB 105)	0.033	0.081	0.078	0.035
4'-B-2,3,3',4,5-CB (PXB 156)	0.022i	<0.065	0.095	0.047

i – indicative value

Table 3 (cont'd): Concentrations of PXDDs, PXDFs and PXBs in foods.

OPHA Sample No.	12477	12479	12493	12495	12473	13426	15369	16166	13670
Sample Details:	Butterfish fillet portions	Fresh whole sprats	Freshwater Eel -whole	Whole eels	Conger Eel Steaks	Hot smoked trout fillets (Scotland)	Whole mackerel	Whole Cornish mackerel	Smoked mackerel
Fat content (% of whole)	28.8	9.6	27.0	23.6	3.3	5.7	12.2	24.8	28.0
ng/kg fat									
PXDD/Fs									
2-B-7,8-CDD	0.010	0.032	0.030	<0.005	<0.012	0.018	0.180	0.091	<0.005
2-B-3,7,8-CDD	<0.005	<0.005	<0.005	<0.005	<0.018	<0.012	<0.006	<0.005	<0.005
2,3-B-7,8-CDD	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
1-B-2,3,7,8-CDD	<0.005	<0.005	<0.005	<0.005	<0.016	<0.011	<0.008	<0.005	<0.005
2-B-1,3,7,8-CDD	<0.005	<0.007	<0.005	<0.005	<0.015	<0.011	<0.01	<0.006	<0.005
2-B-3,6,7,8,9-CDD	<0.005	<0.008	<0.005	<0.006	<0.02	<0.014	<0.014	<0.009	<0.005
2-B-7,8-CDF	0.006	0.012	0.010	0.007	<0.015	0.016	<0.01	<0.007	0.008
3-B-2,7,8-CDF	<0.005	0.021	<0.005	<0.005	0.020	<0.009	0.013	0.006	<0.005
2-B-6,7,8-CDF	<0.005	0.14i	<0.009	<0.005	0.037i	<0.011	0.036	0.023	0.01i
2,3-B-7,8-CDF	<0.005	0.032i	<0.006	<0.005	<0.017	<0.012	0.014i	0.006	<0.005
1-B-2,3,7,8-CDF	<0.005	<0.008	<0.005	<0.005	<0.011	<0.008	<0.013	<0.008	<0.005
4-B-2,3,7,8-CDF	<0.005	0.017	<0.005	<0.005	<0.012	0.016	0.015i	<0.006	0.006
13-B-2,7,8-CDF	<0.005	<0.01	<0.007	<0.005	<0.013	<0.009	<0.011	<0.007	<0.005
PXBs									
4'-B-3,3',4,5-CB (PXB126)	0.058	0.114	0.044	0.017	0.192	0.111	0.059	0.049	0.020
3,4-B-3',4',5'-CB (PXB126 di-Br)	<0.005	0.01i	<0.005	<0.005	<0.009	<0.006	<0.008	<0.005	<0.005
3',4',5'-B-3,4-CB (PXB126 tri-Br)	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.011	<0.007	<0.005
4'-B-2,3',4,5-CB (PXB 118)	0.579	0.286	0.922	0.629	5.964	2.244	1.105	0.853	0.441
4'-B-2,3,3',4-CB (PXB 105)	0.102	0.059i	0.584	0.283	1.717	1.212	0.573	0.764i	0.303i
4'-B-2,3,3',4,5-CB (PXB 156)	0.154	0.039	0.191	0.111	0.989	0.414	0.188	0.061	0.075

i – indicative value

Table 3 (cont'd): Concentrations of PXDDs, PXDFs and PXBs in foods.

