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Research Article

Brominated and chlorinated dioxins, PCBs and brominated flame retardants in Scottish shellfish: Methodology, occurrence and human dietary exposure

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The most commonly consumed shellfish species produced in Scotland – mussels, oysters and scallops – were investigated for the occurrence of a range of brominated and chlorinated contaminants in order to establish current levels and estimate human dietary exposure. Flesh from individual sub-samples was representatively pooled and 35 composites were analysed for brominated and chlorinated dioxins (PBDD/Fs, PCDD/Fs), brominated and chlorinated biphenyls (PBBs, PCBs), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA). The analytical methodology used $^{13}C_{12}$ labelled surrogates of the target compounds, with GC coupled to (usually) high resolution MS, and LC-MS/MS for HBCD and TBBPA analysis. Positive identifications were made in the majority of samples for most analytes with the exception of TBBPA and most PBDD congeners measured. None of the levels detected for PCDD/F and PCB were above the maximum permitted levels specified in European Union regulations. The levels of brominated furans predominated over brominated dioxins, reflecting the environmental distribution and source emission profiles of these contaminants, and relatively high levels of the tri-brominated congeners were observed. Levels of the flame retardant chemicals reflected current and legacy use, with appreciable concentrations of PBDEs and HBCDs (predominantly alpha-HBCD) but far lower levels of PBBs. TBBPA was not detected in any of the species. In general, mussels and oysters displayed relatively higher levels of contamination than scallops, although the gonad tissue of the latter showed significant levels of brominated dioxins. The estimated adult dietary intakes of PCDD/Fs and PCBs arising from the consumption of a typical portion of these foods in combination with an otherwise average UK diet were in the range 0.5–0.6 pg World Health Organisation (WHO)-toxic equivalent (TEQ)(2005)/kg bodyweight per day. These estimated dietary intakes are well within the Tolerable Daily Intake for dioxins and dioxin-like PCBs of 2 pg WHO-TEQ(2005)/kg bodyweight/day endorsed by the independent expert Committee on Toxicology of Chemicals in Food, Consumer Products and the Environment. The corresponding intakes for sumPBDEs and sumHBCDs were 5.6–6.1 and 5.9–7.9 ng/kg bodyweight/day respectively.

Keywords: BFRs / Dietary exposure / Dioxins / PBDDs / PBDFs / PCBs / Shellfish

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1 Introduction

Shellfish are a popular food in many parts of the world and this is reflected in the rising number of seafood restaurants that have emerged within the UK in recent years. The production of shellfish is economically important for Scotland, both for national consumption as well as export, and species

Abbreviations: BFRs, brominated flame retardants; **COT,** UK committee on toxicity of chemicals in food, consumer products and environment; **HBCDs,** hexabromocyclododecanes; **PBBs,** brominated biphenyls; **PBDD/Fs**, polybrominated dibenzo-p-dioxins and polybrominated dibenzofurans; **PBDEs**, polybrominated diphenyl ethers; **PCBs,** chlorinated biphenyls; **PCDD/Fs,** chlorinated dibenzo-p-dioxins and polybrominated dibenzofurans; **TBBPA**, tetrabromobisphenol A; **TEF,** toxicity equivalency factor; **TEQ,** toxic equivalent

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such as mussels (*Mytilus edulis*), oysters (*Crassotrea gigas, Ostrea edulis*) and scallops (*Pecten maximus*) are among the most popular produced. However, shellfish have a recognised potential for bio-accumulating contaminants and some species, *e. g.* mussels, are commonly used as early indicators of the pollution of local waters. This is because bivalve shellfish like oysters and mussels feed by filtering nutrients from seawater and, at the same time, absorb contaminants which they are unable to metabolise and only very slowly excrete. The resulting bioaccumulation within the species used for food is particularly relevant in the case of environmental contaminants with long half-lives, such as chlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/Fs) and chlorinated biphenyls (PCBs). There is very little information [1] on the occurrence of other emerging persistent pollutants such as brominated flame retardants (BFRs) and polybrominated dibenzo-p-dioxins and polybrominated dibenzofurans (PBDD/Fs) in marine species. The reasons for this are two-fold; the relatively recent recognition of the global environmental distribution and toxicological significance of these contaminants, and the difficulties in analytical accessibility for the measurement of some of these contaminants [2] such as the PBDD/Fs.

PCDD/F and PCBs are recognised environmental and food contaminants that are known to bio-accumulate in fish and shellfish. The extent of this accumulation is evident from the levels of these contaminants reported in various studies. In the UK Total Diet Studies [3] carried out over the last two decades, fish (including shellfish) have consistently been one of the food groups containing the highest levels of PCDD/Fs and PCBs. Reports from other recent studies on the levels in fish and shellfish also support this observation [3–5]. Specific surveys on marine and farmed fish and shellfish [5–11] confirmed the relatively high concentrations of PCDD/Fs and PCBs in marine species and also showed that fish with a high lipid content, *i. e.* oily fish, and bottom feeding fish, such as plaice, contained a higher concentration of the contaminants as compared to other, white fish. Shellfish species, particularly crabs, oysters and mussels, also showed relatively high concentrations of PCDD/F and PCB. Human dietary exposure can therefore be significantly influenced by the fish and shellfish component of the diet, particularly in high level consumers and low bodyweight individuals. PCDD/F levels in marine species used for food have been regulated by the EU following the setting of maximum permitted levels in 2002 [12], and more recently, maximum permitted levels have also been set for dioxin-like PCBs, applicable from March 2007 [13].

