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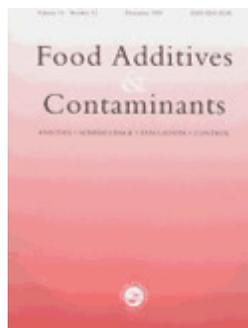
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Brominated dioxins (PBDD/Fs) and PBDEs in Marine Shellfish in the UK

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ABSTRACT

The occurrence of brominated dioxins (PBDD/Fs) and polybrominated diphenyl ethers (PBDEs) was investigated in commonly consumed species of marine shellfish in the UK. Individual samples of Pacific oysters (*Crassostrea gigas*), native oysters (*Ostrea edulis*), mussels (*Mytilus edulis*), scallops (*Pecten maximus*), and cockles (*Cerastoderma edule*) were collected from different coastal regions between 2006-2007. Samples of a particular species from each site were composited and 60 samples were analysed. Polybrominated dibenzofurans (PBDFs) occurred more frequently and generally at a higher level than polybrominated dibenzodioxins (PBDDs), except for 237-TriBDD which was the predominant PBDD/F congener in some of the species, notably oysters. This profile may reflect the environmental distribution of these compounds and the effects of removal mechanisms - degradation, selective uptake and metabolism. PBDEs were detected in all samples. The dominant congeners were BDEs 47, 49, 99 and 100 and, to a lesser extent, BDEs 66 and 154. The occurrence of BDE-209 was observed in most samples and appears to be species selective, with the highest values occurring almost exclusively in mussels and cockles. Among the species studied, oysters and mussels displayed relatively higher levels of both sets of contaminants; native oysters in particular, showed elevated levels of 237-TriBDD (up to 14.5 ng/kg). In general, contaminant levels appeared to be consistent with the extent of local industrialisation with lower levels observed in more remote areas such as the north of Scotland. Polybrominated biphenyls (PBBs) were also measured and PBBs 49, 52 and 77 were the most frequently detected, although levels were very low. Dietary intakes, estimated for PBDD/Fs showed that 237-TriBDD from single portions of oysters constituted a high proportion of the total dietary intake of the congener, but otherwise, dietary intakes of PBDD/Fs from shellfish were relatively low.

INTRODUCTION

Fish and shellfish are generally recommended by nutritionists and the medical profession as healthy foods that provide a good source of protein. Many oily fish species contain nutrients such as omega-3 fatty acids, which may reduce the risk of heart disease and stroke, and it is suggested that the consumption of one to two fish meals per week is helpful in preventing heart disease. The Food Standards Agency advises that consumers should eat two portions of fish a week, one of which should be oily, as part of a balanced diet, and also recommends maximum amounts of fish that should be consumed (Food Standards Agency, 2004). Similarly, bivalve shellfish are an excellent source of protein and are high in essential minerals, and low in calories and fat. However, fish and shellfish can accumulate contaminants from the water in which they live or from the food they eat. Shellfish classed as bivalve molluscs feed by filtering plankton from the surrounding water that washes through their habitat. This feeding mechanism leads to the bio-accumulation of pollutants of anthropogenic and biogenic origin from the surrounding waters even at a considerable distance from pollution sources.

Polybrominated diphenyl ethers (PBDEs), also known as polybrominated diphenyl oxides, and polybrominated biphenyls (PBBs) are mass-produced additive brominated flame retardants (BFRs) used in a variety of plastics, textiles, surface coatings, foams and manmade fibres. Their use has undoubtedly resulted in a reduction in human injury and fatality as a result of fires (Spiegelstein, 2001, Emsley et al 2002). However, the unrestricted application of these materials in the past has allowed diffusion of the contaminants into the environment during manufacture, use and disposal and continues to do so. This release is evident from the occurrence of PBDEs in environmental compartments such as water, sediments and biota (D'Silva et al 2004) and accompanies an increasing amount of evidence on potential detrimental human health effects (D'Silva et al 2004, Darnerud 2003, Hakk and Letcher 2003). Emerging toxicological data shows that PBDEs can cause liver and neurodevelopmental toxicity and affect thyroid hormone levels. In recent years the EU has carried out a comprehensive risk assessment under the Existing Substances Regulation (793/93/EEC) of commercial PBDE products. The outcome was a ban on

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2
3 the use of mixtures such as Penta- and Octa-BDE since 2004, whilst deca-BDE
4 remains under review until additional toxicological and occurrence data are finalised.
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9 One of the principal sources of PBDD/Fs is widely accepted as being combustion
10 processes such as incineration. However they can also occur as trace contaminants in
11 brominated flame retardants such as PBDEs, and studies on formation chemistry show
12 that the incineration of products containing BFRs as well as thermolysis of BFR
13 material such as PBDEs is an important source of PBDD/F emissions. The substantial
14 usage of BFRs will ensure that they remain a significant source of these contaminants.
15 It has also been demonstrated that PBDD/Fs can be formed during ultra-violet
16 irradiation of decabromodiphenyl ether (Olsman et al 2002). Recently, there have
17 been reports that some lower brominated PBDD congeners (tri- tetra-) may be
18 produced through biogenic formation via precursor pollutants in the marine
19 environment and bio-accumulate in some marine species such as shellfish (Malmvern
20 et al 2005, Haglund et al 2007). Toxicologically, studies that have been carried out on
21 PBDD/Fs show biological responses that are comparable to the chlorinated dioxins.
22 ~~Structure activity relationship studies on PBDD/Fs suggest a similar mode of~~
23 ~~biological activity to the chlorinated analogues, which is likely to be initiated by Ah~~
24 ~~receptor binding (Mason et al 1987, Birnbaum et al 2003).~~ There are of course likely
25 to be subtle biochemical differences even between laterally-substituted compounds
26 within the same homologue group. This would be due not only to the difference in
27 substitution pattern as observed for the chlorinated dioxins but also to the differences
28 in size and reactivity of the bromine and chlorine atoms and the difference in bond
29 strengths for the organic carbon-bromine (weaker) and carbon-chlorine (stronger)
30 bonds. Additionally, the larger size of the bromine atom and the degree of
31 halogenation is also likely to alter the elicitation of biological effects (Birnbaum et al
32 2003).
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53 The occurrence of PBDEs in shellfish has been documented in a number of
54 publications, some of which have used shellfish as indicators of marine and aquatic
55 pollution rather than as food. Reports on PBDD/Fs are far less frequent and may be a
56 reflection of the greater difficulty in measuring PBDD/Fs reliably at comparable
57 concentrations to the chlorinated dioxins. More recently, structured studies that are
58 directed towards the estimation of human dietary exposure to these compounds have
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3 investigated occurrence in different foods including fish and shellfish. Data for the
4 sum of PBDE congeners in different foods in North America from a market basket
5 survey showed that the maximum whole weight median concentrations (1725 ng/kg)
6 occurred in fish (Schechter et al 2004). A recent survey of fish in Canada showed
7 whole weight mean PBDE values ranging from 100 ng/kg for shrimp and tilapia to
8 2200 ng/kg for farmed salmon (Health Canada 2005). Similarly a study on different
9 foods collected in the Catalonian region of Spain showed that the highest whole
10 weight concentrations of PBDEs (1010 ng/kg) were found in blue fish. A recent
11 Japanese Total Diet Study (TDS) found the highest average PBDE concentrations
12 (1259 ng/kg) in the fish group (Ashizuka et al 2005), and a similar TDS study in the
13 UK (Fernandes et al 2005) also found the highest average PBDE concentrations (500
14 ng/kg) in the fish group (not including BDE-209). Some recent studies have also
15 shown evidence of the occurrence of these contaminants in shellfish. A study on a
16 range of fish and shellfish species showed the occurrence of PBDEs and brominated
17 dioxins in a number of the species, but particularly shellfish (Food Standards Agency
18 2006). Certain PBDEs were present in most or all of the shellfish analysed, the most
19 abundant congeners being PBDEs 28, 47, 49, 66, 99, 100, 153 and 154 and among the
20 PBDD/F congeners more PBDFs were detected than PBDDs.
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37 This study aimed to investigate commonly consumed shellfish species such as oysters,
38 mussels, scallops and cockles collected from different coastal regions around the UK.
39 The occurrence levels of these brominated contaminants were determined and will be
40 discussed in the context of currently available information. The human exposure
41 arising from the consumption of these foods will also be discussed.
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51 **EXPERIMENTAL**

