Occurrence and Spatial Distribution of Chemical Contaminants in Edible Fish Species Collected from UK and Proximate Marine Waters

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Key-Words – PCDD/Fs, PXDD/Fs, PCNs, PBDEs, PFAS, Food, Occurrence trends

Abstract

The occurrence of a range of regulated and emerging organic environmental contaminants was investigated in 182 samples of edible marine fish sampled mainly from UK marine regions, but extending northerly to the coast of Norway and south to the Algarve. These species (sprats, mackerel, turbot, halibut, herring, grey mullet, sea bass, grey mullet, sardines, etc.) are among those considered to be at the highest risk of contamination with regulated contaminants such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs, dioxins), and polychlorinated biphenyls (PCBs), but the occurrence of polybrominated diphenylethers (PBDEs) and polybrominated biphenyls (PBBs) was also investigated. Sub-sets of samples (50 - 75) were also analysed for emerging contaminants: polychlorinated naphthalenes (PCNs), polybrominated and mixed halogenated dibenzo-p-dioxins, dibenzofurans and biphenyls (PBDD/Fs, PXDD/Fs and PXBs) and perfluoroalkyl substances (PFAS). Contaminant occurrence varied with species and location, but all measured contaminants were detected, with sprats, sea bass, sardines, mackerel, and herring showing higher tissue concentrations. The concentrations of the different contaminants in the various samples were mapped utilising the GPS coordinate data of the capture locations to visualise spatial distribution levels. In terms of catch location, fish sampled from the coasts of southern Britain, north-western France and the Irish Sea appeared to contain proportionately higher levels of some contaminants - e.g. samples from the Irish Sea tended to show higher PCN concentrations, whereas higher levels of PCBs were observed in some fish sampled off the coasts of northern France. Similarly, samples of mullet from the southeast coast of UK showed much higher concentrations of BDE-99 than the other regions. In terms of occurrence trends, PCDD/F and PCB concentrations show a modest decline over the last decade but where limited background data is available for emerging contaminants, there is no evidence of downward trends.

1. Introduction

As a protein-rich and generally low fat food, seafood forms an important part of the human diet, either because of personal taste or for nutritional reasons. However it is increasingly recognised that marine fish and shellfish bio-accumulate contaminants and some species, such as dabs and mussels, have been used as indicators of local pollution. In recent times marine fish have been shown to contribute significantly to the dietary exposure of a number of organic environmental contaminants.

Within the EU, the Marine Strategy Framework Directive (MSFD) encourages collaboration and coordination between member countries in order to reduce pollution inputs and improve the sustainability of marine ecosystems. Under the directive, one of the descriptors for Good Environmental Status (GES) involves the reduction of fish and seafood contamination, including compliance with regulated maximum contaminant levels or other relevant standards. However, in addition to regulated contaminants, this study also targets a number of other contaminants that are either listed within the Stockholm Convention or are under assessment by the European Commission Expert Committee on persistent organic pollutants (POPs) in Food.

Retail fish in the UK markets are sourced both locally and from other parts of the world. However, within the geographical scope of this study, the main areas targeted for investigation

focussed on marine locations around the UK and the European coastal North Atlantic. Other proximate relevant fishing grounds such as Biscay, the Algarve and the Irish Sea with Celtic sea sub-regions were also included, specifically because fish from these regions is widely sold in UK markets.

Commonly consumed fish species were targeted, including oily fish. Earlier studies (Fernandes et al., 2009; 2009B) had shown that these species showed relatively high contamination levels and were likely to indicate the upper margin of the contamination range. Thus the focus was on species such as herring, mackerel, sea bass, sardines, etc. but other species e.g. dogfish, turbot etc. were also included.

The contaminants selected for this study represent a range of established/regulated and emerging contaminants that are recognised to be persistent, bio-accumulative and toxic, with the potential to undergo long-range transport. Most - polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), polybrominated biphenyls (PBBs), polybrominated diphenylethers (PBDEs), perfluorooctane sulphonate (PFOS) - are listed under the Stockholm Convention.

Dietary intake is recognised to be the major pathway of human exposure to PCDD/Fs and PCBs, and concentrations of these contaminants in food is subject to EU regulations (European Commission, 2012). Earlier studies (Fernandes et al., 2004; 2009B) have shown a higher prevalence of these contaminants in fish and seafood. This was confirmed by the last UK Total Diet Study (TDS) (Fernandes et al., 2012) which showed a clear elevation of these contaminants in fish relative to other food groups. The study also noted a decline in the concentration for the fish group, of 4.6 ng/kg to 3.5 ng/kg WHO-TEQ when compared to the previous TDS, although this could in part, be due to the revision of the WHO-TEF values (Van den Berg et al., 2006) that were used in the latter study, which tend to yield lower TEQ values.

PBDEs are a widely studied class of brominated flame retardants (BFRs) that were formerly mass produced. Although manufacturing has been restricted in recent years, they still occur in many existing products either as a result of imports or through the recycling of older materials. Open-ended applications, can result in PBDE diffusion out of materials during manufacture, use and disposal of the product. Toxicological data shows that PBDEs can cause liver and neurodevelopmental toxicity, affect thyroid hormone levels and may be particularly harmful during a critical window of brain development during pregnancy and early childhood (Rose and Fernandes, 2012). A number of studies (Bichon et al., 2016; Fernandes et al., 2009; 2014, 2016, Martellini et al., 2016; Schecter et al., 2010) have established their frequent and widespread occurrence which generally tend to show higher concentrations in fish relative to other foods. Following an earlier call (European Commission, 2014) for occurrence data and the establishment of a European Union Reference laboratory, it is possible that PBDE levels in food will be regulated within the EU.

PCNs were industrial chemicals widely used in the 20th century. With physico-chemical properties similar to PCBs they had very similar industrial applications with the exception that PCNs were also used as flame retardants. Environmentally, PCNs also demonstrate properties of persistence and high bioaccumulation potential, coupled with a similarity in structural configuration to PCDD/Fs. Many congeners have been reported to contribute to dioxin-like

toxicity (Falandysz et al., 2014; Fernandes et al., 2017) eliciting a range of toxic responses such as mortality, embryotoxicity, hepatotoxicity, dermal lesions, teratogenicity and carcinogenicity, although not all can be attributed to a dioxin-like pathway (Behnisch et al., 2003; Blankenship et al., 2000). Earlier reports ((Fernandes et al., 2010, Fernandes, 2013) and a recent review of their occurrence in human tissue and foods (Fernandes et al., 2017) show higher occurrence levels in fish relative to other foods.

Following similar thermodynamic pathways as their chlorinated counterparts, PBDD/Fs can be formed during incineration, particularly of bromine containing waste, or as inadvertent by-products during chemical manufacture of brominated products. PBBs however, were manufactured in large volumes as flame retardants. Both of these classes of contaminants have been detected in earlier studies on food (FSA, 2006, 2006B) in the UK, including an investigation on marine fish. These studies showed that PBDF occurrence was more frequent relative to PBDDs, whilst PBBs were rarely detected or occurred at very low levels. This pattern of occurrence was confirmed in later studies on individual foods including fish and shellfish (Fernandes et al., 2008, 2009, Zacs et al., 2013, 2016).