PBDEs, brominated biphenyls (PBBs), hexabromocyclododecanes (HBCDs) and tetrabromobisphenol A (TBBPA) are mass-produced BFRs which are incorporated into a number of commonly used commercial materials such as plastics, rubbers, textiles and electronic components. These chemicals are used specifically to slow down or inhibit the initial phase of a developing fire and their use has undoubtedly resulted in a reduction in human injury and fatality. However, the commercial applications of these compounds are generally open-ended and the BFRs are available to diffuse out of materials into the environment, a process that can occur over the lifetime of the material during manufacture, use and disposal. The occurrence of BFRs in environmental compartments such as water, sediments and biota [2] accompanies an increasing amount of evidence that suggests that these chemicals may cause potential detrimental human health effects [2, 14, 15]. Unlike BFRs, PBDD/Fs are unintentional by-products of incineration processes and have physico-chemical properties that are similar to their chlorinated analogues. They originate from similar anthropogenic sources as PCDD/Fs, such as incineration, or chemical manufacture, *e.g.* PBDD/Fs are formed as by-products during the manufacture of PBDEs. Studies of incineration processes [2, 16] show that the formation of these compounds is consistent with the "*de novo*" hypothesis and is thus governed by the occurrence of bromine or chlorine sources in incinerator feed. There are studies [2, 17, 18] to show that the incineration of products containing BFRs as well as the thermolysis of BFR material such as PBDEs is an important source of PBDD/F emissions. PBDD/Fs can also be formed from PBDEs during thermal processing procedures such as extrusion, moulding and recycling, and degradation [2]. Additionally it has been demonstrated that PBDD/Fs can also be formed during ultra-violet irradiation of decabromodiphenyl ether [19].

Although there is a considerable lack of data on the occurrence of BFRs (other than PBDEs) and PBDD/Fs in food, one of the food types that has been studied more than others has been seafood, particularly fish. Some of these studies have considered fish as environmental pollution indicators rather than food and the species studied and the sampling strategies have varied accordingly. Data for the sum of PBDE congeners in different foods in North America from a market basket survey showed that the maximum whole weight median concentration (1725 ng/kg) occurred in fish [20]. A recent survey of fish in Canada showed whole weight mean PBDE values ranging from 100 ng/kg for shrimp and tilapia to 2200 ng/kg for farmed salmon [7]. In a Dutch study, where levels of PBDEs in individual food samples from the national Food Consumption Survey were reported, the highest whole weight concentration (21 100 ng/kg) was found in eel [21]. Similarly, a study on various foods collected in the Catalonian region of Spain showed that the highest whole weight concentration of PBDEs (1010 ng/kg) was in blue fish. A recent Japanese total diet study [10] found the highest average PBDE concentration (1259 ng/kg) in the fish group and a similar study in the UK [22] also found the highest average PBDE concentration (500 ng/kg) in the fish group (not including deca-BDE). High levels of PBDEs (up to 288 μg/kg) in river fish have been recorded in the UK although these were caught in the vicinity of a BFR manufacturing facility [23].

Some measure of caution should be applied when comparisons between PBDE data sets are made, because of the differences in the congeners for which data is measured and reported. In the data listed above (all as sum of PBDEs) most of the studies have included the major contributors (BDEs 47, 99, 100, 153 and 154) to total PBDE concentration.

In a recent study in the UK, PBDD/Fs, PBBs and BFRs (PBDEs, HBCDs and TBBPA) were analysed in 48 composite samples of fish and shellfish and ten samples of fish oil dietary supplements [1]. These included farmed and wild, oily fish and white fish, shellfish, canned fish and fish paste, and supplements based on cod liver, halibut liver, shark liver, salmon and tuna oils. Certain PBDEs were present in most or all of the samples analysed, the most abundant congeners being PBDEs 28, 47, 49, 66, 99, 100, 153 and 154. HBCDs and PBBs were detected less frequently (alpha-HBCD being the most abundant) and brominated dioxins only occasionally. TBBPA was not found above the limit of detection in any samples. In a complementary study, the same fish and shellfish samples plus individual samples of some oily fish species were also analysed for PCDD/Fs and PCBs. These were detected in all of the samples analysed, with total World Health Organisation $(\mathrm{WHO})_{1998}$-toxic eqivalent (TEQ) concentrations in the range 0.02–9.5 ng WHO-TEQ/kg fresh weight, with the exception of one individual sample of mackerel that contained a level of 28 ng WHO-TEQ/kg fresh weight.

This study aimed to investigate the current levels of these contaminants in shellfish produced in Scotland. The analytes were all determined by high resolution GC-MS except for ortho-substituted PCBs, which were detected using low resolution MS and HBCD enantiomers and TBBPA, which were measured using HPLC-MS/MS.

2 Materials and methods

Individual sub-samples of mussels, oysters and scallops were collected between January and March 2006. A map showing the location of the sampling sites is given in Fig. 1. The sampling time was selected to capture the pre-spawning period for the species of interest, and also coincides with the time when fat levels are highest and the shellfish are most suitable for consumption.

The samples were representatively pooled and homogenised to yield 35 composite analytical samples. As scallops are sometimes retailed as the adductor muscle alone, these samples were divided into separate adductor and gonad portions prior to pooling. The composite samples were freeze-dried and the resulting powders were thoroughly mixed before taking sub-samples for analysis.