52 Individual sub-samples of mussels, oysters and scallops were collected from coastal
53 locations around Scotland between January and March 2006. Further samples of
54 oysters, mussels and cockles from England, Wales and Northern Ireland (NI) were
55 collected during the latter half of 2006 to early 2007. The individual samples were
56 shucked and the flesh obtained from this process was representatively pooled and
57 homogenised to yield 60 analytical samples – 17 mussels, 19 oysters, 4 cockles and
58 10+10 scallops. As scallops are sometimes retailed as the adductor muscle alone,
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3 these samples were divided into separate adductor and gonad portions prior to
4 pooling. The composite samples were freeze-dried and ground and the resulting
5 powders were thoroughly mixed before taking sub-samples for analysis.
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10 The composite samples were analysed for the following compounds:

11 Brominated dioxins - 2,3,7-triBDD, 2,3,8-triBDF, 2,3,7,8-Br substituted PBDD/Fs:
12 tetra – hexa brominated congeners (note that this includes only one hexa-Bromo-
13 substituted furan as no standards were available for the other three congeners).
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15 Polybrominated diphenylethers (PBDEs) - IUPAC numbers 17, **28**, **47**, 49, 66, 71, 77,
16 85, **99**, 100, 119, 126, 138, **153**, **154**, **183** and **209**. PBB congeners: IUPAC numbers
17 15, 49, **52**, **77**, 80, 101, **126**, 169, **153** and 209. (Those for which ¹³Carbon labeled
18 standards were used as internal or sensitivity standards are shown in bold type and
19 these also included six PBDD/F congeners). Additionally, chlorinated dioxins and
20 PCBs and, in some cases, tetrabromobisphenol-A and hexabromocyclododecane were
21 also determined but these are reported elsewhere (Driffield et al 2008, Fernandes et al
22 2007, Fernandes et al 2008,).
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33 The analytical standards used, native as well as ¹³Carbon labeled for the individual
34 analyte groups, were obtained as nonane solutions either from Cambridge Isotope
35 Labs, Mass. USA or from Wellington Laboratories Inc. Ontario, Canada.
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40 The methodology used for the analysis has been robustly validated and accredited to
41 the ISO17025 standard. A full description of the procedures has been reported
42 elsewhere (Fernandes et al 2008, Fernandes et al 2004). In brief, samples were
43 fortified with ¹³C-labelled analogues of target compounds and exhaustively extracted
44 using mixed organic solvents. PBDEs were chromatographically fractionated from
45 the brominated dioxins and furans on activated carbon. The two fractions were further
46 purified using adsorption chromatography on alumina. Analytical measurement was
47 carried out using high resolution gas chromatography coupled to high resolution mass
48 spectrometry (HRGC-HRMS, Waters Autospec Ultima instrument fitted with a
49 Hewlett Packard 6890N gas chromatograph). Additional control was provided by the
50 inclusion of methods blanks and a reference material. Where reliable inter-calibration
51 schemes exist for food matrices (PBDEs), the methodology has been further validated
52 by successful participation in these studies (e.g. Dioxins in Food, Quasimeme) over
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3 the last 3 years (Quasimeme 2004, Norwegian Institute of Public Health 2005, 2007).
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5 The Z-scores achieved for fish and fish based matrices in these studies, ranged from –
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7 0.61 to 0.81.
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10 **RESULTS AND DISCUSSION**