Mixed bromo/chloro-substituted dioxins, furans and biphenyls (PXDD/Fs and PXBs) are also formed during incineration processes and elicit similar toxicological responses as the other analogues. Unlike PCBs or PBBs, PXBs were never intentionally produced as industrial chemicals. Analysis of this class of contaminants is complex due to the large numbers of possible compounds (4600 PXDD/Fs and 9180 PXBs) and the potential for false positive detection during mass spectrometric measurement, as these compounds share ions with other more abundant and less toxic contaminants. Toxicologically, the potency of some PXDD/F congeners is similar to the most toxic PCDD/Fs, but some congeners reportedly demonstrate a greater potency (Wall et al., 2015). A difficult analytical access has limited the number of studies on these contaminants, but occurrence had been demonstrated in foods including fish (Ohta et al., 2008; Fernandes et al., 2011, 2014; Zachs et al., 2013, 2016) and the current study will provide a baseline for levels in marine fish.

Perfluoroalkyl substances (PFAS), are a group of persistent and bio-accumulative group of contaminants which include the widely studied perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA). These industrial chemicals were manufactured for their non-stick and water repellent properties which found applications as coatings for fabrics and furnishings. They were also used in fire-fighting foams. PFAS bio-accumulate up the food chain through utilisation or disposal routes, or enter directly into food through primary contamination events. Food has been shown to be an important pathway to human exposure and PFAS are commonly detected in foods (Clarke et al., 2010; Noorlander et al., 2011; Pico et al., 2011; Fernandes et al., 2012; Stahl et al., 2014; Vassiliadou et al. 2015). All studies report positive detection of PFAS compounds in fish.

This study aims to characterise the occurrence and spatial distribution of these contaminants in commonly consumed fish species from UK proximate waters and from other proximate fishing areas from which retail fish in the UK is commonly sourced. There are a number of possible outputs from such a study – definition of an occurrence baseline for some hitherto unmeasured contaminants, the current occurrence levels of the studied contaminants, the geographical distribution of these contaminants in marine environments around the UK, risk assessment

arising from human dietary intake through fish consumption - some of which will be addressed in this report – and it provides a baseline of evidence for GES for Descriptor 9 under the MSFD.

2. Sampling and Analysis

2.1 Sampling and Sample Preparation

182 samples covering a range of marine species (sea bass, mackerel, herring, sprats, grey mullet, sardines, turbot, halibut, various shark species etc.) were collected mainly from the waters around the UK and the European coastal North Atlantic. The wider sampling area extended north to the coast of Norway and south to the Algarve. This area included proximate relevant fishing grounds such as the North Sea and the Greater North Sea sub-region, Biscay, the Algarve and the Irish Sea with Celtic sea sub-regions.

Samples were dissected to collect edible muscle tissue excluding skin, organs and bones. However whole fish were used for some of the smaller species, e.g. sprats. In general, the preparation of samples was guided by domestic fish preparation procedures. Samples thus prepared were minced and homogenised by blending with an aliquot set aside for PFAS analysis. The remainder of the sample was lyophilised and re-homogenised to yield a dry powder which was aliquoted for the other analyses.

2.2 Measurands

The following analytes were determined: Regulated contaminants are highlighted in bold.

- Dioxins - **all 17, 2378-Cl substituted PCDDs and PCDFs**.
- Dioxin-like PCBs - IUPAC numbers **77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189.**
- Non Dioxin-like PCBs - IUPAC numbers 18, **28**, 31, 47, 49, 51, **52**, 99, **101**, 128, **138, 153**, and **180**.
- PBDE congeners: IUPAC numbers 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 183 and 209.
- PBB congeners: IUPAC numbers 15, 49, 52, 77, 80, 101, 126, 153, 169 and 209.
- PCNs - PCN-52/60, 53, 66/67, 68, 69, 71/72, 73, 74, & 75.
- Brominated dioxins - 2,3,7-T_3BDD, 2,3,8-T_3BDF, and ten, 2,3,7,8-Br substituted tetra – hepta- brominated PBDD/F congeners (Fernandes et al 2008).
- Mixed halogenated dioxins and biphenyls (PXDD/F and PXBs) - 13, tri - hexa halogenated PXDD/DFs and 6 coplanar and mono-ortho substituted biphenyls. (Fernandes et al 2011).
- PFAS - Perfluorooctanesulfonylamide (PFOSA), Perfluorobutane sulfonate (PFBSH), Perfluorohexane sulfonate (PFHxS), Perfluorooctane sulfonate (PFOS), Perfluorooctanoic acid (PFOA), Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDeA), Perfluoroundecanoic acid (PFUnA) and Perfluorododecanoic acid (PFDoA).

2.3 Analysis of dioxin-like contaminants and PBDEs

The analytical methodology used for the extraction, purification and instrumental measurement of chlorinated, brominated and mixed halogenated dioxins/furans and biphenyls have been reported previously (Fernandes et al., 2004B, 2008, 2011). Similarly, the methodology for PBDE and PCN analysis has also been reported earlier (Fernandes et al., 2004B, 2010). Summarising these procedures, aliquots of the selected samples were fortified with ^{13}C-labelled analogues of target compounds and exhaustively extracted using mixed organic solvents. Extracts were fractionated on activated carbon, concentrated and purified using adsorption chromatography on alumina. Measurement was carried out using high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) at a resolution of 10,000, except for the PXDD/Fs and PXBs for which 13,000-15,000 resolution was used.

The methodology used for the analysis has been extensively used in other studies (Fernandes et al., 2008, 2009, 2009B, 2010, 2011, 2012, 2014, 2016) and was robustly validated prior to sample analysis. Method performance parameters have been reported before (Fernandes et al., 2004B, 2008, 2010, 2011). The analytical process that was used for many of the contaminants was accredited to the ISO 17025 standard. Equivalent standards were used for other contaminants, with the inclusion of in-house reference materials and method blanks which were evaluated prior to quantitation and reporting. Further quality assurance measures included the successful participation in international inter-comparison exercises on PCDD/Fs, PCBs and PBDEs (Dioxins in Food, 2013, 2014, 2015) over the course of this project. Analytical recoveries based on the use of ^{13}C labelled surrogates were typically in the range of 50 to 110% for PCDD/Fs, PCBs, PBDEs, PXDD/Fs and PXBs. Due to their higher volatility, PCN recoveries were typically in the range of 40 to 80%. More details on quality control aspects can be found in the sponsor report (Fernandes et al., 2015). Measurement uncertainty (expanded uncertainty with a coverage factor of 2) estimates range from around 20% (at $\geq$ 10x the limit of detection, to around 200% at the limit of detection.

2.4 Analysis of PFAS

A detailed description of this procedure has been given elsewhere (Clarke et al., 2010). Briefly, replicate samples were fortified with the appropriate unlabelled standards and labelled internal standards, extracted overnight with methanol, concentrated and treated with aqueous KOH. Extracts were purified by methanol elution through a preconditioned weak anion exchange SPE cartridge and analysed using LC-MS/MS (Agilent 1290 LC - Agilent 6490 triple quadrupole mass spectrometer) in multiple reaction monitoring (MRM) mode.

The specificity of the measurement process for these compounds owes much to the use of LC-MS/MS in MRM mode in combination with the use of ^{13}Carbon labelled and deuterated analogues as internal standards. All samples were analysed in duplicate with procedural blanks and additionally with an aliquot over-spiked with the target compounds to validate the measurement and quantitation process.