The following analytes were determined:

(i) The 17 2,3,7,8-chloro substituted dibenzo-p-dioxins and dibenzo-furans (PCDD/Fs)
(ii) The dioxin-like, non-ortho substituted polychlorinated biphenyls (PCBs) – IUPAC numbers **77, 81, 126** and **169**.
(iii) Mono to tetra-ortho substituted PCBs – IUPAC numbers 18, **28**, 31, 47, 49, 51, **52**, 99, **101**, **105, 114, 118, 123**, 128, **138, 153**, **156, 157, 167**, **180, 189**, 33, 41, 44, 60, 61, 74, 66, 87, 110, 129, 141, 149, 151, 183, 185, 187, 191, 193, **194**, 201, **202**, 203, 206, 208 and 209.
(iv) Polybrominated diphenyl ethers (PBDEs) – IUPAC numbers 17, **28, 47**, 49, 66, 71, 77, 85, **99**, 100, 119, **126**, 138, **153, 154**, **183** and **209**.
(v) **2,3,7,8**-Bromo substituted dibenzo-p-dioxins and dibenzo-furans (PBDD/Fs) – tetra to hexa substituted congeners; and **2,3,7-TBDD** and 2,3,8-TBDF.
(vi) Polybrominated biphenyls (PBB): IUPAC numbers 15, 49, **52**, **77**, 80, 101, **126**, 169, **153** and 209.
(vii) **TBBPA** and HBCD: **α**, **β**, and **γ** diasteriomers

All analytical standards, native as well as ^{13}Carbon labeled (^{13}Carbon labeled standards used as internal or sensitivity standards are given in bold), for the individual analyte groups were prepared by the dilution and/or combination of commercial standards. These were obtained either from Cambridge Isotope Labs, (MA, USA) or from Wellington Laboratories, (Ontario, Canada) and were prepared gravimetrically in n-nonane, apart from TBBPA and HBCD which were prepared in methanol for LC-MS/MS determination. The solvents used were obtained from Rathburns Chemicals (Scotland).

An aliquot of the dry, homogenised sample was fortified with a known amount (typically 50 μL) of $^{13}C_{12}$ labeled surrogates for each of the analyte groups. The size of the aliquot was dependent on the proportion of lipid present and the equivalent of up to 1 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 1:1.5, H_2SO_4: Silica, for minimum 6 h). The mixture was quantitatively transferred to the top of a multi-layer column (70 × 600 mm) packed from top to bottom with; 30 g of anhydrous sodium sulphate, 25 g of acid modified silica gel, 50 g of base modified silica gel (YMC Gel, prepared by mixing in the ratio 3:1, 5 M KOH in methanol:Silica and allowing evaporation of methanol and stabilisation for 24 h), 10 g of sodium sulphate and silanised glass wool. The column was plugged with a glass fibre frit and connected in series to a carbon column (20 × 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 dichloromethane:hexane (40:60 v/v, 400 mL). The collected eluate represented the fraction containing mono- to tetra-ortho substituted PCBs and PBBs, and of all the PBDEs. The carbon column was disconnected and reverse-eluted with 200 mL of toluene to yield a fraction

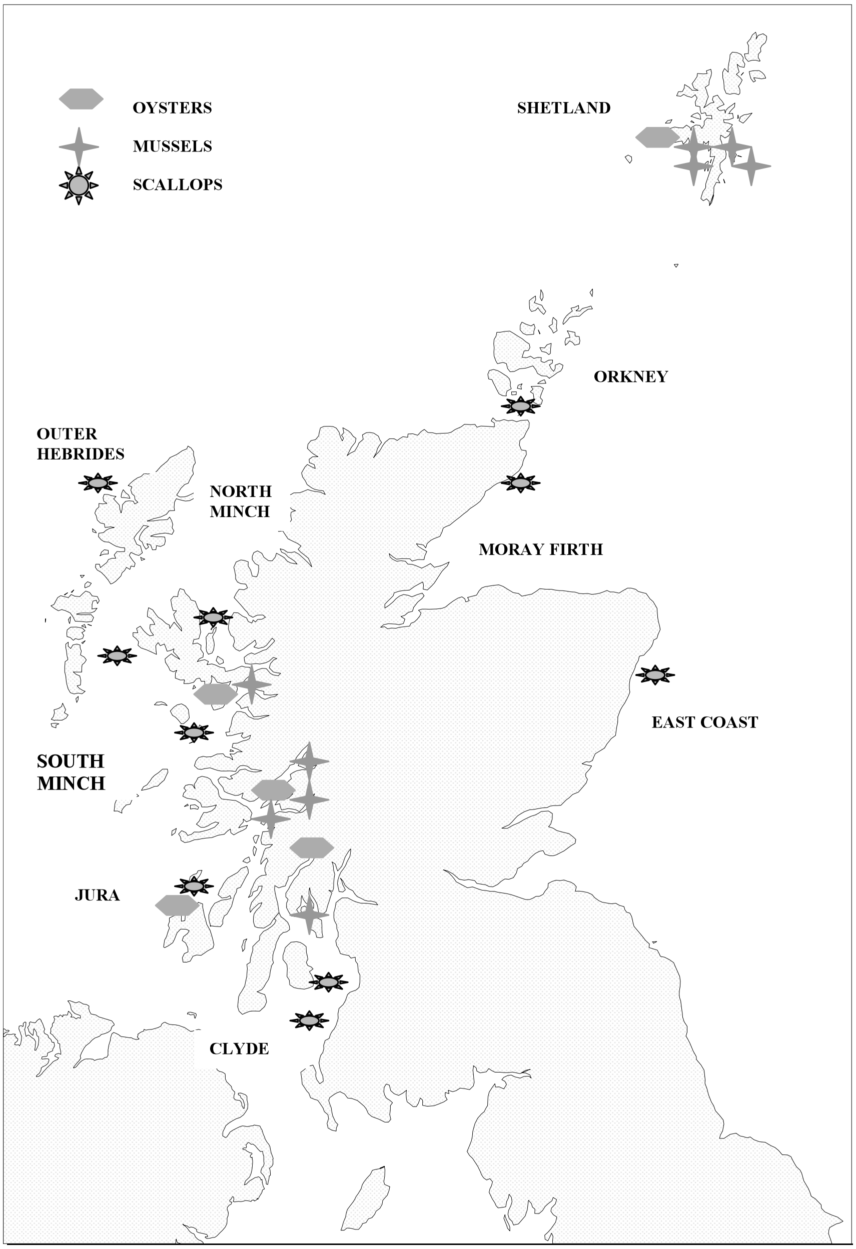

Figure 1. Location of sampling sites.

containing the non-ortho substituted PCBs and PBBs together with PCDD/Fs and PBDD/Fs.