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13 A full version of the detailed results for all of the analytes described in this work is
14 presented elsewhere (Fernandes et al 2006, Fernandes et al 2007) and contains in
15 addition to the PBDD/Fs and PBDEs described in this paper, data on PBBs
16 chlorinated dioxins/PCBs and for some samples, speciated HBCD and TBBPA. Due
17 to the large volume of PBDD/F and PBDE data, only a summarised version of the
18 results are presented in this paper. These are shown in Table 1. Data for the sum of
19 the 17 PBDEs measured and for the PBDD/F TEQ are reported as *upper-bound*, i.e.
20 where congeners were not detected they were assumed to be present at the level of the
21 limit of detection. All concentrations are expressed on a whole weight basis to allow
22 comparison with other data. The key statistics for this data are summarised in Table 2.
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33 PBDEs are presented as the sum of 17 different congeners but, due to the high level of
34 current interest in BDE-209, data for this congener is presented separately, as is data
35 for BDE-47, BDE-99 and BDE-100. PBDD/F data is presented as toxic equivalents
36 (TEQs) based on the use of the analogous chlorinated dioxin and furan (PCDD/F)
37 toxic equivalent factors (TEFs) (Van den Berg et al 1998), an approach that has been
38 used in other studies (Ohta et al 2004, Colles et al 2008, Fernandes et al 2008, Food
39 Standards Agency 2006). Although the TEF scheme was updated in 2005 (Van den
40 Berg et al 2006) the 1998 scheme values are ones used by regulators, and in current
41 legislation. Similarly the comparative literature quoted here also uses the 1998
42 scheme. It should be recognised that this is an interim measure until a more rigorously
43 evaluated set of TEF values specifically for the brominated dioxin/furan congeners
44 become available (Food Standards Agency 2006B). The detection of brominated
45 dioxins in foods, particularly fish and shellfish (Fernandes et al 2006B, Fernandes et
46 al 2008) makes this a very necessary requirement, particularly as an obvious
47 limitation of the approach used here is the exclusion of toxicity relating to the tri-
48 brominated congeners which have been shown to exhibit a similar mode of Ah
49 receptor activity as the 2378-substituted dioxins and furans (Mason et al 1987,
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3 Birnbaum et al 2003). The approach however provides data to allow comparisons
4 with other studies that have provided similar data (Ohta et al 2004, Fernandes et al
5 2005, Fernandes et al 2008, Food Standards Agency 2006).
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10 PBDEs were detected in all the shellfish species and, although the relative
11 distributions of the lower- to mid-brominated congeners (BDE-47, 99, 100) measured
12 in this study were very similar across the species, the relative distributions of the
13 higher brominated congeners (BDE-183, BDE-209) varied. This was evident for
14 BDE-209 in mussels and, particularly, in cockles (Table 1). The two groupings of
15 congeners may be associated with commercial mixtures such as “Penta” which
16 contains BDE-47, 99 & 100, and “Deca” which is predominantly BDE-209 (BDE-183
17 is an expected breakdown product of “Deca”). Analysis of the congener distribution
18 also shows that the levels of BDE-47 correlate well ($R^2 > 0.98$) with the total PBDE
19 level for all species except cockles. As observed elsewhere (D’Silva et al 2004),
20 BDE-47 is the major component of “Penta”. On the other hand, BDE-209 does not
21 correlate well with total PBDE in oysters or scallops, but shows strong correlation in
22 cockles ($R^2 = 0.95$). These distributions of BDE congeners within the species may be
23 indicative of the differences in bio-accumulative potential between species, with
24 mussels showing the potential to bio-accumulate both Penta and Deca; oysters show
25 very low levels for Deca and cockles the highest. It is unlikely that spatial distribution
26 influences the correlation between BDE-209 and mussels through the selective
27 loading of this contaminant at particular locations, because different species collected
28 in the same area do not show relatively similar amounts of this congener. It is
29 pertinent at this stage to mention the potential difficulties with the measurement of
30 BDE-209 (De Boer 2004, Fernandes et al 2008). Laboratory blanks invariably show
31 the presence of this congener, so blank subtraction is necessary, but removal
32 mechanisms such as degradation during sample extraction/purification due to UV
33 exposure (Olsman et al 2002), and other processes such as adsorption, are also known
34 to occur. Hence the monitoring of the measurement process with the use of the
35 commercially available ^{13}C labelled BDE-209 as used in this work is strongly
36 recommended in order to provide better measurement control (Fernandes et al 2008).
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In terms of absolute concentrations, higher levels of PBDEs were observed in mussels compared to the other species, with the lowest levels being observed in cockles. The

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3 observed predominance of BDE-47, 49, 99 and 100 and to a lesser extent BDE-66 and
4 BDE-154 is similar to that observed in other studies (Ashizuka et al 2005, Fernandes
5 et al 2008, Food Standards Agency 2006, Van Leeuwen and De Boer 2008) and
6 demonstrates the persistence of these contaminants, as the use of the commercial
7 formulations from which these congeners derive has been banned for some years now.
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14 There are very few reports on the occurrence of brominated dioxins and furans in food
15 or biota. Recently however, PBDDs have been reported as occurring in marine biota,
16 including shellfish taken from the Baltic Sea (Malmvern et al 2005, Haglund et al
17 2007). These studies targeted the brominated dibenzo-p-dioxin rather than
18 dibenzofuran molecules and the occurrence of specific di and tri-brominated dioxins
19 was recorded, with lower levels of tetrabrominated congeners. The authors suggest
20 that this specific distribution originates from marine biogenic processes. The
21 formation of individual brominated dioxin congeners is thought to proceed through
22 condensation reactions of naturally occurring bromophenols mediated by the action of
23 bromoperoxidases in the presence of bromide (Haglund et al 2007). This formation
24 pathway is likely to be governed by kinetic processes and would explain the relative
25 abundances of the individual congeners. However, the shellfish samples analysed in
26 this work showed not only the congener profiles discussed above (for PBDDs); they
27 also showed the presence of significant levels of PBDFs (Figure 1). The
28 chromatographic profiles for the furans (tri- to penta-brominated) show similarities to
29 those observed for environmental samples, in that a wide range of furan congeners are
30 observed. This observed occurrence of a range of congeners rather than specific
31 compounds suggest an origin from thermodynamic processes and it is likely that the
32 observed profile and levels are due to combustion processes such as incineration. The
33 predominance of PBDFs over PBDDs has also been observed in other studies
34 involving combustion. Thus it is likely that the PBDD/Fs observed in these samples
35 reflect both types of sources, biogenically mediated (Haglund et al 2007) as well as
36 anthropogenic.
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56 PBDD/Fs were detected in most of the samples at varying concentrations depending
57 on the species. The calculated TEQs were higher in scallop gonad than in mussels
58 (0.083 ng/kg compared to 0.055 ng/kg whole weight respectively), although mussels
59 showed a more complete range of detectable congeners, particularly the PBDFs
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(Figure 1). Relatively lower TEQ levels were detected in the scallop adductor muscle and this may relate to the lower lipid content of the adductor. The contribution to TEQ was derived mainly from 2,3,7,8-TBDF, 2,3,4,7,8-PBDF and 2,3,7,8-TBDD (Fernandes et al, 2007). This composition is similar to the TEQ distribution of PCDD/Fs where, for fish and shellfish, these congeners, along with 1,2,3,7,8-PCDD, are often the main contributors. Most samples in this study showed the presence of tri-bromo dioxins and furans. In particular, 2,3,7-tribromo dioxin was the predominant congener in oysters, native oysters (*Ostrea edulis*) showing relatively elevated levels (up to 14.5 ng/kg whole weight). The toxicology of the tri-brominated dioxins and furans is the subject of continuing international study (Hornung et al 1997, Birnbaum 2003, Behnisch et al 2003,) with available toxicological data indicating that these compounds elicit more potent biological responses than their chlorinated analogues (Behnisch et al 2003). It should particularly be noted that the concentrations of tri-bromo substituted PBDD/F congeners reported here have not been included in the summed TEQs, as there are no recognised analogous TEF values for tri-chloro substituted PCDD/Fs. Moreover, although the levels of tri- and tetra- BDD/BDF congeners are elevated in comparison to the other 2,3,7,8-Br substituted compounds, they occur at a relatively low level in comparison to other non-laterally substituted tri- and tetra- congeners that were present in the samples. The greater abundance of these congeners (some are orders of magnitude higher in occurrence), merits further research, both in terms of toxicology – none is currently available - as well as occurrence in other marine and aquatic species, particularly those used as food. Although PBDD/Fs exposure in humans has been reported (Ohta et al, Colles et al), data on the tri-brominated compounds was not available. However, apart from the levels reported in this work, tri-brominated compounds have also been detected in other foods (Food Standards Agency, 2006c), which makes it likely that humans are exposed to these compounds. Apart from 2,3,7-tribromoBDD, the occurrence of PBDFs generally predominates that of PBDDs, reflecting profiles observed for environmental samples which in turn mirror the formation chemistry of these molecules through thermodynamic pathways that are a feature of combustion processes.