2.5 Spatial Distribution

To better visualise the geographical dispersion of the contaminants, an interactive webpage (www.fishplots.droppages.com) was designed based on Google Maps which utilised sample GPS location data and the sample concentrations. Proportionate concentration levels contained within samples may be efficiently represented by the size of circles located at the associated sample spatial coordinates of the catch site. This technique provides rapid visualisation of the spatial distributions of selected contaminants within species.

3.0 Results & Discussion

As would be expected from a study of this magnitude, the volume of raw data generated is very large, and has been presented in a sponsor report (Fernandes et al., 2015). The results are statistically summarised in Tables 3.1 to 3.4, by species. As per convention, the concentrations of PCDD/Fs and dioxin-like PCBs has been summarised as toxic equivalents (WHO-TEQ), using the 2005 toxic equivalent factors (TEF_{2005} - Van den berg et al., 2006). The TEQ approach has also been used for other AhR active contaminants (PBDD/Fs and PCNs) and, given the scarcity of data for PXDD/Fs & PXBs, the occurrence ranges have been summarised. Also in keeping with convention, upper bound (UB) TEQ values have been reported for PCDD/Fs, PCBs and PCNs. This is appropriate mainly because the vast majority of measured congeners were detected, so UB TEQs would be more representative, but additionally, as a theme of this work is food safety, UB TEQs also reflect the higher risk limit. However a significant proportion of PBDDs were not detected, so for this class of contaminants, both, UB and lower bound TEQ has been reported.

The reporting limits (quoted as "<") for all analytes incorporate the relevant procedural blank and were estimated as a dynamic parameter following the current guidance on LOQ estimation (European Commission, 2017). The resulting limits were better than those required for the regulated contaminants, but for all reported contaminants, the limits were generally either better than or similar to those reported in current literature.

It is important to note that one of the main foci of the study was food safety and the analytical samples were composed of edible fish tissue, rather than the whole fish (except for smaller species where the entire fish is consumed e.g. sprats). Given the physiological characteristics of fish in general and the lipophilicity of the contaminants studied, the reported concentrations (which exclude organs such as fish liver, in particular) are likely to be underestimates of the whole fish concentrations.

3.1 PCDD/F and PCBs

The PCDD/F and PCB concentrations for all the major fish species studied are summarised in Table 3.1. The levels of occurrence ranged from 0.03 to 12.5 ng sum WHO-TEQ/kg whole weight (ww), with an average concentration of 1.4 ng WHO-TEQ/kg ww. The corresponding summed ICES-6 PCB concentrations ranged from 0.1 to 145 µg/kg ww. The extent of occurrence varied, with some species (sea bass, sprats, sardines) showing higher levels of bioaccumulation with average sum WHO-TEQ concentrations of 2.5, 2.0 and 2.0 ng/kg respectively. In comparison to a study conducted approximately twelve years ago (Fernandes

et al., 2009B), with sum WHO-TEQ concentrations of 3.7 and 4.3 ng/kg for sea-bass and sprat respectively, the current results represent a modest decline in occurrence levels. However, data from the earlier study would have been calculated using TEF_{1998} factors which generally result in higher WHO-TEQ values. The existing EU regulation (European Commission, 2011), specifies a maximum limit for fish muscle of 3.5 ng/kg for PCDD/F WHO-TEQ and 6.5 ng/kg for summed PCDD/F and PCB WHO-TEQ, respectively. It was found that two of the samples (one each of sea-bass and mackerel) that were taken from waters off northern France, showed sum WHO-TEQ concentrations of 12.5 and 7.5 ng/kg respectively. The corresponding summed ICES-6 PCB concentration for the sea-bass was 145 µg/kg ww relative to the maximum limit of 75 µg/kg ww. In general, PCBs made a greater contribution to TEQ relative to PCDD/Fs, an observation that was consistent with other studies on fish and with the earlier study (Fernandes et al., 2009B).

3.2 PBDEs

With the exception of BDE-126, all measured PBDE congeners were detected at various levels (Fernandes et al., 2015). A summary of the data is presented in Table 3.1 which provides descriptive statistics for each of the major fish species for the sum of all measured PBDEs (17 congeners), as well as the sum of the ten PBDEs (EU_{10}) specified for EU monitoring (European Commission, 2014). There are only minor differences between the average values for the sum of the 17 congeners and the EU_{10}, which confirms an informed choice of congeners for the EU list. For the sum of all measured PBDEs, concentrations ranged from 0.04 µg/kg to 8.87 µg/kg ww (corresponding to 0.04 µg/kg to 8.63 µg/kg for EU_{10}). The highest average values were observed for herring, sea bass, mackerel and sprat (2.08, 2.0, 1.45 and 1.27 µg/kg respectively). The average concentration across all samples was 1.2 µg/kg (or approximately 35 µg/kg on a fat weight basis). When compared to earlier fish data from 2007 (Fernandes et al., 2014B), on individual foods including fish (n=36 mostly oily species) the average concentrations are not dissimilar (25 and 35 µg/kg fat weight for the 2007 study and current study respectively). Thus this data provides no evidence of a downward trend in PBDE concentrations in marine species.

PBBs were detected less frequently and at lower concentrations (Fernandes et al., 2015), confirming other reported data (Fernandes et al., 2008, 2012, 2016). The highest concentration observed was 0.65 µg/kg for BB-52 for grey mullet from France. In general, most of the higher PBB concentrations were observed for samples taken from waters off the southern coast of England and northern France. PBBs are generally not detected, or occur at very low concentrations in foods in the UK (Fernandes et al., 2016), so these higher concentrations may reflect a higher level of PBB utilisation in France.

3.3 PCNs

PCNs were measured in a sub-set of 75 samples representing seven species (Table 3.2). Concentrations are reported as the sum of twelve measured congeners, ranging from 0.7 ng/kg ww for a turbot sample to 265 ng/kg ww for a sample of sprats. The highest concentrations

were recorded for sprats and mackerel with mean concentrations of 67 ng/kg ww and 68 ng/kg ww respectively. Converting to TEQ (Fernandes et al 2010), these corresponded to mean PCN TEQ concentrations of 0.17 and 0.26 ng TEQ/kg ww respectively. An earlier study on individual UK foods (Fernandes et al., 2010) showed a mean concentration for fish (individual samples of salmon, herring, sprats, eels, trout, etc.), of 20 ng/kg ww for the sum of 12 congeners, and in a later TDS (Fernandes et al., 2012) the concentration in the fish group was 6.6 ng/kg ww. The TDS fish group is comprised of both white and oily fish, and also includes shellfish, in comparison to the mostly oily species targeted in this study. In the current study, the highest PCN concentrations were recorded for samples from the Irish sea, although locations across the southern/eastern UK coasts and northern France showed a majority of the higher concentrations.

3.4 PBDD/Fs

As reported in earlier studies on PBDD/Fs (Fernandes et al., 2008, 2009), PBDFs occurred at a greater frequency than PBDDs, with some congeners such as the penta- and hexa-BDD remaining undetected. In order to enable comparison with other studies the concentration data were summarised to yield TEQ values, using the analogous chlorinated dioxin TEFs. The limitation of this conversion must be recognised as there is no universally recognised TEF scheme as yet for PBDD/Fs. The resulting TEQs were lower than the corresponding PCDD/F TEQs ranging from 0.001 to 0.04 ng/kg TEQ ww (Table 3.2) which is comparable to the PBDD/F TEQ concentration in the fish group in the last TDS (Fernandes et al., 2012) at 0.02 ng/kg ww.