The toluene extract was concentrated using a TurboVap II^{TM} (Zymark Corporation) apparatus and solvent exchanged to ∼0.5 mL of hexane. The concentrate was treated with 37 N sulphuric acid (five drops) and mixed by rotary shaking. The mixture was allowed to stand for 15 min to allow the aqueous acid and organic layers to separate. The bottom aqueous layer was discarded and the process was repeated a further two times. The organic layer was separated on two micro-columns (6 mm × 100 mm) in series, the upper column packed with acid modified silica gel (∼3.5 cm) and base modified silica gel (∼3.5 cm) eluting directly onto the lower column containing activated ∼7 cm alumina (WB5-Basic, Sigma Aldrich, Germany). 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 dichloromethane:hexane (30:70). This eluate was concentrated with the addition of the $^{13}C_{12}$ labelled PCDD/F and PBDD/F sensitivity standard contained in the keeper solvent to approximately 50 μL.

The fraction containing ortho PCB/PBBs and PBDEs was concentrated and solvent exchanged to ∼0.5 mL of hexane. The concentrate was separated on the two micro-column system described above but eluted with 10 mL hexane to waste followed by disposal of the silica column and elution of the alumina column with 20 mL of dichloromethane:hexane (30:70). As described for the planar (toluene) fraction the eluate from the two micro-column system was concentrated, with the addition of the $^{13}C_{12}$ labelled PCB or PBDE sensitivity standard contained in the keeper solvent, to approximately 50 μL.

2.1 Instrumental methods

All analyte groups except the mono to tetra-ortho substituted PCBs were analysed by high resolution GC-MS. These measurements were performed on either one of two Micromass Autospec Ultima instruments coupled to a Hewlett Packard 6890N gas chromatograph and a CTC Analytics PAL GC autosampler or a CTC A200S autosampler. The gas chromatograph was fitted with a 60 mm × 0.22 mm id J&W DB-5 MS fused silica capillary column and operated in constant flow (∼1 mL/min helium) mode. PCDDs, PCDFs and non-ortho-PCBs were monitored in a single run using a GC oven temperature programme consisting of a 5 min isothermal period at 60°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 280°C with a final isothermal period of 10 min. PBDEs and PBDD/Fs were monitored in two further runs using the following GC oven temperature programme: 80°C (5 min), 10°C/min, 170°C (1 min), 35°C/min, 240°C (1 min), 2°C/min, 280°C (1 min), 10°C/min 325°C (19.5 min). Decabromo analytes were measured in a separate run using a 15 mm ZB5-MS column (Zebron, Phenomenex) operated with the following oven temperature programme: 3 min at 60°C, 20°C/min to 205°C over 21 min and finally 66°C/min to 325°C for 10 min.

The GC-MS interface was set to 260°C (300°C for PBDEs PBBs and PBDD/Fs). 10 μL injections were made with a PTV injector using a temperature programme which consisted of a 3 min isothermal period at 60°C followed by heating at 12°C/sec to 320°C for 3 min and finally 12°C/sec to 350°C to the end of the run.

The high resolution MS instruments were operated in electron ionisation mode at a mass resolution of ∼10 000 (at 10% peak height). SIM was used to record the two most intense ions in the molecular ion cluster for each homologue. An acceleration voltage of 8 kV was used for the PCDD/Fs and PCBs, but more stable mass calibration was obtained for the brominated compounds at 7 kV. An electron energy of 33–40 eV was used with a trap current range of 440–480 μA.

The mono to tetra-ortho substituted PCBs were analysed by HRGC with detection by unit resolution MS, performed on an Agilent 5973N mass selective detector coupled to a 6890 GC, fitted with a 7683 auto-sampler. Chromatographic separation was performed using a 60 m × 0.25 mm id J&W DB-5 capillary column used in conjunction with constant flow (∼1 mL/min helium) conditions. Five microlitres of extract was injected into a PTV injector programmed with a 1 min isothermal period at 50°C followed by heating at 10°C/sec to 150°C then 10°C/sec to 260°C, hold for 1 min, then at 10°C/sec to 320°C for 40 min. The gas chromatograph temperature programme consisted of a 1 min isothermal period at 60°C followed by heating at 20°C/min to 190°C for 3 min, then at 1.4°C/min to 248°C and finally at 10.0°C/min to 310°C with an isothermal period of 12 min. The mass spectrometer was operated in electron ionisation mode. Selected ion monitoring was used, and the two most intense ions in the molecular ion cluster were measured for each ^{13}C labelled PCB and native PCB homologue group.

Quantification was carried out on the basis of stable isotope dilution of the ^{13}C labelled surrogates and internal standardisation. Masslynx^{TM} software was used for the targeting and quantitation of all the analytes.

All PCDD/F and PCB data were assessed for compliance with published acceptance criteria [24] and the method performance criteria guidelines laid down in EU commission directives 2002/69/EC and 2002/70/EC [25, 26]. Similar acceptance criteria were used for the PBDEs, PBBs and PBDD/Fs. A blank and a BCR reference material were analysed with every batch of samples. The GC-MS analytical run for each set of analyses was preceded by a reference standard solution used to check system performance and calibration validity prior to continuation of the run. The reference standard solution was also analysed during and at the end of the analytical run. All integrated chromatograms were scrutinised to assess chromatographic peak shape, resolution and S/N; and, for high resolution MS, lock-mass traces were examined for evidence of ionisation suppression. Isotope ratios for signal peaks were assessed for agreement with theoretical abundances and the variation in response factors for reference standard solutions within a run was limited to 15%.