OPHA Sample No.	13675	15450	16189	13752	15315	16159	13895	11655	15564
Sample Details:	Hot smoked Scotish mackerel fillets	Whole herring	Herring - filleted by fishmonger	Kipper Fillets	Organic boned Scottish salmon fillets	Lochmuir Scottish salmon portions	Arran salmon	Salmon pate	Wild Atlantic salmon
Fat content (% of whole)	20.7	24.1	9.7	18.3	13.8	16.5	10.7	11.5	7.8
ng/kg fat									
PXDD/Fs									
2-B-7,8-CDD	<0.005	<0.007	0.022i	<0.005	<0.005	<0.005	0.065	0.080	0.123
2-B-3,7,8-CDD	<0.006	<0.005	<0.007	<0.005	0.008	<0.005	<0.01	<0.005	<0.008
2,3-B-7,8-CDD	<0.005	<0.005	<0.006	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
1-B-2,3,7,8-CDD	<0.006	<0.005	<0.009	<0.005	<0.006	<0.005	<0.009	<0.006	<0.007
2-B-1,3,7,8-CDD	<0.005	0.007	<0.01	<0.005	<0.005	<0.005	<0.008	<0.005	<0.007
2-B-3,6,7,8,9-CDD	<0.007	<0.009	<0.015	<0.006	<0.007	<0.006	<0.011	<0.006	<0.009
2-B-7,8-CDF	<0.005	<0.007	0.025	0.007	0.012	0.008	0.156	<0.01	0.018
3-B-2,7,8-CDF	0.007	0.007	0.052	0.005i	0.017i	<0.005	0.014	0.011	0.023
2-B-6,7,8-CDF	0.015i	<0.007	0.218i	<0.005	0.021i	0.009i	0.034	0.009i	0.03i
2,3-B-7,8-CDF	<0.006	<0.006	0.092	<0.005	0.008	0.007	<0.009	0.011	0.011
1-B-2,3,7,8-CDF	<0.005	<0.008	<0.014	<0.005	<0.005	<0.005	<0.006	<0.007	<0.005
4-B-2,3,7,8-CDF	0.007	<0.006	0.047	0.008	0.01i	<0.005	0.018	0.006	0.022
13-B-2,7,8-CDF	<0.005	<0.007	<0.012	<0.005	<0.005	<0.005	<0.007	<0.005	<0.006
PXBs									
4'-B-3,3',4,5-CB (PXB126)	0.024i	0.033	0.439	0.048	0.120	0.017	0.076	0.049	0.076
3,4-B-3',4',5'-CB (PXB126 di-Br)	<0.005	<0.005	0.011	<0.005	<0.005	<0.005	<0.005	<0.005	0.017
3',4',5'-B-3,4-CB (PXB126 tri-Br)	<0.005	<0.007	<0.012	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
4'-B-2,3',4,5-CB (PXB 118)	0.627	0.587	11.836	0.687	1.835	0.329	1.799	0.980	1.423
4'-B-2,3,3',4-CB (PXB 105)	0.537i	0.688i	4.768	0.516	0.905	0.174i	1.107i	0.250	1.319i
4'-B-2,3,3',4,5-CB (PXB 156)	0.092	0.098	1.825	0.128	0.327	0.067	0.301	0.150	0.256

i – indicative value

Table 3 (cont'd): Concentrations of PXDDs, PXDFs and PXBs in foods.