Insert figure 1 here

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3 PBDE commercial mixtures are reported to be one of the major sources of PBDD/Fs
4 (Hayakawa 2004 et al 2004, D'Silva et al 2004, Hagberg 2008), which occur as
5 contaminants in the mixtures. Hayakawa et al report a positive correlation between
6 these two groups in atmospheric deposition. There is very little information on
7 pathways for PBDD/Fs or the occurrence of these compounds in sediments or soils,
8 but given the similarities in physical and chemical properties to the chlorinated
9 dioxins, it is not unreasonable to expect similar transfer mechanisms, although the
10 PBDD/Fs are more likely to suffer degradation due to the higher susceptibility of the
11 C-Br bond. In these samples, apart from the set of cockles (which should be
12 interpreted with care because of the low number of samples) there is poor correlation
13 between concentrations of PBDD/F and PBDEs. This is perhaps unsurprising given
14 the various degradation/absorption/metabolic/bio-accumulation processes that define
15 the occurrence of both these sets of contaminants in shellfish.
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28 Although the data for PBBs is reported elsewhere (Fernandes et al 2007, Fernandes et
29 al 2008), they were measured in all the samples and generally showed relatively low
30 levels of occurrence. The most frequently detected congeners were PBB 49 and PBB
31 52 and these occurred typically in the range 0.2 – 1.0 ng/kg. The non-ortho substituted
32 PBBs (congeners PBB77, PBB126 and PBB169) were also measured and of these
33 PBB 77 was the most frequently detected, typically in the range of 0.01 – 0.05 ng/kg.
34 The relative concentrations of the flame retardants – PBBs (low levels) and PBDEs
35 (higher levels) is consistent with the greater and more recent usage of PBDEs in the
36 UK. The low levels of PBBs observed are likely to arise from long range marine and
37 aerial transport as observed in the detection of this contaminant in tissue from Arctic
38 polar bear (D'Silva et al 2006).
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50 Geographically, the spatial distribution of the sampling sites covers most of the
51 shellfish harvesting areas around the UK coastline. The different levels of
52 contaminants observed appear to be consistent with the levels of industrial activity in
53 these regions. In general, mussels from locations in Scotland, particularly the north
54 and north west (the Orkneys, Western Isles and Northern Highlands) showed, on
55 average, lower levels of PBDEs and broadly similar levels of PBDD/Fs to locations in
56 the rest of Britain and Northern Ireland. For Pacific oysters the situation was
57 reversed, with higher levels observed in Scottish samples. The concentrations of the
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3 tri-brominated dioxins, however, appear to be species dependent with average
4 concentrations over an order of magnitude higher in samples of native oysters
5 compared with Pacific oysters. This observation is valid even for samples of the two
6 species harvested in the same location and may be related to the individual uptake and
7 metabolism processes of the different species. The detection of most contaminants,
8 albeit at low levels in all samples, some taken from the more remote areas confirms
9 the long-range transport of these compounds, which is a defining characteristic of
10 persistent organic pollutants.
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21 **Dietary Intakes**

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24 Dietary intakes from the shellfish alone were estimated from the average
25 concentrations found in the different types of shellfish, assuming a portion size of 70
26 g. Dietary intakes from the whole diet excluding fish and shellfish were estimated
27 from the results of a survey for brominated chemicals in samples from a Total Diet
28 Study (TDS) (Food Standards Agency, 2006c). The TDS is a model of the typical
29 UK diet. Foods were purchased from 24 randomly selected locations in the United
30 Kingdom, and these were combined into 20 food groups. Foods that are consumed in
31 large quantities such as bread, milk and potatoes, and foods that are susceptible to
32 contamination such as fish (which includes shellfish) and offals, are kept separate.
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42 Table 3 shows the estimated dietary intakes by 60 kg adults, of PBDD/Fs and dioxin-
43 like PBBs, from single 70 g portions on their own, and from one and two weekly 70 g
44 portions in combination with the rest of the diet, from shellfish.. In the case of
45 oysters, especially native oysters, the estimated dietary intake of 2,3,7-triBDD by
46 those who consume the species exceeds the average dietary intake from the rest of the
47 diet by the UK population by a large margin. Otherwise, the estimated dietary intakes
48 of brominated chemicals from shellfish alone are a low proportion of those from the
49 rest of the diet. The difference between upper and lower bound values is likely due to
50 the absence of PBDDs (apart from tri- and tetra-brominated dioxins) which have
51 higher TEF values and would therefore have contributed to ~ two-thirds of the TEQ.
52 This contrasts with PCDD/Fs in shellfish where most PCDDs and PCDFs are usually
53 present.
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5 The results of a previous survey for brominated chemicals in farmed and wild fish and
6 shellfish (Food Standards Agency, 2006a) were assessed by the independent expert
7 Committee on Toxicity of Chemicals in Food, Consumer Products and the
8 Environment (COT). The COT concluded that consumption of the shellfish was
9 unlikely to pose a hazard to human health (Food Standards Agency, 2006b). The
10 current results were similar to those for shellfish tested in the previous survey.
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19 CONCLUSION

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22 The data presented here confirms the widespread occurrence of PBDEs and PBDD/Fs
23 in shellfish. The differences in levels for some congeners, notably 2,3,7-triBDD may
24 suggest differences in bioaccumulation potential among the species. The dioxin-like
25 toxicity arising from the occurrence of PBDD/F TEQ levels are lower than those
26 reported for chlorinated dioxins (Fernandes et al 2008), and the assessment of the
27 average dietary intake of these contaminants in the UK as a result of shellfish
28 consumption shows that it is unlikely that toxicity arising from these contaminants
29 alone is of concern. However, the TEQ from PBDD/Fs is an important contribution to
30 the overall burden of human exposure to dioxin-like TEQ that results from PCDD/Fs,
31 PCBs, PCNs and other similar halogenated aromatic compounds, and may be
32 particularly significant for high level shellfish consumers. The exact magnitude of the
33 contribution will remain indicative until toxicological studies provide a specific and
34 comprehensive set of toxicity factors for PBDD/Fs including the contribution from
35 the tri-brominated compounds.
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50 The universal occurrence of PBDEs in these samples, characterised by the dominance
51 of BDE-47, 99, 100 (and to a lesser extent BDE 209) in the congener profiles,
52 demonstrates the persistence of these contaminants, as the use of the commercial
53 formulations from which these congeners derive have seen a reduction in usage or
54 have been banned for a few years. With the exception of 2,3,7-triBDD from oysters,
55 estimated dietary intakes of brominated chemicals from shellfish were low compared
56 to those from the rest of the diet. No change to the Food Standards Agency's advice
57 on fish and shellfish consumption was needed on the basis of these results.
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REFERENCES

Ashizuka Y, Nakagawa R, Hori T Tobiishi K Lida T (2005) Determination of PBDEs and PBDD/Fs in marine products. *Journal of Agric. and food Chem*, **53**, 3807-3813.