The regular use of reference material shows control of rigorously validated methodology used within the laboratory, but greater confidence of method performance is provided by participation in external trials. Where reliable inter-calibration schemes exist for food matrices (for, *e.g.* PCDD/Fs, PCBs and PBDEs) the methodology has been further validated by successful participation in these studies over the last three years [27–34]. Measurement uncertainty has been estimated for all PCDD/Fs, PCBs, PBDD/Fs, PBDEs and PBBs as per the Eurachem guide [35]. Typical uncertainties, for example, for dioxins are of the order of 20% at the 1 ng/kg fat level, but can rise to around 200% at the limit of detection (typically 0.01 ng/kg fat, but dependent on the fat content and sample size)

2.2 LC-MS/MS analysis

The methodology for the analysis of speciated HBCD (α, β, and γ diasteriomers) and TBBPA used LC-MS/MS and has been described in detail elsewhere [36]. In brief, samples were fortified with $^{13}C_{12}$ labelled surrogates of all four analytes and the sample matrix was subjected to acid hydrolysis using sulphuric acid suspended on silica gel. The hydrolysed sample was extracted using hexane:dichloromethane (60:40 v/v) and hexane, concentrated and solvent exchanged to methanol:water (4:1). Samples were analysed in duplicate and measurements were carried out using LC-MS/MS in the multiple reaction monitoring mode [36]. A reference material and method blank were included with each set of samples, and the reference material data was evaluated for accuracy to the assigned values.

3 Results and discussion

3.1 Occurrence

Due to the large volume of data produced in this work, only a summarised version of the results are presented in this paper. These are shown in Table 1. All data are reported as *upper-bound*, which means that where congeners were not detected they were assumed to be present at the level of the limit of detection. All concentrations are expressed on a whole weight basis. A full version of the detailed results for all of the analytes described in this work is presented elsewhere [36].

Concentrations of chlorinated dioxins and furans and dioxin-like PCBs are normally reported as a TEQ, which is calculated by multiplying the concentration of each congener of interest by its toxicity equivalency factor (TEF). The TEFs are based on the toxicity of each congener relative to 2,3,7,8-TCDD. The WHO defined a set of TEFs in 1998 [14], but conducted a review and revised some of the values in 2005 [37]. Current EU regulations stipulate the use of the 1998 TEFs and these must therefore be used in assessing TEQ levels against regulatory limits. The UK Committee on Toxicity of Chemicals in Food, Consumer Products and Environment (COT) has reviewed the new WHO TEFs and has endorsed their use in assessing dietary intakes. Therefore, the newer system has been used in comparing exposure against the UK Tolerable Daily Intake [38].

Table 1 also shows concentrations for the PBDD/Fs. These are presented as WHO-TEQs based on the use of the analogous chlorinated dioxin and PCB TEFs for PBDD/Fs and non-ortho PBBs, an approach that has been endorsed by the COT as an interim measure until a more rigorously evaluated set of TEF values specifically for the brominated congeners become available [39]. It provides data to allow comparisons with other studies that have used the same approach [1, 40, 41]. Other data presented in Table 1 include the results for PBDEs as a sum of 17 congeners and the sum of α, β, and γ HBCD enantiomers. These are presented as upper bound concentrations in μg/kg whole weight.

This report represents the first comprehensive study of this range of chlorinated and brominated environmental contaminants in Scottish shellfish. Positive identifications of these contaminants were made in all samples, apart from TBBPA and some PBDD and PBB congeners (notably penta and hexa-brominated compounds) for which no positive identifications were made. No levels exceeded relevant regulatory limits.

Data summarising the findings are given in Table 2. The concentrations of dioxins and PCBs (on average, less than 0.5 ng WHO-TEQ/kg on a whole weight basis for the three species studied) are similar to those reported in an earlier study of fish and shellfish in the UK in 2005 [6] and also similar to those reported for Scotland in 2000 [11]. The similarity of the concentrations over time does not reflect the general downward trend in contaminant levels observed for foods within the UK [42], but the comparison is limited due to the small number of samples analysed in the earlier studies. On average, higher values were observed for oysters and mussels (0.42 and 0.43 ng WHO-TEQ/kg than for the scallop tissues (0.25 and 0.04 ng WHO-TEQ/kg for gonad and adductor, respectively). These values are at least an order of magnitude below the maximum permissible level (8 ng WHO-TEQ/kg) for fish and fisheries products [43]. Unlike other marine species studied [6, 8] PCDD/Fs generally make a greater contribution than PCBs to the total TEQ. The major contributors to the total TEQ were 1,2,3,7,8,–PeCDD, 2,3,4,7,8-PeCDF, 2,3,7,8-TCDD, 2,3,7,8-TCDF and PCBs 118 and 126.

In contrast to the observations for PCDD/Fs and PCBs, levels of PBDD/Fs (WHO-TEQ basis) were relatively higher in scallop gonad tissue than oysters and mussels (0.083 ng/kg compared to 0.053 and 0.058 ng/kg for oysters and mussels, respectively. However, mussels showed a more complete range of detectable congeners, particularly PBDFs. The toxicology of the tribrominated dioxins and furans is the subject of continuing international study [40, 44]. This is particularly relevant in the context of the data presented here (especially for oysters) where relatively higher concentrations of these congeners have been detected. There have been reports of similar high tri-BDD levels in mussels from the Baltic sea by researchers in Sweden [45] who report that apart from anthropogenic activity, biogenic processes involving the dimerisation or biotransformation of precursor molecules such as brominated phenols and hydroxylated PBDEs may give rise to the formation of tri-BDD (and to a lesser extent tetra-BDD) congeners. It should be noted in particular that the concentrations of tribromo- substituted PBDD/F congeners reported here have not been included in the summed TEQs as there are no analogous WHO-TEF values for tri-chloro substituted PCDD/Fs. In general, the occurrence of brominated furans is more pronounced than brominated dioxins, reflecting the environmental distribution and source emission profiles of these contaminants. Similarly, the relative concentrations of the PBBs (low) compared with PBDEs (higher) is consistent with the greater and more recent usage of PBDEs as