3.5 PXDD/Fs and PXBs

With the exception of two samples of sea-bass, at least one PXDD/F congener was detected in all 59 samples analysed in this sub-set (Fernandes et al., 2015). Concentrations were low in comparison to the PCDD/Fs. The data is summarised by species in Table 3.3. PXBs were detected at a greater frequency than PXDD/Fs, and occurred in all samples with the highest concentrations being observed in mackerel, sprats and sea-bass. In general, the frequency of detection was similar to that observed in an earlier study on foods (Fernandes et al., 2014) and followed the order PXBs>PXDFs>PXDDs. In the earlier study, a set of 40 fish samples were analysed with concentrations ranging from <0.005 to 1.12 ng/kg fat for PXDD/Fs and <0.005 to 14.7 for the PXBs. In the current study a similar range for PXDD/Fs (<0.005 to 1.62 ng/kg fat) was observed, but the upper end of the range for PXBs (<0.005 to 42 ng/kg fat) was approximately a factor of 3 higher than the earlier study. In general, the samples associated with the higher PXB concentrations were taken from northern France/southern UK waters and the Irish Sea.

3.6 PFAS

A sub-set of 50 fish samples covering 6 species was analysed for PFAS with positive detection in all samples. The higher concentrations were generally seen in sardines, sprats and sea bass, with PFOS, PFOSA and PFOA usually showing the highest values (Table 3.4). Higher concentrations tended to be seen more frequently in samples from southern UK waters and the Irish Sea. It is difficult to make comparison to earlier studies on fish in the UK because of the very different method sensitivities, which resulted in most analytes remaining undetected in earlier work. More recently, a total concentration of 12.6 µg/kg ww recorded for the fish group in the last TDS (Fernandes et al., 2012) was comparable to the recorded range (0.64 to 15.3 µg/kg ww) in this study.

3.7 Geographical distribution of a single contaminant in single/multiple fish species

As an example of the spatial mapping, Figure 1 displays the concentration distribution of BDE-99 in sea bass along the south coast of England, which clearly shows that the samples from the southeast coast contain higher concentration of BDE-99 than the other regions. Sea bass may be a particularly good local indicator as it is both territorial and highly predatory.

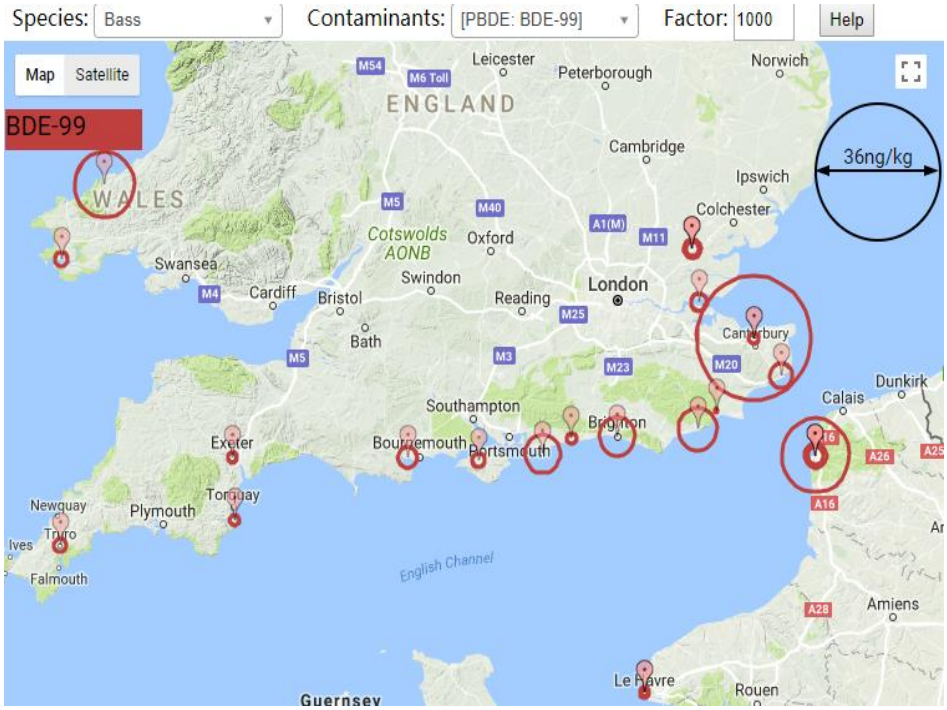


Figure 1. Example of the distribution of BDE-99 in Sea Bass on the UK south coastal area.

Furthermore，the distribution of a single contaminant (e.g. BDE-99) in multiple fish species may be compared by attaching different colours to different fish species as shown in Figure 2. Generally, the samples from north of England and English Channel showed much higher concentration of BDE-99 than the other regions, and it is clearly shown that mackerel and herring exhibited higher concentration relative to the other species. Compared with BDE-99, the concentration of BDE-47 in sea bass presented a different distribution pattern along the

south coast of England with samples from the middle reaches of the coast showing relatively lower concentrations. Most of higher concentrations of BDE-47 in this region were seen in sea bass and mullet. Similarly, the southern coast also showed the highest concentrations of PCB-153 in sea bass and other fish species.

3.8 Geographical distribution of multiple contaminants in single/multiple fish species

Similarly in Figure 2, different colours may be used to represent different contaminants in a single species. Figure 3 shows a spatial distribution of all PBDE congeners in turbot. No clear geographical distribution trend was found for the PBDEs in turbot, but it is clear that BDE-47 occurs at a higher concentration. Another way of visualisation would be to incorporate TEQ values to demonstrate the toxicity distribution. Figure 4 demonstrates effective method representation by showing the spatial distribution of PCN52 in different fish species across the south of the UK and northern coast off France.