OPHA Sample No.	15555	15565	15516	11582	14039	12332	14040	13317
Sample Details:	Whitebait	Whitebait	Whole Cornish sardines - frozen	Blanchbait (smelt)	Mussels in shell	Oysters Scottish	Native oysters in shell	Red Deer Liver - Millden, Glenesk
Fat content (% of whole)	9.1	2.1	5.5	2.1	1.4	1.9	0.7	3.7
ng/kg fat								
PXDD/Fs								
2-B-7,8-CDD	0.053	1.120	0.147	<0.071	43.308	21.634	624.278	<0.045
2-B-3,7,8-CDD	<0.007	0.018	<0.006	<0.014	0.033	0.143	0.333	0.056
2,3-B-7,8-CDD	<0.006	0.044i	<0.005	<0.009	0.354	0.468	2.923	0.058
1-B-2,3,7,8-CDD	<0.009	<0.023	<0.01	<0.024	<0.033	<0.031	<0.06	0.022
2-B-1,3,7,8-CDD	<0.011	0.041	<0.008	<0.018	<0.025	<0.037	<0.045	0.025
2-B-3,6,7,8,9-CDD	<0.016	<0.039	<0.011	<0.025	0.095i	<0.053	0.119i	0.059
2-B-7,8-CDF	0.019	0.063	0.026	<0.038	0.835	0.878	0.369	<0.024
3-B-2,7,8-CDF	0.012	0.122	0.011	<0.02	0.315	0.173	0.721	0.068
2-B-6,7,8-CDF	0.015i	0.729i	<0.011	0.073i	0.209	0.605	1.214i	<0.016
2,3-B-7,8-CDF	<0.012	0.119	<0.008	0.022	<0.027	0.558i	<0.048	0.147
1-B-2,3,7,8-CDF	<0.015	0.040	<0.012	<0.027	<0.039	<0.049	0.109	0.052i
4-B-2,3,7,8-CDF	0.050	0.113	<0.01	0.024	0.215	2.585	0.559	2.454
13-B-2,7,8-CDF	<0.013	<0.032	<0.008	<0.018	<0.025	<0.043	0.054	0.045
PXBs								
4'-B-3,3',4,5-CB (PXB126)	0.244	0.463	0.081	0.141	0.114i	0.352	0.332i	0.973
3,4-B-3',4',5'-CB (PXB126 di-Br)	0.012	<0.022	<0.007	<0.016	<0.023	<0.029	0.071	0.266i
3',4',5'-B-3,4-CB (PXB126 tri-Br)	<0.013	<0.033	<0.007	<0.015	<0.022	<0.044	<0.039	0.061
4'-B-2,3',4,5-CB (PXB 118)	3.296	14.720	1.741	3.341	3.657	6.115i	4.545	0.206
4'-B-2,3,3',4-CB (PXB 105)	1.581	4.901	0.602	1.26i	1.908	2.308i	0.90i	0.118i
4'-B-2,3,3',4,5-CB (PXB 156)	0.490	1.742	0.312	0.675	<0.054	<0.044	1.019	0.096

i – indicative value

Table 3 (cont'd): Concentrations of PXDDs, PXDFs and PXBs in foods.

OPHA Sample No.	11522	11372	11389	11424	11449	11520	11529	11444	11440
Sample Details:	Roe venison liver	Lambs Liver	Lambs Liver	Ox Liver	British pork liver	Pigs liver	Chicken livers	Halal lambs kidney	Ox Kidney
Fat content (% of whole)	3.7	5.7	6.1	3.5	2.7	3.9	3.6	4.8	7.0
ng/kg fat									
PXDD/Fs									
2-B-7,8-CDD	<0.051	<0.035	<0.032	<0.038	<0.046	<0.016	<0.017	<0.016	<0.012
2-B-3,7,8-CDD	0.130	0.011	0.006	<0.036	<0.043	<0.016	<0.016	<0.015	<0.011
2,3-B-7,8-CDD	0.058	<0.005	<0.005	0.026	<0.02	<0.01	<0.007	<0.007	<0.005
1-B-2,3,7,8-CDD	<0.017	<0.012	<0.011	<0.012	0.038	<0.015	<0.005	<0.005	<0.005
2-B-1,3,7,8-CDD	0.021	<0.009	<0.008	<0.018	<0.022	<0.018	<0.008	<0.007	<0.006
2-B-3,6,7,8,9-CDD	0.047	<0.012	0.016	0.062	<0.059	0.024	<0.021	<0.02	<0.016
2-B-7,8-CDF	<0.027	<0.019	<0.017	<0.026	<0.031	<0.02	<0.011	<0.01	<0.008
3-B-2,7,8-CDF	0.016	<0.01	<0.009	<0.012	0.023	<0.017	<0.005	<0.005	<0.005
2-B-6,7,8-CDF	<0.019	<0.013	<0.012	<0.009	<0.011	<0.018	<0.005	<0.005	<0.005
2,3-B-7,8-CDF	0.014	<0.009	0.020	<0.015	<0.018	<0.013	<0.006	<0.006	<0.005
1-B-2,3,7,8-CDF	<0.02	<0.013	<0.012	<0.03	<0.036	<0.018	<0.013	<0.012	<0.01
4-B-2,3,7,8-CDF	0.629i	0.098	0.088	0.097	0.05i	0.073	<0.011	<0.01	0.013
13-B-2,7,8-CDF	<0.013	<0.009	<0.008	<0.032	<0.038	<0.022	<0.014	<0.013	<0.01
PXBs									
4'-B-3,3',4,5-CB (PXB126)	2.507	0.211	0.195	0.094	0.060	0.023	<0.014	0.019i	0.020
3,4-B-3',4',5'-CB (PXB126 di-Br)	0.905	0.083	0.038	0.040	<0.036	<0.014	<0.013	<0.012	<0.01
3',4',5'-B-3,4-CB (PXB126 tri-Br)	0.165i	<0.008	0.011	<0.026	<0.031	<0.006	<0.011	<0.01	<0.008
4'-B-2,3',4,5-CB (PXB 118)	0.798	0.025	<0.011	0.402	0.084	<0.016	<0.01	0.020	0.120
4'-B-2,3,3',4-CB (PXB 105)	0.307i	<0.026	<0.023	<0.019	0.032	<0.02	<0.008	0.018i	0.009
4'-B-2,3,3',4,5-CB (PXB 156)	0.671	0.052	0.071	<0.021	<0.025	<0.031	<0.009	0.041	<0.007