Table 1. Concentrations of chlorinated dioxins (PCDD/Fs) and dl-PCBs (WHO$_{1998}$-TEF values), brominated dioxins (PBDD/Fs), PBDEs and HBCD

Sample Code	Sample Details	PCDD/F WHO-TEQ ng/kg	PCB WHO-TEQ ng/kg	PBDD/F WHO-TEQ ng/kg	Sum PBDEs µg/kg	Deca-BDE µg/kg	Sum HBCD µg/kg
				(Upper bound fresh weight basis)			
Oysters							
13554	Shetland	0.242	0.107	0.035	0.886	0.018	0.564
13555	South Shian Bay	0.194	0.110	0.037	0.219	0.006	0.831
13556	Loch nan Ceol	0.193	0.082	0.031	0.172	0.013	0.472
13557	Loch Fyne	0.449	0.236	0.121	0.585	0.014	1.261
13559	Craigens	0.284	0.186	0.042	0.327	0.014	0.541
Mussels							
13558	Linga	0.190	0.128	0.028	0.845	0.041	0.516
13560	Troustan	0.414	0.556	0.064	2.737	0.089	12.1
13563	Loch Etive	0.233	0.098	0.118	0.373	0.040	0.893
13567	Whalwick	0.196	0.442	0.037	0.227	0.038	0.892
13568	Glenvig Bay	0.200	0.426	0.035	0.271	0.094	0.280
13569	Catfirth	0.134	0.085	0.037	0.175	0.036	0.192
13570	Wadbister	0.165	0.117	0.038	0.195	0.032	0.297
13592	Loch Leven	0.176	0.082	0.097	0.749	0.066	0.280
13593	Lismore	0.260	0.135	0.063	0.323	0.032	0.681
13594	Mussel composite	0.168	0.109	0.061	0.715	0.080	2.564
Scallop Gonad							
13571	Clyde 8	0.248	0.118	0.054	0.702	0.019	0.477
13572	South Minch 10/11	0.175	0.053	0.055	0.239	0.017	0.260
13573	Jura	0.202	0.063	0.233	0.31	0.022	0.285
13574	East Coast	0.178	0.117	0.178	0.727	0.026	0.330
13575	South Minch 1/2	0.170	0.051	0.056	0.241	0.019	0.191
13576	Orkney	0.117	0.033	0.047	0.126	0.011	0.425
13577	Clyde 5	0.217	0.180	0.061	1.251	0.044	0.090
13578	Outer Hebrides	0.091	0.034	0.040	0.116	0.010	0.125
13579	South Minch 3	0.180	0.060	0.040	0.306	0.029	2.140
13580	Moray Firth	0.126	0.043	0.068	0.195	0.027	1.210
Scallop Adductor							
13582	East Coast	0.034	0.011	0.041	0.11	0.017	0.050
13583	South Minch 1/2	0.026	0.009	0.039	0.067	0.022	0.046
13584	South Minch 10/11	0.026	0.006	0.033	0.059	0.012	0.080
13585	South Minch 3	0.042	0.006	0.033	0.083	0.017	0.074
13586	Outer Hebrides	0.029	0.006	0.035	0.048	0.017	0.090
13587	Jura	0.028	0.007	0.032	0.058	0.012	0.080
13588	Orkney	0.022	0.004	0.040	0.039	0.006	0.170
13589	Moray Firth	0.028	0.005	0.024	0.081	0.027	0.100
13590	Clyde 5	0.038	0.013	0.024	0.164	0.026	0.220
13591	Clyde 8	0.028	0.008	0.022	0.097	0.024	0.030

flame retardants in this country. Data for PBBs has not been presented in this paper as they occurred only at very low levels [36], mostly in mussels and oysters and, where detected, were typically in the range 0.01–0.1 µg/kg. As there has not been any substantial use of PBBs in the UK, the low levels observed are likely to arise from long range marine and aerial transport as observed in the detection of this contaminant in polar bear tissue from the Arctic [46].

On average, higher concentrations of PBDEs were observed in mussels compared to the other species, with the lowest levels being observed in scallop adductor tissue, although the relative distributions of the 16 different congeners (not including deca-BDE) measured in this study were very similar across the three species. The predominance of BDEs 47, 99, 100 and, to a lesser extent, 154 and 209 is similar to that observed in other studies [1, 2, 10, 21] and reflects the use of commercial PBDE formulations [2] such as commercial "penta". The levels of BDE 47 correlate well (R = 0.98) with the total PBDE level for all species and this accords well with commercial "penta" as a source, since BDE 47 is the major component of it. On the other hand, BDE 209 does not correlate well (R = 0.53) with total PBDE and appears to be species selective, with the highest values occurring almost exclusively in mussels. Unlike the