Behnisch P, Hosoe K and Sakai S (2003) Brominated dioxin-like compounds: in vitro assessment in comparison to classical dioxin-like compounds and other polyaromatic compounds. *Environ. Int.* **29**, 861-877

Birnbaum L, Staskal D and Diliberto J, (2003) Health Effects of PBDDs and PBDFs *Environment International* **29**, 855-860

Colles A, Koppen G, Hanot V, Nelen V, Dewolf M, Noel E, Malisch R. Kotz A, Kypke K, Biot P, Vinkx C, Schoeters G (2008), Fourth WHO-coordinated survey of human milk for persistent organic pollutants: Belgian results. *Chemosphere*, **73**, 907-914

Darnerud P, (2003). Toxic effects of brominated flame retardants in man and in wildlife *Environment International*, **29**, 841-853.

De Boer J (2004) Brominated flame retardants in the environment – the price for our convenience. *Environ. Chem*, **1**, 81-85

D'Silva K, Fernandes A, and Rose M, (2004) Brominated Organic Micropollutants – Igniting the flame retardant issue. *Critical Reviews in Env Sci and Tech*, **34(2)** p141-207

D'Silva K, Fernandes A, Rose M, Andersen M and A Derocher A (2006) “Halogenated Organic Contaminants in Polar Bears (*Ursus Maritimus*)”, Proceedings, First Network conference on persistent organic pollutants, Univ. Birmingham, March 2006

1
2
3
4
5 Emsley A, Lim L. and Stevens G. (2002). International fire statistics and the potential
6 benefits of fire counter-measures. Paper presented at Flame Retardants 2002.
7
8 Interscience Communications Limited, London.
9

10
11
12 Fernandes A, White S, DSilva K, and Rose M (2004) Simultaneous Determination of
13 PCDDs, PCDFs, PCBs and PBDEs in Food, *Talanta*, **63**, 1147-1155
14
15

16
17
18 Fernandes A, DSilva K, Driffield M, White S, and Rose M (2005) Brominated flame
19 retardants and brominated dioxins in 2003 Total Diet samples. Report to the Food
20 Standards Agency, CSL Report FD 04/37
21
22

23
24
25 Fernandes A, Smith F, Driffield M, White S, and Rose M (2006) Brominated and
26 Chlorinated contaminants and PAHs in shellfish flesh from Scottish Innshore and
27 Offshore harvesting areas. Report to the Food Standards Agency, Scotland. CSL
28 Report FD 06/04
29
30

31
32
33 Fernandes A, Smith F, Petch R, White S, and Rose M (2007) Brominated and
34 chlorinated contaminants in shellfish. Report to the Food Standards Agency, CSL
35 Report FD 07/05
36
37

38
39
40 Fernandes A, Dicks P, Mortimer D Gem M, Smith F, M, White S, and Rose M
41 (2008), Brominated and Chlorinated Dioxins and Brominated Flame Retardants in
42 Scottish Shellfish: Methodology, Occurrence and Human Dietary Exposure
43
44 *Molecular Nutrition and Food Research* **52(2)**, 238-249
45
46

47
48
49 Food Standards Agency (2004) New oily fish advice issued. Food Standards Agency
50 News Release, available at
51
52 <http://www.food.gov.uk/news/newsarchive/2004/jun/oilyfishwebcast>.
53
54

55
56
57 Food Standards Agency (2006a) Brominated chemicals in farmed and wild fish and
58 shellfish and fish oil dietary supplements Food Survey Information Sheet 04/06
59 Available at:
60

<http://www.food.gov.uk/science/surveillance/fsisbranch2006/fsis0406>

1
2
3
4
5 Food Standards Agency. (2006B) Committee on Toxicity of Chemicals in Food,
6 Consumer Products and the Environment. Statement on organic chlorinated and
7 brominated contaminants in shellfish, farmed and wild fish, available at
8
9 <http://www.food.gov.uk/multimedia/pdfs/cotstatementfishsurveys.pdf> .
10
11

12
13
14 Food Standards Agency (2006c) Brominated chemicals: UK dietary intakes. Food
15 Surveillance Information Sheet 10/06 available at
16 www.food.gov.uk/multimedia/pdfs/fsis1006.pdf
17
18

19
20
21 Hagberg J (2008) Analysis of PBDD/Fs by high resolution GC-MS
22
23 Journal of Chromatography (in press)
24

25
26 Haglund P, Malmvarn A, Bergek S, Bignert A, Kautsky L, Nakano T, Wiberg K and
27 Asplund L (2007), Brominated dibenzo-p-dioxins: A new class of marine toxins *Env*
28 *Sci and Technol*, **41**, 3069-3074
29
30

31
32
33 Hakk H.and Letcher R, (2003) Metabolism in the toxicokinetics and fate of
34 brominated flame retardants—a review, *Environment International*, **29**, 801-828.
35
36

37
38
39 Harmer N, Driffield M, Fernandes A, Bradley E, Rose M, Mortimer D and Dicks P
40 (2008) The determination of brominated flame retardants in food by liquid
41 chromatography with tandem mass spectrometric detection: diastereoisomer specific
42 hexabromocyclododecane and tetrabromobisphenol A
43
44 *Food Additives and Contaminants*, **25(7)**, p895
45
46

47
48
49 Hayakawa K, Takatsuki H, Watanbe I and Sakai S (2004) PBDEs, PBDD/Fs and
50 MoBPXDD/Fs in the atmosphere and bulk deposition of Japan. *Chemosphere* 57 343-
51 356
52
53

54
55
56 Health Canada (2005) Fish and Seafood survey, Available at:
57 [www.hc-sc.gc.ca/food-aliment/ cs-ipc/fr-ra/e_seafood_survey.html](http://www.hc-sc.gc.ca/food-aliment/cs-ipc/fr-ra/e_seafood_survey.html) - 19k - 1 Mar
58
59 2005
60

1
2
3 Hornung L, Zabel E and Peterson R (1996), TEFs of PBDD/F, PBB and PBDE
4 congeners based on rainbow trout early life stage mortality.

5
6
7 *Toxicology and Applied Pharmacology*, **140**, 227- 234

8
9
10 Malmvarn A, Zebuhr Y, Jensen S, Kautsky L, Greyerz E, Nakano T & Asplund L
11 (2005) Identification of PBDDs in blue mussels (*mytilus edulis*) from the Baltic sea.