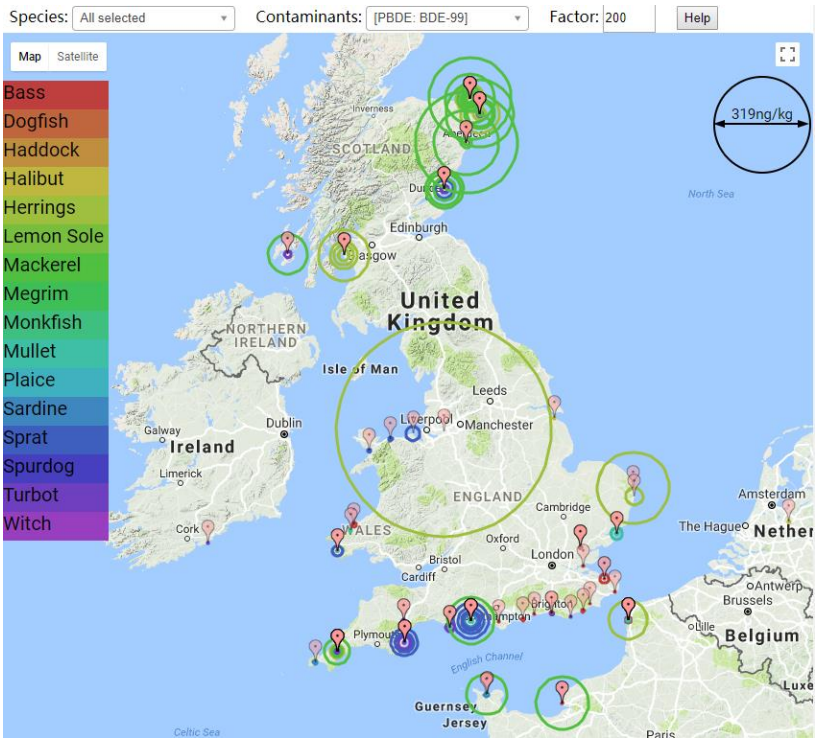
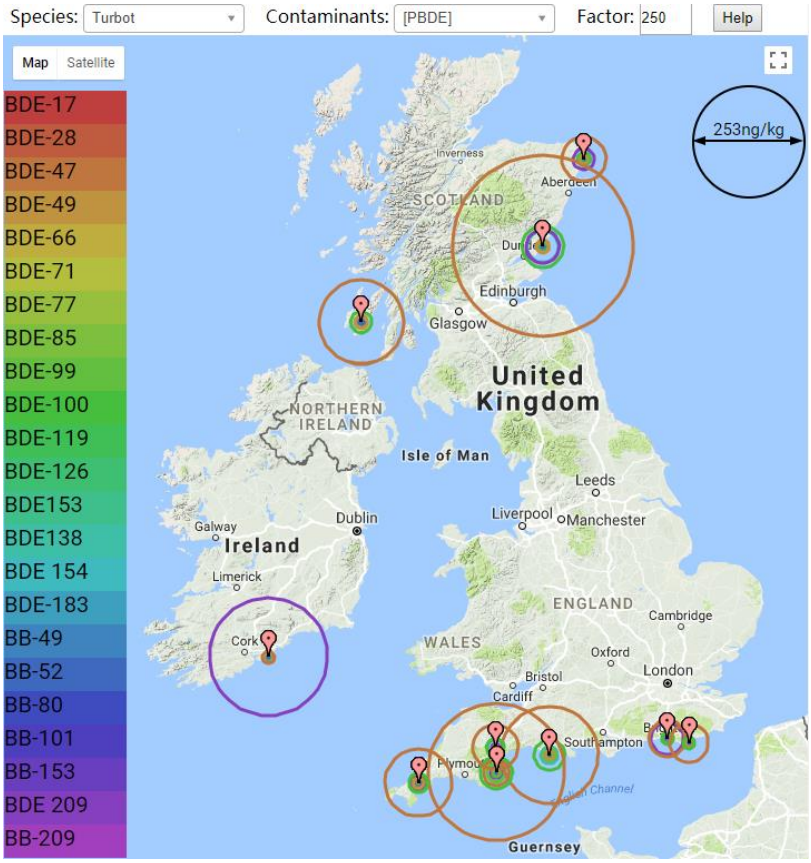


Figure 2 Geographical distribution of BDE-99 across different fish species



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401 **Figure 3** Geographical distribution of PBDE in Turbot in various locations across the UK.

Figure 4 Spatial distribution of PCN52 in different fish species. The interactive inset box provides specific details (concentration, location, date, etc) in a sample of mullet.

3.9 Discussion

The data generated by this study provides a number of different aspects for investigation. Given that edible species were measured, a major consideration was food safety and the trend in contaminant concentrations from previous studies. As some of the species included had not previously been tested and some emerging contaminants had not previously been measured, this was only possible for PCDD/Fs, PCBs, PCNs and PBDEs in some species. For sea-bass, sprat, herring and mackerel measured in 2003-2004 (Fernandes et al., 2009), PCDD/Fs concentrations reduced from 3.7, 4.3, 3.6 and 1.9 ng/kg ww WHO-TEQ to 2.5, 2.0, 1.2 and 1.4 ng/kg ww WHO-TEQ respectively. The corresponding summed ICES-6 PCB concentrations declined from 25, 21, 20 and 14 µg/kg ww to 22, 11, 8.5 and 10.5 respectively. This decline in occurrence levels would correspond to a modest reduction in the dietary exposure of these contaminants relative to earlier estimates on the consumption of varying portions of these species per week (COT, 2006). The compliance of the vast majority of samples with the regulatory limits specified in European commission regulations for PCDD/Fs and PCBs (European Commission, 2011) taken together with the reduction in mean levels suggest a small

downward trend in the concentrations of these contaminants. This concurs well with other reported declines for fish species from European waters (Airaksinen et al., 2014; Perello et al., 2015). Vuorinen et al., 2017, note a decreasing trend in Baltic herring for PCDD/F plus PCB TEQ since the late 1970s, although older herring specimens exceeded the maximum limit set by the EC. Spatial variation was also observed with PCB contamination in Baltic herring being higher in the eastern part of the Gulf of Finland relative to the western part (Jarv et al., 2017). This decline is not mirrored for other contaminants where a comparison is possible. PBDEs, PBDD/Fs and PFAS, for example, show no discernible trend and the mean PCN concentration of 45 ng/kg ww for the samples in Table 3.2 is higher than the mean concentrations reported earlier (20 ng/kg ww) for fish in the UK (Fernandes et al., 2010) or that reported (22 ng/kg ww) for fish from Ireland (Fernandes et al., 2011). These earlier studies were carried out in the same laboratory using the same methodologies.

For the fish species studied here, the dietary exposure for PCDD/Fs and dioxin-like PCBs resulting from the consumption of one portion of non-oily fish such as shark and sea-bass was earlier estimated to be in the range of 0.7 to 1.9 pg TEQ/kg bodyweight/day, and 1.3 to 2.1 pg TEQ/kg bodyweight/day for oily species such as mackerel and sprat (COT, 2006). When other dioxin-like contaminants such as PBDDs, PBDFs and PBBs were included, the exposure increased to range from 1.1 to 2.3 pg TEQ/kg bodyweight/day for non-oily species and 1.7 to 2.5 pg TEQ/kg bodyweight/day for oily species. In very general terms, the reduction in occurrence levels reported here for PCDD/F and PCB TEQ in these species would correspond to a modest reduction in dietary exposure as compared to earlier estimates.

Direct comparisons of data from marine species may not be straightforward because individual sample characteristics such as age of the fish, location of catch, time of year, etc., all contribute to the observed contaminant concentrations. Nonetheless given the numbers of samples measured in this study, the average levels suggest variations in trends for emerging contaminants, rather than the modest decline observed for PCDD/Fs and PCBs. Where levels in terrestrial based foods show declines, these can be attributed to local and regional emission control regulations or the voluntary phasing out of contaminants such as PBDEs. It is evident that the marine environment does not respond to control as easily as regional land controls and that the effects of controls become evident over a much longer time-scale within the marine environment as inputs from anthropogenic activity decline.

The other aspect considered in this paper was the spatial distribution of the measured contaminants in different species and locations. Spatial analysis showed that mackerel from waters south of the UK and north-west of France appeared to show relatively higher levels of PCDD/F and PCB contamination, but PBDE levels for this species were higher for samples from the southern coast of England/north-western France and the Irish Sea (mean concentrations of 1.6 and 2.1 µg/kg respectively for EU_{10} PBDEs, compared to the mean value of 1.35 µg/kg for the whole group. Corresponding PCN mackerel levels were generally highest for Irish Sea samples. Sprats and sea-bass showed relatively higher PCDD/F, PBDE and PCN

460 contamination in waters off the south of the UK and north-west of France. Herring from the
461 waters off the east coast of England and the Irish Sea showed relatively higher levels of
462 contamination, but the highest levels of PBDE and PCN contamination were more evenly
463 distributed around the UK. For most of the contaminants studied here, turbot appeared to show
464 low occurrence levels. This spatial contaminant distribution accords well with known
465 anthropogenic activity in the areas where fish were found to be more contaminated – e.g. the
466 English Channel (southern and south-eastern UK/northern France) experiences one of the
467 highest proportions of maritime traffic, with high levels of industrialisation near the coastal
468 areas. The findings are also consistent with a known contamination problem in the Seine Bay,
469 arising from a high loading of PCBs from the river Seine, which led to a French government
470 ban on sardine fishing in the area (Prefecture de la Seine-Maritime, 2010). Similarly, the coastal
471 areas around the northern Irish Sea contain pockets of heavy industry such as ship building.
472 The spatial analysis thus additionally provides an indication of the status of the regional marine
473 environment with regard to GES and supports evidence based decisions for assessors and
474 policy makers within the MSFD. The designed interactive webpage provides a convenient
475 method for the visualization of the geographical distribution of contaminants in different fish
476 species.