Table 2. Summary of contaminant concentrations in shellfish species (upper bound fresh-weight basis)

	ng/kg WHO-TEQ	PCDD/F WHO-TEQ	PCDD/F & PCB WHO-TEQ	PBDD/F TEQ	PBDD/F & PBB TEQ
Oysters	Min	0.19	0.28	0.031	0.032
	Mean	0.27	0.42	0.053	0.054
	Median	0.24	0.35	0.037	0.038
	Max	0.45	0.69	0.121	0.122
	µg/kg	α HBCD	β HBCD	γ HBCD	Sum PBDEs
	Min	0.30	0.04	0.03	0.17
	Mean	0.52	0.13	0.08	0.44
	Median	0.42	0.15	0.07	0.33
	Max	0.98	0.21	0.15	0.89
	ng/kg WHO-TEQ	PCDD/F WHO-TEQ	PCDD/F & PCB WHO-TEQ	PBDD/F TEQ	PBDD/F & PBB TEQ
Mussels	Min	0.13	0.22	0.028	0.029
	Mean	0.21	0.43	0.058	0.059
	Median	0.19	0.32	0.049	0.050
	Max	0.41	0.97	0.118	0.119
	µg/kg	α HBCD	β HBCD	γ HBCD	Sum PBDEs
	Min	0.13	0.01	0.03	0.18
	Mean	1.36	0.26	0.24	0.66
	Median	0.43	0.09	0.09	0.35
	Max	8.93	1.60	1.52	2.74
	ng/kg WHO-TEQ	PCDD/F WHO-TEQ	PCDD/F & PCB WHO-TEQ	PBDD/F TEQ	PBDD/F & PBB TEQ
Scallops Gonad (Adductor)	Min	0.09 (0.02)	0.12 (0.03)	0.040 (0.022)	0.041 (0.023)
	Mean	0.17 (0.03)	0.25 (0.04)	0.083 (0.032)	0.085 (0.034)
	Median	0.18 (0.03)	0.23 (0.04)	0.056 (0.033)	0.058 (0.034)
	Max	0.25 (0.04)	0.40 (0.05)	0.233 (0.041)	0.235 (0.043)
	µg/kg	α HBCD	β HBCD	γ HBCD	Sum PBDEs
	Min	0.06 (0.01)	0.01(0.01)	0.01 (0.01)	0.12 (0.04)
	Mean	0.46 (0.04)	0.05 (0.03)	0.04 (0.02)	0.42 (0.08)
	Median	0.26 (0.04)	0.02 (0.02)	0.03 (0.02)	0.27 (0.07)
	Max	1.75 (0.12)	0.24 (0.08)	0.16 (0.05)	1.25 (0.16)

Note: PBDD/Fs and PBB TEQ values are based on PCDD/F and PCB WHO_{1998}-TEFs

penta formulation, "deca" which is predominantly BDE 209, is still in use and a number of studies have published occurrence data in biota for this congener [47–49]. BDE 209 generally shows lower analytical recovery (40–60%) than the other BDEs (typically 60–110%). This suggests that some removal mechanisms are active during analysis and it is therefore essential that labelled BDE 209 is used as an internal standard in order to provide the necessary control.

Of the other BFRs studied, no detectable levels of TBBPA were recorded in any of the shellfish species even though limits of detection were typically as low as 0.01 µg/kg. This is consistent with the results of other recent studies [1, 21, 22] where levels were very low or undetectable. In general production processes, TBBPA is chemically bonded to the polymeric matrices of material in which it is incorporated as a flame retardant, unlike PBDEs or HBCD [2, 50]. The nature of this application, limits the potential for release of this contaminant and may account for the lower frequency of detection of this compound, although TBBPA has been reported in sediments. In the case of HBCDs, the predominance of the alpha-enantiomer relative to the beta and gamma diasteriomers was observed in all of the shellfish species studied here, with the highest levels observed in mussels. Although commercial formulations and sediments show gamma-HBCD as being dominant, the predominance of the alpha-enantiomer has been documented in fish and other mammalian species and probably arises as a

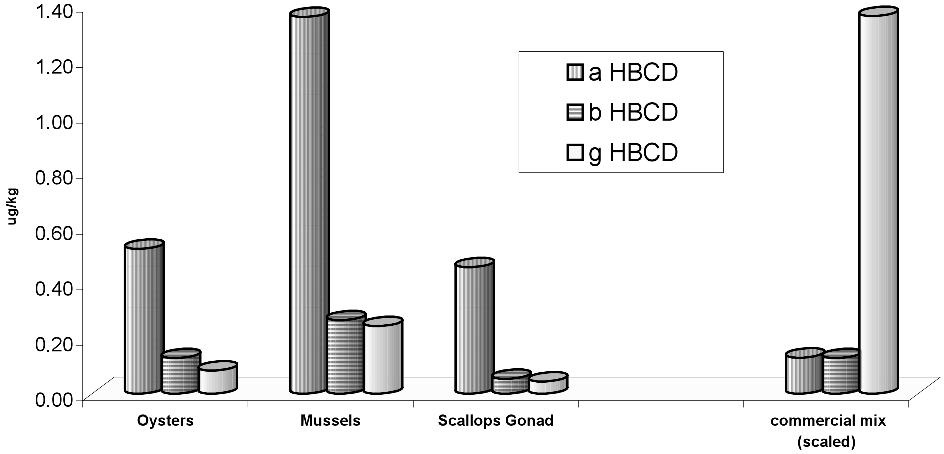

Figure 2. Hexabromocyclododecane profiles: Average concentrations in shellfish compared to typical commercial mix.

result of selective metabolism of the different enantiomers and/or biotransformation processes [51, 52]. The contrast in profiles for the two matrices is shown in Fig. 2. The HBCD levels recorded in this work are similar to those reported for shellfish and fish species elsewhere [53].

Geographically, the samples of shellfish studied here, particularly oysters and mussels, reflect the harvesting areas that are representative of the Scottish shellfish industry. Sampling locations for the scallops also reflect the spatial distribution of the species. In general, locations in the north and north west (the Orkneys, Outer Hebrides and Northern Highlands) contained lower levels of contaminants. Locations in the Southern reaches of the Highlands (S Minch) and the Clyde region generally provided samples with greater levels of contaminants. This is consistent with the levels of industrial activity in these areas. However the detection of most contaminants albeit at low levels in some of the more remote areas confirms the long-range transport of these compounds, which is a defining characteristic of persistent organic pollutants.