12
13
14 *Env Sci and Technol*, **39**, p 8235-8242

15
16
17 Mason G Zacharewski T, Denomme M, Safe L and Safe S (1987) PBDDs and related
18 compounds: quantitative in-vivo and in-vitro structure activity relationships.

19
20
21 *Toxicology* **44**, 245-255

22
23
24 Norwegian Institute of Public Health, Oslo, Norway, (2005) “Interlaboratory
25 Comparison on dioxins in food – Sixth round of an International Study” Rapport
26
27 2005:7 ISBN 82-8082-145-7

28
29
30 Norwegian Institute of Public Health, Oslo, Norway, (2007) “Interlaboratory
31 Comparison on dioxins in food – Eight round of an International Study” Rapport
32
33 2007:7 ISBN 978-82-8082-216-1

34
35
36 Ohta S, Okumura T, Nishimura H, Nakao T, Shimizu Y, Ochiai F, Aozasa O and
37
38 Miyata H (2004) Levels of PBDEs, TBBPA, TBPs, PCDD/Fs PxDD/Fs and PBDD/Fs
39
40 in human milk of nursing women and dairy milk products in Japan. *Organohalogen*
41
42 *Compounds*, **66**, 2891

43
44
45 Olsman H et al (2002) Formation of dioxin-like compounds as photoproducts of
46
47 DeBDE during UV-irradiation, *Organohalogen Compounds*, **58**, (2002), 41-44.

48
49
50 Quasimeme Round 37 exercise 618, Data Assessment report. (Nov 2004) Quasimeme
51
52 Project Office, Aberdeen ,UK

53
54
55 Schecter A, Papke O, Kuang-Chi T, Staskal D and Birnbaum L (2004). PBDE
56
57 contamination of United States food, *Env Sci and Technol*, **38(20)**:5306-5311

1
2
3 Spiegelstein M, (2001) Proceedings, BFR 2001, Stockholm, (p41) .
4

5 Pubs.AB Firmatryck, Stockholm, Sweden
6
7

8
9 Van den Berg M., Birnbaum L., Bosveld A.T.C., Brunström B., Cook P., Feeley M.,
10 Giesy J.P., Hanberg A., Hasegawa R., Kennedy S.W., Kubiak T., Larsen J.C., van
11 Leeuwen F.X.R., Liem A.K.D., Nolt C., Peterson R.E., Poellinger L., Safe S.,
12 Schrenk D. Tillitt D., Tysklind M., Younes M., Waern F. and Zacharewski T. (1998)
13 Toxic Equivalency Factors (TEFs) for PCBs PCDDs and PCDFs for humans and
14 wildlife. *Environmental Health Perspectives*, **106**, 775-792
15
16
17
18

19
20
21 Van den Berg, M.; Birnbaum, L. S.; Denison, M.; De Vito, M. ;Farland, W.; Feeley,
22 M.; Fiedler, H.; Hakansson, H.; Hanberg, A.; Haws, L.; Rose, M.; Safe, S.; Schrenk,
23 D.; Tohyama, C.; Tritscher, A.; Tuomisto, J.; Tysklind, M.; Walker, N.; Peterson, R.
24 E. (2006). The 2005 World Health Organization Re-evaluation of Human and
25 Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds.
26 *Toxicol. Sci.* **93**, 223–241.
27
28
29
30
31
32

33
34 Van Leeuwen S and De Boer J (2008), Brominated flame retardants in fish and
35 shellfish- levels and contribution of fish consumption to dietary exposure of Dutch
36 citizens to HBCD. *Molecular Nutrition and Food Research* **52(2)**, 194
37
38
39

40
41 Weber R, Kuch B, Ohno T and Sakurai T. De Novo synthesis of mixed brominated
42 – chlorinated PXDD/PXDF. (2002), *Organohalogen Compounds*, **56**, 181.
43
44
45

46
47 Weber R and Kuch B., Relevance of BFRs and thermal conditions on the formation
48 pathways of brominated and brominated–chlorinated dibenzodioxins and
49 dibenzofurans (2002), *Environment International*, **29**, 699-710.
50
51
52
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Figure 1: HRMS ion chromatograms for lower brominated PBDD/Fs in shellfish (Most co-eluting peaks fulfil acceptance criteria for positive identification as PBDD/Fs)

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Table 1: Occurrence levels of PBDEs and PBDD/Fs in shellfish (fresh weight basis)

Sample ID.	BDE-47 ng/g	BDE-99 ng/g	BDE-100 ng/g	BDE-209 ng/g	Sum of 17 PBDEs ng/g	237-T ₃ BDD pg/g	238-T ₃ BDF pg/g	PBDD/F TEQ pg/g
Pacific Oysters (<i>Crassostrea gigas</i>)								
Shetland	0.25	0.32	0.12	0.02	0.89	0.11	0.23	0.035
South Shian Bay	0.08	0.04	0.03	0.01	0.22	0.28	0.16	0.037
Loch nan Ceol	0.05	0.04	0.02	0.01	0.17	0.13	0.11	0.031
Loch Fyne	0.23	0.09	0.08	0.01	0.58	0.32	0.51	0.121
Craigens	0.11	0.05	0.04	0.01	0.33	0.63	0.32	0.042
Norfolk	0.79	0.29	0.25	< 0.03	2.13	0.74	0.34	0.028
Northern Ireland	0.12	0.05	0.05	0.02	0.32	0.26	0.10	0.016
Anglesey	0.21	0.09	0.10	0.05	0.72	0.52	0.14	0.025
Exeter	0.29	0.10	0.08	< 0.03	0.68	0.36	0.07	0.014
Dorset	0.04	0.02	0.01	0.01	0.12	0.09	0.01	0.011
Northumberland	0.12	0.05	0.05	< 0.01	0.34	0.57	0.05	0.025
Northern Ireland	0.12	0.07	0.04	0.07	0.39	0.10	0.17	0.016
Cornwall	0.14	0.06	0.06	< 0.02	0.38	0.30	0.07	0.015
Cornwall	0.45	0.18	0.15	< 0.03	1.02	0.23	0.11	0.013
Native Oysters (<i>Ostrea edulis</i>)								
Dorset	0.06	0.03	0.02	0.02	0.17	6.59	0.01	0.047
Portsmouth	0.32	0.11	0.13	0.01	0.78	14.53	0.05	0.065
Cornwall	0.10	0.05	0.04	0.03	0.34	0.73	0.02	0.014
Hampshire	0.04	0.02	0.02	< 0.01	0.12	5.30	0.03	0.033
Kent	0.38	0.10	0.15	0.01	0.94	3.51	0.05	0.030
Mussels (<i>Mytilus edulis</i>)								
Linga	0.37	0.21	0.11	0.04	0.84	0.13	0.08	0.028
Troustan	1.22	0.53	0.33	0.09	2.74	0.04	0.40	0.064
Loch Etive	0.11	0.09	0.05	0.04	0.37	0.11	0.26	0.118
Whalwick	0.07	0.04	0.03	0.04	0.23	< 0.03	0.08	0.037
Glenvig Bay	0.07	0.04	0.03	0.09	0.27	0.03	0.07	0.035
Catfirth	0.06	0.03	0.02	0.04	0.18	< 0.04	0.06	0.037
Wadbister	0.06	0.03	0.02	0.03	0.20	0.04	0.07	0.038
Loch Leven	0.24	0.21	0.10	0.07	0.75	0.06	0.26	0.097
Lismore	0.10	0.07	0.04	0.03	0.32	0.06	0.21	0.063
Mussel composite	0.24	0.21	0.08	0.08	0.72	0.02	0.11	0.061
Northern Ireland	0.17	0.07	0.06	0.03	0.44	0.10	0.07	0.013
Anglesey	0.14	0.06	0.07	0.07	0.53	0.21	0.06	0.032
Dorset	0.06	0.03	0.02	< 0.01	0.17	0.15	0.02	0.027
Cumbria	0.87	0.55	0.14	0.23	2.13	0.02	0.26	0.030
Cornwall	0.16	0.06	0.06	0.02	0.44	0.10	0.09	0.018
Devon	0.12	0.04	0.04	0.02	0.32	0.04	0.09	0.025
Belfast Lough	1.34	0.46	0.34	0.53	3.23	0.08	0.36	0.205