Table 3.1 Summary of whole weight PCDD/F & PCB WHO-TEQ, ICES-6 PCB and PBDE concentrations (upper bound)

Species→	Sardines	(n=16)			mackerel	(n=41)			Herring	(n=19)			GreyMullet	(n=26)		
	MIN	**MEDIAN**	**MEAN**	**MAX**	**MIN**	**MEDIAN**	**MEAN**	**MAX**	**MIN**	**MEDIAN**	**MEAN**	**MAX**	**MIN**	**MEDIAN**	**MEAN**	**MAX**
WHO-TEQ ng/kg																
PCDD/F	0.13	0.36	0.40	1.20	0.04	0.26	0.43	1.62	0.34	0.55	0.64	1.55	0.02	0.10	0.14	0.51
Non ortho-PCB	0.47	1.10	1.48	3.16	0.06	0.63	0.90	5.56	0.23	0.40	0.56	1.27	0.07	0.32	0.47	1.91
Mono-ortho-PCB	0.03	0.06	0.09	0.33	0.01	0.04	0.07	0.37	0.02	0.04	0.05	0.12	0.01	0.04	0.06	0.22
Sum WHO-TEQ	**0.63**	**1.51**	**1.97**	**4.37**	**0.10**	**1.05**	**1.40**	**7.51**	**0.64**	**1.00**	**1.24**	**2.78**	**0.11**	**0.48**	**0.67**	**2.36**
Sum ICES-6 PCBs µg/kg	**5.41**	**12.35**	**16.62**	**54.89**	**0.86**	**6.73**	**10.59**	**63.64**	**3.76**	**7.68**	**8.49**	**17.84**	**0.89**	**6.92**	**12.16**	**43.76**
Sum PBDEs µg/kg	**0.145**	**0.394**	**0.504**	**2.18**	**0.15**	**1.24**	**1.45**	**3.86**	**0.61**	**1.14**	**2.08**	**8.87**	**0.09**	**0.58**	**1.10**	**5.41**
Sum EU-10 PBDEs µg/kg	**0.13**	**0.38**	**0.49**	**2.12**	**0.14**	**1.16**	**1.35**	**3.65**	**0.58**	**1.10**	**2.00**	**8.63**	**0.08**	**0.57**	**1.08**	**5.36**

Species→	Sprat	(n=25)			Sea Bass	(n=25)			Turbot	(n=16)			Shark (various sp.)	(n=14)		
WHO-TEQ ng/kg																
PCDD/F	0.13	0.87	0.91	2.55	0.09	0.34	0.44	1.34	0.02	0.14	0.17	0.44	0.02	0.08	0.12	0.30
Non ortho-PCB	0.09	1.13	1.02	2.25	0.23	1.26	1.92	10.38	0.05	0.42	0.47	1.37	0.01	0.08	0.14	0.46
Mono-ortho-PCB	0.01	0.08	0.07	0.15	0.02	0.09	0.14	0.84	0.01	0.02	0.03	0.10	0.01	0.03	0.07	0.21
Sum WHO-TEQ	**0.23**	**2.14**	**2.00**	**4.35**	**0.35**	**1.65**	**2.50**	**12.49**	**0.07**	**0.66**	**0.67**	**1.91**	**0.03**	**0.22**	**0.32**	**0.93**
Sum ICES-6 PCBs µg/kg	**1.35**	**11.49**	**11.07**	**28.32**	**2.76**	**12.87**	**22.16**	**144.92**	**0.52**	**3.97**	**4.98**	**17.20**	**0.11**	**1.97**	**9.82**	**33.97**
Sum PBDEs µg/kg	**0.33**	**1.09**	**1.27**	**4.59**	**0.28**	**1.75**	**2.00**	**5.71**	**0.07**	**0.33**	**0.37**	**0.84**	**0.04**	**0.13**	**0.54**	**2.02**
***Sum EU-10 PBDEs µg/kg**	**0.31**	**1.05**	**1.23**	**4.56**	**0.27**	**1.73**	**1.97**	**5.64**	**0.06**	**0.31**	**0.35**	**0.79**	**0.04**	**0.12**	**0.51**	**1.91**

*EU-10 PBDEs – BDEs 28, 47, 49, 99, 100, 138, 153, 154, 183 and 209.

Measurement uncertainty is typically 15-20% for TEQ and sum PBDE, and around 15% for sum ICES-6. Values approaching the LOQ will show higher (up to 200%) uncertainty

Table 3.2 PCN and PBDD/F TEQ concentrations in marine fish species

Species (number)		Sum PCNs lower bound	Sum PCNs upper bound	*PCN TEQ upper bound	PBDD/F TEQ lower bound	PBDD/F TEQ upper bound
		ng/kg whole weight			ng/kg whole weight	
Sardines (12)	MIN	5.1	5.4	0.004	<0.001	0.012
	MEDIAN	16.6	16.6	0.007	0.003	0.019
	MEAN	19.7	19.8	0.009	0.006	0.021
	MAX	63.1	63.1	0.031	0.021	0.042
Mackerel (14)	MIN	10.0	10.1	0.002	<0.001	0.010
	MEDIAN	50.3	50.5	0.024	0.003	0.015
	MEAN	67.9	68.0	0.035	0.004	0.015
	MAX	243.0	243.0	0.170	0.012	0.031
Herring (6)	MIN	18.3	18.3	0.009	<0.001	0.014
	MEDIAN	29.5	29.7	0.016	0.002	0.016
	MEAN	38.5	38.7	0.024	0.005	0.019
	MAX	89.5	89.5	0.069	0.013	0.034
Grey mullet (9)	MIN	4.2	4.2	0.001	<0.001	0.008
	MEDIAN	12.2	12.4	0.006	0.003	0.012
	MEAN	14.6	14.7	0.007	0.005	0.013
	MAX	33.5	33.5	0.014	0.017	0.029
Sprat (15)	MIN	29.4	29.4	0.014	<0.001	0.007
	MEDIAN	46.0	46.0	0.027	0.002	0.016
	MEAN	66.4	66.5	0.044	0.004	0.016
	MAX	264.5	264.8	0.204	0.012	0.026
Sea Bass (13)	MIN	13.7	14.2	0.004	<0.001	0.010
	MEDIAN	28.6	29.2	0.008	0.002	0.012
	MEAN	29.3	29.4	0.010	0.003	0.014
	MAX	48.5	48.5	0.026	0.010	0.022
Turbot (6)	MIN	0.7	0.7	<0.001	<0.001	0.001
	MEDIAN	3.4	3.5	0.002	<0.001	0.008
	MEAN	5.3	5.3	0.003	0.002	0.008
	MAX	15.5	15.5	0.009	0.008	0.013

*Sum of PCN TEQ calculated using TEF values given in Fernandes et al., 2017.