3.2 Dietary intakes

The data generated from this study was used to estimate dietary intakes for adults and these are summarised in Table 3. Although dietary surveys of UK consumers in various age groups have been carried out, they were too few or no recorded consumers to provide robust consumption data in the case of the shellfish species included in this survey. Instead, dietary intakes of chlorinated and brominated chemicals from shellfish alone have been estimated from the measured concentrations, assuming an average adult portion size of 70 g for all species. Average dietary intakes of the contaminants of interest by adults from the non-fish part of the diet were estimated by combining the results of the most recent total dietary study surveys for the various groups of chemicals [3, 41] with food consumption data from the National Diet and Nutrition Survey: adults aged 19 to 64 years [54], which recorded the food consumed by each of 1724 adults over a seven day diary period. Daily intake can then be estimated by combining the intake from one portion of shellfish with the intake from the rest of the diet.

The *upper bound* dietary intakes of the different groups of chemicals estimated by this method are 0.5–0.7 pg WHO-TEQ/kg bodyweight/day for PCDD/Fs and PCBs (based on the 2005 TEFs, which are more relevant to intake assessment), 0.4 pg WHO-TEQ/kg bodyweight/day for PBDD/Fs, 5.6–6.1 ng/kg bodyweight/day for total PBDEs, and 5.9–7.9 ng/kg bodyweight/day for total HBCDs.

The dietary exposure of adults to PCDD/Fs dioxin-like PCBs arising from a typical level of consumption of these shellfish in combination with the average consumption of the rest of the diet is well within the UK Tolerable Daily Intake of 2 pg WHO-TEQ/kg bodyweight/day endorsed by the COT. Because toxicological data for PBDEs and HBCDs are limited, the COT has not been able to set Tolerable Daily Intake for these substances. However, the COT have previously concluded that the concentrations of the brominated compounds reported in the UK Food Standards Agency's surveys for the chemicals in farmed and wild fish and shellfish [1] and Total Diet Study samples [41] do not raise toxicological concerns. The ranges of concentrations found in the Scottish shellfish samples were similar to those in the farmed and wild fish and shellfish survey and the contribution from shellfish to exposure to the contaminants measured is not significant when compared to exposure from the rest of the diet.

4 Concluding remarks

The levels reported of the various contaminants that were measured in this work are consistent with literature obser-

Table 3. Summary of estimated dietary intakes contaminants from one weekly portion of shellfish in combination with the rest of the diet

	pgWHO-TEQ/kg bodyweight/day		PCDD/F & PCB 2005 WHO-TEQ	PBDD/F & PBB 2005 TEQ	
Oysters	Min		0.55	0.41	
	Mean		0.57	0.41	
	Median		0.56	0.41	
	Max		0.61	0.43	
	ng/kg bodyweight/day	α HBCD	β HBCD	γ HBCD	Sum PBDEs
	Min	0.01	0.005	0.005	0.03
	Mean	0.07	0.02	0.01	0.07
	Median	0.07	0.01	0.007	0.05
	Max	0.16	0.04	0.02	0.15
	pgWHO-TEQ/kg bodyweight/day		PCDD/F & PCB 2005 WHO-TEQ	PBDD/F & PBB 2005 TEQ	
Mussels	Min		0.54	0.41	
	Mean		0.57	0.41	
	Median		0.56	0.41	
	Max		0.64	0.42	
	ng/kg bodyweight/day	α HBCD	β HBCD	γ HBCD	Sum PBDEs
	Min	0.02	0.002	0.005	0.03
	Mean	0.23	0.04	0.04	0.11
	Median	0.07	0.02	0.02	0.06
	Max	1.49	0.27	0.25	0.46
	pgWHO-TEQ/kg bodyweight/day		PCDD/F & PCB 2005 WHO-TEQ	PBDD/F & PBB 2005 TEQ	
Scallops Gonad (Adductor)	Min		0.53 (0.52)	0.41 (0.41)	
	Mean		0.55 (0.52)	0.42 (0.41)	
	Median		0.55 (0.52)	0.42 (0.41)	
	Max		0.57 (0.52)	0.44 (0.41)	
	ng/kg bodyweight/day	α HBCD	β HBCD	γ HBCD	Sum PBDEs
	Min	0.01 (0.002)	0.002 (0.002)	0.002 (0.002)	0.02 (0.01)
	Mean	0.08 (0.007)	0.009 (0.005)	0.007 (0.004)	0.07 (0.01)
	Median	0.04 (0.006)	0.003 (0.003)	0.005 (0.003)	0.05 (0.01)
	Max	0.29 (0.02)	0.04 (0.01)	0.03 (0.008)	0.2 (0.03)

vations made for shellfish, as well as the environmental and biological characteristics of contaminant bio-accumulation. Thus for example, scallop muscle tissue (adductor) generally shows relatively lower contaminant levels as compared to the gonad, reflecting the fat content of the latter. Apart from the PBDD/Fs, oysters and mussels generally showed higher levels of contaminants compared to the scallops. Although the availability of data for dioxin and PCB WHO-TEQ in shellfish resulting from structured studies is low, the findings presented in this work do not suggest that the downward trend observed for other foods [42] is repeated in shellfish concentrations. Nevertheless, the reported levels are already low compared with other foods. The general lack of data on the brominated contaminants does not allow observations on the trend in occurrence for these compounds. The continued use of BFRs and the resulting potential of PBDD/F formation from the disposal of these materials make it prudent to continue surveillance for the presence of these contaminants.

The estimated levels of human exposure to chlorinated and brominated contaminants as a result of shellfish consumption do not raise any cause for concern.

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