i – indicative value

Table 3 (cont'd): Concentrations of PXDDs, PXDFs and PXBs in foods.

OPHA Sample No.	11422	12200	12412	12414	12198	12327	12433	12191	12330
Sample Details:	Chicken liver	British Beef Topside/ Top Rump	Beef Sausages	Corned beef premium slices	British Lamb Half Bone In Shoulder	Lamb	Welsh Lamb Mince	Mutton	Organic chicken
Fat content (% of whole)	3.2	10.0	22.4	13.6	13.4	9.8	21.6	13.9	11.2
ng/kg fat									
PXDD/Fs									
2-B-7,8-CDD	<0.028	<0.013	0.011i	0.025	<0.008	<0.01	<0.01	<0.007	<0.006
2-B-3,7,8-CDD	<0.026	<0.012	<0.007	<0.012	0.054	0.013	<0.009	<0.005	<0.005
2,3-B-7,8-CDD	<0.012	0.007	<0.005	<0.005	0.011	<0.005	0.005	<0.005	<0.005
1-B-2,3,7,8-CDD	<0.009	<0.005	<0.005	<0.005	0.008	<0.007	<0.005	<0.005	<0.005
2-B-1,3,7,8-CDD	<0.014	<0.006	<0.005	<0.006	<0.005	<0.005	<0.005	<0.005	<0.005
2-B-3,6,7,8,9-CDD	<0.036	<0.017	<0.01	<0.016	0.016	<0.01	<0.013	0.012	<0.006
2-B-7,8-CDF	0.029	0.019	0.008	0.015	<0.008	<0.01	<0.007	<0.007	<0.006
3-B-2,7,8-CDF	0.019	<0.005	<0.005	<0.005	<0.005	<0.006	<0.005	<0.005	<0.005
2-B-6,7,8-CDF	<0.007	<0.005	<0.005	<0.006	<0.005	<0.006	<0.005	<0.005	<0.005
2,3-B-7,8-CDF	0.041	<0.005	<0.005	<0.005	0.006	0.009	<0.005	<0.005	<0.005
1-B-2,3,7,8-CDF	<0.022	<0.01	<0.006	<0.01	<0.005	<0.007	<0.008	<0.005	<0.005
4-B-2,3,7,8-CDF	0.025	0.012	0.005	<0.008	0.014	0.019	<0.007	<0.006	<0.005
13-B-2,7,8-CDF	<0.024	<0.011	<0.007	<0.011	<0.007	<0.009	<0.008	<0.006	<0.005
PXBs									
4'-B-3,3',4,5-CB (PXB126)	0.027i	0.018	0.015	0.011	0.072i	0.019	0.020	0.013	0.010
3,4-B-3',4',5'-CB (PXB126 di-Br)	<0.022	<0.01	<0.006	<0.01	<0.007	<0.009	<0.008	0.010	<0.005
3',4',5'-B-3,4-CB (PXB126 tri-Br)	<0.019	<0.009	<0.005	<0.008	<0.008	<0.011	<0.007	<0.007	<0.006
4'-B-2,3',4,5-CB (PXB 118)	0.034	0.140	0.131	0.074i	0.154	0.11i	0.045	0.042	0.168
4'-B-2,3,3',4-CB (PXB 105)	<0.014	<0.007	0.022i	<0.006	0.028	<0.016	0.014i	0.043	<0.009
4'-B-2,3,3',4,5-CB (PXB 156)	<0.016	<0.007	0.040	0.013	0.099	<0.015	0.034i	0.055	<0.008