506 Table 3.3 Summary of PXDD/F and PXB concentrations in marine fish species

PXDD/Fs	Sardines n=7	Mackerel n=13	Sprats n=13	Sea bass n=15	Turbot n=4
	Range, ng/kg *fat weight				
2-B-7,8-CDD	<0.01 - <0.145	<0.018 - 0.097	<0.009 - 0.199	<0.005 - <0.197	<0.027 - 0.186
2-B-3,7,8-CDD	<0.006 - <0.033	<0.008 - 0.078	<0.009 - 0.134	<0.005 - <0.16	<0.007 - <0.071
2,3-B-7,8-CDD	<0.005 - <0.074	<0.008 - <0.03	<0.005 - <0.07	<0.005 - 0.101	<0.007 - <0.067
1-B-2,3,7,8-CDD	<0.005 - <0.093	<0.008 - <0.046	<0.005 - <0.073	<0.005 - <0.111	<0.011 - <0.106
2-B-1,3,7,8-CDD	<0.006 - <0.076	<0.006 - <0.035	<0.006 - <0.049	<0.005 - <0.097	<0.007 - <0.061
2-B-3,6,7,8,9-CDD	<0.006 - <0.092	<0.009 - <0.064	<0.008 - <0.122	<0.005 - <0.191	<0.008 - <0.085
2-B-7,8-CDF	<0.014 - <0.075	<0.012 - 0.083	<0.01 - <0.094	<0.007 - 0.231	<0.011 - 0.133
3-B-2,7,8-CDF	<0.005 - <0.056	<0.017 - 0.09	<0.008 - 0.134	<0.005 - <0.172	<0.015 - 0.091
2-B-6,7,8-CDF	<0.005 - <0.05	0.051 - 0.508	0.036 - 1.627	<0.005 - <0.241	<0.006 - 0.3
2,3-B-7,8-CDF	<0.005 - <0.704	<0.014 - <0.19	<0.009 - 0.619	<0.011 - 1.267	<0.025 - <0.172
1-B-2,3,7,8-CDF	<0.005 - <0.1	<0.006 - <0.066	<0.005 - <0.061	<0.005 - <0.134	<0.005 - <0.06
4-B-2,3,7,8-CDF	<0.011 - 0.175	<0.014 - <0.101	<0.015 - 0.257	<0.005 - 0.255	<0.02 - <0.093
1,3-B-2,7,8-CDF	<0.005 - <0.089	<0.005 - <0.037	<0.005 - <0.039	<0.005 - <0.185	<0.006 - <0.082
PXBs					
4'-B-3,3',4,5-CB (PXB126)	0.033 - 0.495	0.081 - 0.517	0.04 - 0.529	0.008 - 0.192	0.178 - 0.532
3,4-B-3',4',5'-CB (PXB126 di-Br)	<0.005 - 0.069	<0.005 - 0.078	<0.005 - 0.062	<0.005 - 0.084	0.006 - 0.05
3',4',5'-B-3,4-CB (PXB126 tri-Br)	<0.005 - <0.05	<0.005 - <0.048	<0.005 - <0.047	<0.005 - 0.225	<0.007 - <0.1
4'-B-2,3',4,5-CB (PXB 118)	0.567 - 9.428	1.639 - 14.582	0.842 - 17.673	2.13 - 42.032	2.376 - 7.606
4'-B-2,3,3',4-CB (PXB 105)	0.201 - 2.804	0.601 - 4.939	0.317 - 9.159	0.684 - 9.705	0.783 - 3.103
4'-B-2,3,3',4,5-CB (PXB 156)	0.101 - 1.407	0.286 - 2.853	0.118 - 2.753	0.302 - 6.567	0.056 - 1.275

507

508 *Reported on fat weight basis in order to comparison with other reported food PXDD/F and PXB data which is generally
509 reported on a fat weight basis

510

511 Table 3.4 Summary of PFAS concentrations in marine fish species

512

	Species	Sardines n=8	Mackerel n=12	Herring n=9	Mullet n=7	Sprat n=9	Sea Bass n=5
		µg/kg whole weight					
PFOA	Range	0.06 - 0.92	0.06 - 0.35	0.08 - 1.17	0.01 - 0.26	0.13 - 3.82	0.05 - 0.24
	Mean	(0.34)	(0.2)	(0.34)	(0.13)	(1.48)	(0.13)
PFNA	Range	0.01 - 0.27	0.04 - 0.23	0.02 - 0.45	0.02 - 0.19	0.05 - 0.69	0.04 - 0.16
	Mean	(0.16)	(0.1)	(0.1)	(0.07)	(0.26)	(0.07)
PFDeA	Range	0.04 - 0.94	0.07 - 1.07	0.02 - 0.87	0.14 - 0.58	0.05 - 0.45	0.06 - 0.33
	Mean	(0.37)	(0.4)	(0.3)	(0.27)	(0.25)	(0.18)
PFUnA	Range	0.04 - 2.29	0.13 - 1.89	0.06 - 0.58	0.15 - 0.84	0.22 - 1.09	0.12 - 0.59
	Mean	(0.78)	(0.4)	(0.16)	(0.39)	(0.51)	(0.3)
PFDoA	Range	0.02 - 0.51	0.01 - 2.04	0.03 - 0.64	0.13 - 1.34	0.05 - 0.64	0.02 - 0.48
	Mean	(0.26)	(0.35)	(0.17)	(0.42)	(0.25)	(0.17)
PFBSH	Range	0.03 - 0.35	0.01 - 0.1	0.01 - 0.6	0.02 - 0.15	0.02 - 0.5	0.01 - 0.08
	Mean	(0.07)	(0.02)	(0.12)	(0.08)	(0.11)	(0.04)
PFHxSH	Range	0.01 - 0.12	0.01 - 0.14	0.04 - 0.06	0.01 - 0.08	0.02 - 0.15	0.01 - 0.1
	Mean	(0.03)	(0.02)	(0.02)	(0.02)	(0.08)	(0.03)
PFOS	Range	0.78 - 3.59	0.22 - 4.92	0.16 - 1.84	0.37 - 12.83	1.51 - 9.44	1.28 - 10.79
	Mean	(2.18)	(1.12)	(0.59)	(2.58)	(3.94)	(3.82)
PFOSA	Range	0.06 - 3.4	0.04 - 0.39	0.02 - 0.89	0.29 - 0.67	0.08 - 3	0.43 - 2.13
	Mean	(0.92)	(0.22)	(0.38)	(0.36)	(0.85)	(0.84)

513

514 **4.0 Conclusions**

515 The results of this study demonstrate the occurrence of a wide range of environmental
516 contaminants in fish taken from marine regions around the UK and other proximate marine
517 waters from which retail fish in the UK is commonly sourced.
518

All of the different contaminant groups that were targeted were detected at varying concentrations depending on species and location. Sprats, sardines, sea bass, herring and mackerel, appear to show the highest levels of contamination. The spatial distribution of this occurrence showed that fish taken from waters around the Southern UK/Northern French coasts and the Irish Sea tended to show higher levels of most contaminants, but contamination is also evident for locations off the east coast of the UK.