* The sum of the 17, PBDEs and PBDD/F TEQ are presented as upper bound levels

Table 1 (cont'd): Occurrence levels of PBDEs and PBDD/Fs in shellfish (fresh weight basis)

Sample ID.	BDE-47 ng/g	BDE-99 ng/g	BDE-100 ng/g	BDE-209 ng/g	Sum of 17 PBDEs ng/g	237-T ₃ BDD pg/g	238-T ₃ BDF pg/g	PBDD/F TEQ pg/g
Scallops (<i>Pecten maximus</i>) Gonad								
Clyde 8	0.23	0.15	0.07	0.02	0.70	0.09	0.33	0.054
South Minch 10/11	0.07	0.04	0.02	0.02	0.24	0.10	0.25	0.055
Jura	0.08	0.06	0.03	0.02	0.31	0.15	0.35	0.233
East Coast Scotland	0.23	0.14	0.11	0.03	0.73	0.12	0.35	0.178
South Minch 1/2	0.06	0.04	0.02	0.02	0.24	0.14	0.25	0.056
Orkney	0.03	0.02	0.01	0.01	0.13	0.09	0.10	0.047
Clyde 5	0.39	0.32	0.11	0.04	1.25	0.11	0.44	0.061
Outer Hebrides	0.03	0.02	0.01	0.01	0.12	0.28	0.11	0.040
South Minch 3	0.08	0.06	0.03	0.03	0.31	0.11	0.23	0.040
Moray Firth	0.05	0.03	0.02	0.03	0.20	0.10	0.12	0.068
Scallops (<i>Pecten maximus</i>) Adductor muscle								
East Coast Scotland	0.03	0.02	0.01	0.02	0.11	< 0.01	0.03	0.041
South Minch 1/2	0.01	0.01	< 0.01	0.02	0.07	0.01	0.02	0.039
South Minch 10/11	0.02	0.01	< 0.01	0.01	0.06	0.02	0.03	0.033
South Minch 3	0.01	0.02	0.01	0.02	0.08	0.01	0.03	0.033
Outer Hebrides	0.01	0.01	< 0.01	0.02	0.05	0.04	0.02	0.035
Jura	0.01	0.01	< 0.01	0.01	0.06	0.02	0.03	0.032
Orkney	0.01	0.01	< 0.01	0.01	0.04	< 0.01	0.01	0.040
Moray Firth	0.01	< 0.02	0.01	< 0.03	0.08	0.02	0.02	0.024
Clyde 5	0.04	0.04	0.01	< 0.03	0.16	0.01	0.05	0.024
Clyde 8	0.02	0.02	0.01	< 0.02	0.10	0.01	0.03	0.022
Cockles (<i>Cerastoderma edule</i>)								
Dorset	0.01	0.01	< 0.01	0.02	0.06	0.01	< 0.01	0.013
Cornwall	0.02	0.02	0.01	< 0.02	0.09	0.01	0.01	0.010
Kent	0.07	0.06	0.04	0.13	0.40	0.04	0.02	0.026
Swansea	0.04	0.04	0.02	0.22	0.37	0.01	0.01	0.025

* The sum of the 17, PBDEs and PBDD/F TEQ are presented as upper bound levels

Table 2: Summary of statistical parameters describing the occurrence of PBDEs and PBDD/Fs in shellfish

		BDE-47	BDE-99	BDE-100	BDE-209	Sum of 17 PBDEs	237-T ₃ BDD	238-T ₃ BDF	PBDD/F TEQ*
		ng/g	ng/g	ng/g	ng/g	ng/g	pg/g	pg/g	pg/g
Pacific Oysters n=14	Mean	0.21	0.10	0.08	0.02	0.59	0.33	0.17	0.031
	Median	0.13	0.07	0.06	0.02	0.39	0.29	0.13	0.025
	Min	0.04	0.02	0.01	0.01	0.12	0.09	0.01	0.011
	Max	0.79	0.32	0.25	0.07	2.13	0.74	0.51	0.121
Native oysters n=5	Mean	0.18	0.06	0.07	0.01	0.47	6.13	0.03	0.038
	Median	0.10	0.05	0.04	0.01	0.34	5.30	0.03	0.033
	Min	0.04	0.02	0.02	<0.01	0.12	0.73	0.01	0.014
	Max	0.38	0.11	0.15	0.03	0.94	14.53	0.05	0.065
Mussels n=17	Mean	0.32	0.16	0.09	0.09	0.82	0.07	0.15	0.055
	Median	0.14	0.07	0.06	0.04	0.44	0.06	0.09	0.037
	Min	0.06	0.03	0.02	0.01	0.17	0.02	0.02	0.013
	Max	1.34	0.55	0.34	0.53	3.23	0.21	0.40	0.205
Scallops⁺ Gonad (adductor) n=10	Mean	0.12 (0.02)	0.09 (0.02)	0.05 (0.01)	0.02 (0.02)	0.42 (0.08)	0.13 (0.02)	0.25 (0.03)	0.083 (0.032)
	Median	0.07 (0.01)	0.05 (0.01)	0.03 (0.01)	0.02 (0.02)	0.27 (0.07)	0.11 (0.01)	0.25 (0.03)	0.056 (0.033)
	Min	0.03 (0.01)	0.02 (0.01)	0.01 (<0.01)	0.01 (0.01)	0.12 (0.04)	0.09 (0.01)	0.10 (0.01)	0.04 (0.022)
	Max	0.39 (0.04)	0.32 (0.04)	0.11 (0.01)	0.04 (0.03)	1.25 (0.16)	0.28 (0.04)	0.44 (0.05)	0.233 (0.041)
Cockles n=4	Mean	0.04	0.03	0.02	0.10	0.23	0.02	0.01	0.018
	Median	0.03	0.03	0.02	0.07	0.23	0.01	0.01	0.019
	Min	0.01	0.01	<0.01	0.02	0.06	0.01	<0.01	0.010
	Max	0.07	0.06	0.04	0.22	0.40	0.04	0.02	0.026

* TEQ calculated using analogous PCDD/F WHO-TEFs

⁺ Scallop gonad and (adductor) tissue analysed separately.