i – indicative value

Table 3 (cont'd): Concentrations of PXDDs, PXDFs and PXBs in foods.

OPHA Sample No.	12441	12445	11717	12535	11849	12030	11334	11339	12325
Sample Details:	Fresh Mallard	Oven Ready Pigeon	Organic Free Range Eggs	Omega 3 free range eggs	English goats cheese	Bread composite- brown, sunflower multigrain, wholemeal, granary, white	Veg composite- Kale, Leek, spring greens, green cabbage, broccoli	Potatoes, Composite- King Edward, Maris Piper, Juliettes, Charlottes, Estima	Uk Apples, composite- Bramley, George Cave, James Grieve, Discovery, Grenadier
Fat content (% of whole)	22.0	3.5	9.0	8.5	31.5	2.7	1.0	0.2	0.3
ng/kg fat									
PXDD/Fs									
2-B-7,8-CDD	<0.005	<0.016	<0.008	<0.009	<0.009	<0.034	0.078	<0.085	<0.031
2-B-3,7,8-CDD	0.036	0.024	<0.006	<0.006	0.031	<0.025	<0.069	<0.085	<0.031
2,3-B-7,8-CDD	0.014	<0.006	<0.005	<0.005	<0.005	<0.012	<0.044	<0.054	<0.02
1-B-2,3,7,8-CDD	<0.005	<0.011	<0.006	<0.006	<0.006	<0.023	<0.066	<0.081	<0.029
2-B-1,3,7,8-CDD	<0.005	<0.009	<0.005	<0.005	<0.005	<0.018	0.134	<0.092	<0.034
2-B-3,6,7,8,9-CDD	0.012	<0.017	<0.009	<0.009	<0.009	<0.035	0.158	<0.104	<0.038
2-B-7,8-CDF	0.008	<0.017	0.011	<0.009	0.009	<0.035	0.579	<0.104	0.126
3-B-2,7,8-CDF	0.072i	<0.01	0.007	<0.005	<0.005	<0.021	0.077	<0.088	<0.032
2-B-6,7,8-CDF	0.064i	<0.01	0.007i	0.008	<0.005	<0.021	<0.075	<0.092	<0.034
2,3-B-7,8-CDF	0.111	<0.012	0.009	<0.006	<0.006	<0.025	<0.056	<0.069	<0.025
1-B-2,3,7,8-CDF	0.025	<0.011	<0.006	<0.006	<0.006	<0.023	<0.078	<0.096	<0.035
4-B-2,3,7,8-CDF	0.083	<0.014	<0.007	<0.007	<0.007	<0.029	<0.072	<0.088	<0.032
13-B-2,7,8-CDF	0.007	<0.014	<0.007	<0.008	<0.008	<0.03	<0.094	<0.115	<0.042
PXBs									
4'-B-3,3',4,5-CB (PXB126)	0.112i	0.106	<0.009	<0.009	<0.009	0.099i	0.097	<0.096	<0.035
3,4-B-3',4',5'-CB (PXB126 di-Br)	0.122i	0.023i	<0.007	<0.008	<0.008	<0.03	<0.059	<0.073	<0.027
3',4',5'-B-3,4-CB (PXB126 tri-Br)	0.194i	<0.017	<0.009	<0.009	<0.009	<0.036	<0.025	<0.031	<0.011
4'-B-2,3',4,5-CB (PXB 118)	0.602	0.960	0.054i	0.051	0.195	<0.072	0.248	<0.085	<0.031
4'-B-2,3,3',4-CB (PXB 105)	0.315	0.290	0.023	0.031	0.044i	<0.055	<0.087	<0.108	<0.039
4'-B-2,3,3',4,5-CB (PXB 156)	0.173	0.203	<0.012	<0.008	0.047	<0.051	<0.134	<0.165	<0.06

i – indicative value

Table 3 (cont'd): Concentrations of PXDDs, PXDFs and PXBs in foods.

OPHA Sample No.	11836	12480	16151	16169	13698	13692	12081	13869	15529	11442
Sample Details:	Salmon oil	Fresh Sprats	Smoked Eel	Farmed Salmon fillets	Manx Kippers	Hot smoked mackerel	North Atlantic cooked cockles	Smoked scallops	Chicken liver	Pig Kidney
Fat content (% of whole)	100	8.4	35.7	15.5	15.9	19.5	0.8	1.9	4.6	3.5
ng/kg fat										
PXDD/Fs										
2-B-7,8-CDD	<0.006	<0.007	0.009	0.009	<0.006	<0.005	0.328	8.629	0.012	<0.078
2-B-3,7,8-CDD	<0.006	<0.008	<0.005	0.009	<0.006	<0.005	<0.047	0.064	<0.01	<0.013
2,3-B-7,8-CDD	<0.005	<0.011	<0.006	<0.005	<0.009	<0.008	<0.03	0.067	<0.006	<0.014
1-B-2,3,7,8-CDD	<0.006	<0.012	<0.007	<0.006	<0.010	<0.008	<0.045	<0.065	0.013	<0.013
2-B-1,3,7,8-CDD	<0.007	<0.006	<0.005	<0.007	<0.005	<0.005	<0.052	<0.033	<0.011	<0.01
2-B-3,6,7,8,9-CDD	<0.008	<0.01	<0.005	<0.008	<0.005	<0.005	<0.058	<0.005	<0.012	<0.018
2-B-7,8-CDF	0.017	0.010	0.010	0.010	0.010	0.010	0.066	1.844	<0.012	<0.022
3-B-2,7,8-CDF	0.009	0.016	<0.005	0.008	<0.005	0.011	<0.049	0.158	<0.01	<0.01
2-B-6,7,8-CDF	<0.007	0.133i	<0.005	<0.007	<0.005	<0.005	<0.052	0.168	<0.011	<0.015
2,3-B-7,8-CDF	<0.005	0.012i	<0.005	0.008	<0.005	<0.005	0.047	0.062	<0.008	<0.009
1-B-2,3,7,8-CDF	<0.007	0.009	<0.005	<0.008	<0.005	<0.005	<0.054	<0.025	<0.011	<0.014
4-B-2,3,7,8-CDF	<0.007	0.018i	0.009	0.011	0.011	<0.008	0.062	0.146	<0.01	0.017i
13-B-2,7,8-CDF	<0.009	<0.008	<0.005	<0.009	<0.007	<0.006	<0.064	<0.045	<0.013	<0.009
PXBs										
4'-B-3,3',4,5-CB (PXB126)	0.040	0.106	0.029	0.040	0.076	0.043	<0.054	0.111	0.015	<0.053
3,4-B-3',4',5'-CB (PXB126 di-Br)	0.013	0.007	<0.005	<0.006	<0.005	0.013	<0.041	<0.005	<0.009	<0.011
3',4',5'-B-3,4-CB (PXB126 tri-Br)	0.006	<0.008	<0.005	<0.005	<0.007	<0.006	<0.017	<0.045	<0.005	<0.03
4'-B-2,3',4,5-CB (PXB 118)	0.606	2.588	1.946	0.648	0.831	0.558	0.156	1.529	<0.01	0.058
4'-B-2,3,3',4-CB (PXB 105)	0.226	1.337	1.114	0.201	0.646i	0.379i	<0.06	0.625i	<0.013	<0.013
4'-B-2,3,3',4,5-CB (PXB 156)	0.100	0.382	0.201	0.122	0.156	0.089	<0.092	<0.031	<0.019	<0.019