Table 3 Estimated intakes of PBDD/Fs and dioxin-like PBBs

Most significant species	Amount consumed	Brominated dioxins + dioxin-like PBBs, pg ⁵ TEQ/kg BW/day		TriBDD, pg/kg BW/day	TriBDF, pg/kg BW/day
		Lower bound	Upper bound		
(Rest of diet) ¹		0.08	0.40	0.07	0.2
Cockles	single portion ²	0.002	0.004	0.003	0.002
	1 weekly portion ³	0.08	0.41	0.07	0.21
	2 weekly portions ⁴	0.08	0.41	0.07	0.21
Scallops - Adductor	single portion ²	0.0005	0.005	0.003	0.005
	1 weekly portion ³	0.09	0.41	0.09	0.25
	2 weekly portions ⁴	0.09	0.42	0.09	0.26
Scallops -Gonad	single portion ²	0.008	0.01	0.02	0.04
	1 weekly portion ³	0.09	0.42	0.11	0.29
	2 weekly portions ⁴	0.10	0.43	0.13	0.33
Oysters	single portion ²	0.004	0.006	0.31	0.02
	1 weekly portion ³	0.09	0.41	0.38	0.22
	2 weekly portions ⁴	0.09	0.42	0.68	0.25
Mussels	single portion ²	0.006	0.008	0.01	0.03
	1 weekly portion ³	0.09	0.41	0.08	0.23
	2 weekly portions ⁴	0.10	0.42	0.09	0.26

1. Daily intake from rest of diet estimated from Total Diet Study (Food Standards Agency, 2006c).

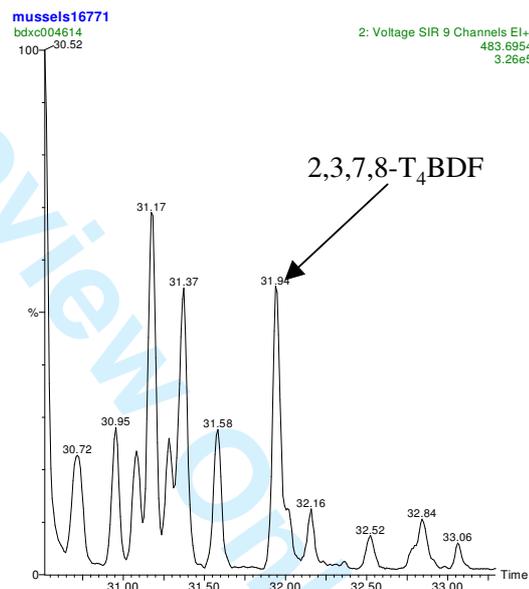
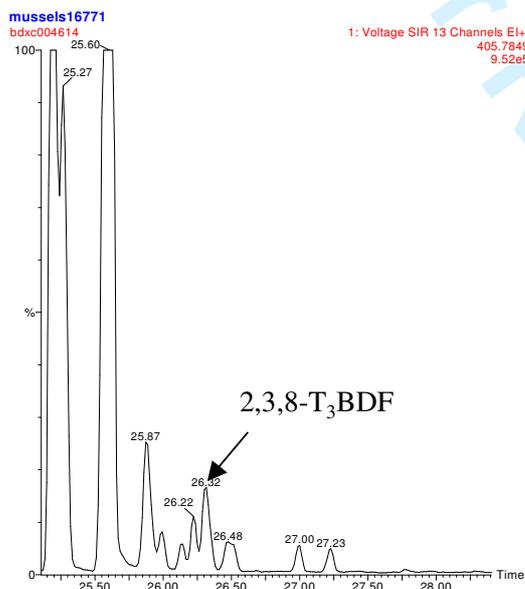
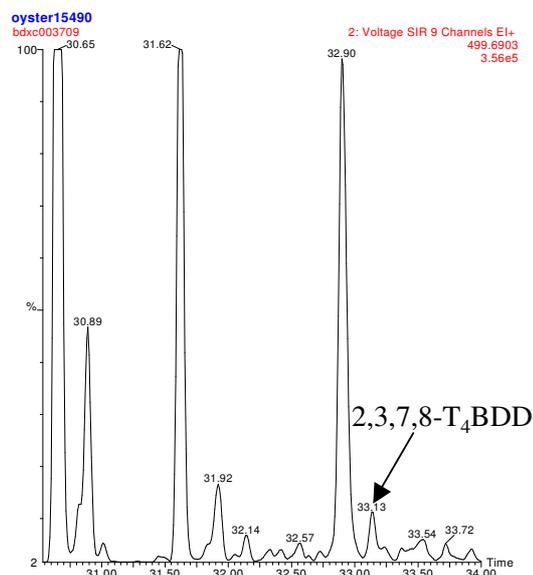
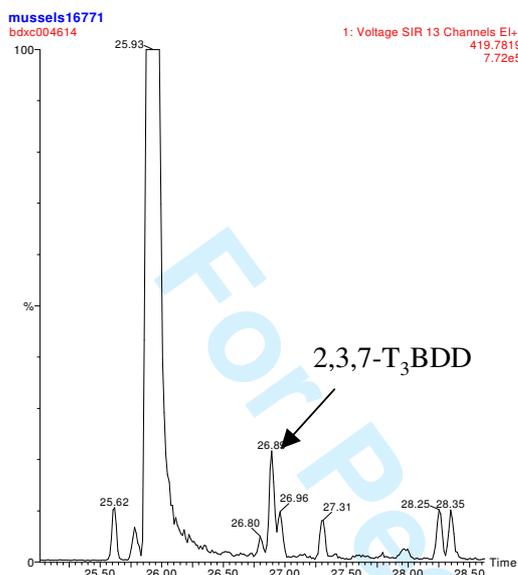
2. Estimated intake from the consumption of a single portion (70 g).

3. Estimated average daily intake from the consumption of one portion per week in addition to normal dietary intake.

4. Estimated average daily intake from the consumption of two portions per week in addition to normal

5. TEQs derived from analogous PCDD/F & PCB WHO-TEFs

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Minutes →