i – indicative value

Table 4: Results of In-House Reference Material* Analysis -

Congener	Fortification level	Measured levels							
	ng/kg whole	B2	B3	B4/7	B5	B6	B8	B9	B10
ng/kg									
2Br78ClDx	3.3	3.47	3.53	3.21	3.71	3.45	3.63	3.44	3.38
2Br378ClDx	3.7	4.89	4.18	4.04	4.25	3.58	3.58	3.90	4.27
23Br78ClDx	3.7	3.85	3.65	3.55	3.70	3.75	3.65	3.70	3.89
1Br2378ClDx	3.7	3.85	3.64	3.67	3.85	3.93	3.91	3.77	3.44
2Br1378ClDx	3.3	3.66	3.65	3.29	3.83	3.64	3.52	3.54	2.98
2Br36789ClDx	3.3	3.38	3.39	3.42	3.46	3.01	3.20	3.66	2.88
8Br78ClDf	3.7	3.71	3.59	3.42	3.71	3.87	3.58	3.75	3.53
3Br278ClDf	3.3	3.36	3.33	3.17	3.36	3.22	3.09	3.50	2.83
2Br678ClDf	3.7	3.66	3.77	3.88	3.97	3.92	3.81	3.93	3.57
1Br2378ClDf	3.7	3.43	3.45	3.42	3.47	3.58	3.70	3.69	3.62
4'Br33'45Cl PXB126	2.2	2.14	2.05	2.11	2.19	2.13	2.21	2.30	2.16
34Br3'4'5'Cl PXB126 di-Br	2.2	2.33	1.82	2.19	2.59	2.16	2.34	2.51	2.60
3'4'5'Br34Cl PXB126 tri-Br	2.2	2.44	1.98	2.36	2.37	2.24	2.56	2.87	3.23
4'Br23'45Cl PXB-118	2.2	3.21	3.86	3.32	3.86	3.61	3.11	3.65	3.51
4'Br233'4Cl PXB-105	2.2	3.30	3.50	3.12	3.50	3.79	2.16	2.14	3.47
4'Br233'45Cl PXB-156	2.2	2.46	2.70	2.46	2.70	2.53	2.70	2.86	2.75

* The in-house reference material used, was a retail fish oil that was fortified with PXDD/Fs and PXBs.

Table 5: Average measurement uncertainty values for the different food types

Average Percent Uncertainty	Fish & Shellfish	Eggs, poultry, game	Offal	Meat & products	Dairy	Other foods
PXDD/Fs						
2-B-7,8-CDD	102	186	130	122	188	189
2-B-3,7,8-CDD	117	88	95	75	100	115
2,3-B-7,8-CDD	143	132	157	128	170	206
1-B-2,3,7,8-CDD	176	165	191	175	211	181
2-B-1,3,7,8-CDD	148	151	158	147	179	134
2-B-3,6,7,8,9-CDD	154	108	98	98	173	126
2-B-7,8-CDF	54	64	82	62	93	48
3-B-2,7,8-CDF	99	90	151	151	164	134
2-B-6,7,8-CDF	43	57	96	68	79	69
2,3-B-7,8-CDF	167	135	193	189	216	237
1-B-2,3,7,8-CDF	232	192	233	247	222	250
4-B-2,3,7,8-CDF	182	190	106	195	190	250
1,3-B-2,7,8-CDF	173	180	160	148	191	145
PXBs						
4'-B-3,3',4,5-CB (PXB126)	180	162	152	209	193	250
3,4-B-3',4',5'-CB (PXB 126 di-Br)	144	96	68	93	148	134
3',4',5'-B-3,4-CB (PXB126 tri-Br)	202	138	153	171	205	223
4'-B-2,3',4,5-CB (PXB 118)	22	25	67	23	23	119
4'-B-2,3,3',4-CB (PXB 105)	26	47	137	90	37	154
4'-B-2,3,3',4,5-CB (PXB 156)	37	92	116	52	94	107