In comparison to a decade ago, a small reduction in concentration levels is evident for some contaminants such as PCDD/Fs and PCBs, but similar trends were not observed for other contaminants. This may be due to a slower rate of decline or because some of the data are unique (e.g. there are none or very little earlier data for PXDD/Fs, PXBs in turbot) and in these cases, the study provides a useful concentration baseline for future assessments. However, all of the data would be useful in allowing risk assessment from dietary consumption.

The high frequency of contaminant occurrence combined with the instances of samples that lie above the regulated limits (where applicable), suggest that continued vigilance of these edible marine fish species is advisable.

Acknowledgement

The authors are grateful to the UK Food Standards Agency for funding this work.

References

Airaksinen, R., Hallikainen, A., Rantakokko, P., Ruokojärvi, P., Vuorinen, P., Parmanne, R., Verta, M., Mannio, J., Kiviranta, H. 2014. Time trends and congener profiles of PCDD/Fs, PCBs, and PBDEs in Baltic herring off the coast of Finland during 1978-2009. Chemosphere, 114, 165-71

Behnisch, P., Hosoe, K., 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.

Bichon, E., Guiffard, I., Vénisseau, A., Lesquin, E., Vaccher, V., Brosseaud, A., Marchand, P., Le Bizec, B. 2016. Simultaneous determination of 16 brominated flame retardants in food and feed of animal origin by fast gas chromatography coupled to tandem mass spectrometry using atmospheric pressure chemical ionisation. J. Chromatogr. A (2016), 120-128

Blankenship, A., Kannan, K., Villalobos, S., Villeneuve, D., Falandysz, J., Imagawa, T., Jakobsson, E., Giesy, J.P., 2000. Relative potencies of Halowax mixtures and individual polychlorinated naphthalenes (PCNs) to induce Ah receptor-mediated responses in the rat hepatoma H4IIE-Luc cell bioassay. Environ. Sci. Technol. 34(15), 3153-3158.

Clarke, D., Bailey, V., Routledge, A., Lloyd, A, Mortimer, D., Gem, M. 2010. Dietary intake estimate for perfluorooctanesulphonic acid and other perfluorocompounds (PFCs) in English retail foods following determination using standard addition LC-MS/MS. Food Addit. Contam. 27(4) 530-545

Committee on toxicity of chemicals in food, consumer products and the environment (COT), 2006. Statement on organic chlorinated and brominated contaminants in shellfish, farmed and wild fish. Available at: https://cot.food.gov.uk/sites/default/files/cot/cotstatementfishsurveys.pdf

Dioxins in Food, 2013. "Interlaboratory Comparison on dioxins in food – Fourteenth round Norwegian Institute of Public Health Report. -Available at: www.fhi.no/ilc

Dioxins in Food, 2014. "Interlaboratory Comparison on dioxins in food – Fifteenth round - Norwegian Institute of Public Health Report. Available at: http://www.fhi.no/dokumenter/2c9eab2243.pdf

Dioxins in Food, 2015. "Interlaboratory Comparison on dioxins in food – Sixteenth round - Norwegian Institute of Public Health Report. Available at: https://www.fhi.no/en/publ/2015/interlaboratory-comparison-on-pops-in-food-2015/

European Commission, 2011. Commission Regulation (EU) No 1259/2011 of 2 December 2011 amending Regulation (EC) No 1881/2006 as regards maximum levels for dioxins, dioxin-like PCBs and non-dioxin-like PCBs in foodstuffs. Official Journal of the European Union, L320/18, 3.12.2011

European Commission, 2014. Commission Recommendation 2014/118/EU of 3 March 2014, on the monitoring of traces of brominated flame retardants in food. Off. J. Eur. Union, L65/39, 5.3.2014

European Commission, 2017. Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Feed and Food. Available at: https://ec.europa.eu/jrc/en/publication/guidance-document-estimation-lod-and-loq-measurements-field-contaminants-feed-and-food

Falandysz, J., Fernandes, A., Gregoraszczuk, E., Rose, M. 2014. The Toxicological Effects of Halogenated Naphthalenes: A Review of Aryl Hydrocarbon Receptor-Mediated (dioxin-like) Relative Potency Factors. J. Environ. Sci. Health, 32, 239-272,

Fernandes, A., Gallani, B., Gem, M., White, S., Rose, M. 2004. Trends in the dioxin and PCB content of the UK diet. Organohalogen Compd. 66, 2053-2060.

Fernandes, A., White, S., D'Silva, K., Rose, M. 2004B, Simultaneous Determination of PCDDs, PCDFs, PCBs and PBDEs in Food, Talanta, 63, 1147-1155.

Fernandes, A., Dicks, P., Mortimer, D., Gem, M., Smith, F., White, S., Rose, M., 2008. Brominated and Chlorinated Dioxins and Brominated Flame Retardants in Scottish Shellfish: Methodology, Occurrence and Human Dietary Exposure. Mol. Nutr. Food Res. 52(2), 238-249.

Fernandes, A., Smith, F., Petch, R., Panton, S., Carr, M., Rose, M. 2009. Investigation into the occurrence of brominated contaminants in selected foods. Report to the Food Standards Agency, Fera Report FD 08/07, 2009

Fernandes, A., Mortimer, D., Rose, M., Knowles, T., Gem, M. 2009B The Occurrence of Dioxins (PCDDs, PCDFs) and PCBs in Wild, Farmed and Processed Fish, and Shellfish
Food Addit. Contam. B, **2(1)**, 15-20

Fernandes, A., Mortimer, D., Gem, M., Smith, F., Rose, M., Panton, S., Carr, M., 2010. Polychlorinated Naphthalenes (PCNs): Congener specific analysis, occurrence in food and dietary exposure in the UK. Environ. Sci. Technol. 44, 3533

Fernandes, A., Rose M, Mortimer, D., Carr, M Panton, S., Smith, F., 2011. Mixed Brominated/Chlorinated Dibenzo-p-Dioxins, dibenzofurans and Biphenyls: Simultaneous Congener-selective Determination in Food. J. Chromatogr. A, 1218, 9279-9287

618 Fernandes, A., Rose, M., Smith, F., Holland, M. 2012. Organic Environmental contaminants in the 2012
619 Total Diet Study samples. Report to the Food Standards Agency, Fera Report FD 12/04, 2012
620
621 Fernandes. A. 2013. in "Persistent organic pollutants and toxic metals in foods" Rose, M. and
622 Fernandes, A. Eds. P 367, ISBN 978-0-85709-245-8 Woodhead Publishing Ltd. Cambridge UK
623
624 Fernandes, A., Mortimer, D., Wall R., Bell D., Rose, M., Carr, M., Panton, S., Smith, F. 2014. Mixed
625 Halogenated Dioxins/Furans (PXDD/Fs) and Biphenyls (PXBs) in Food: Occurrence and Toxic
626 Equivalent Exposure using Specific Relative Potencies. Environ. Int., 73, 104-110
627
628 Fernandes A., Mortimer D., Rose M., Smith F., Panton S. 2014B. Brominated dioxins and PBDEs:
629 Occurrence trend in UK food. Organohalogen Cmpds. 76, 764-7.
630
631 Fernandes, A., Rose, M., Smith, F., Panton, S. 2015. Geographical Investigation for chemical
632 contaminants in fish collected from UK and proximate marine waters. Report FD 15/04 to the UK
633 Food Standards Agency. London, 2015. Available at:
634 https://www.food.gov.uk/science/research/chemical-safety-research/env-cont/fs102005

635 Fernandes, A., Mortimer, D., Rose, M., Smith, F., Panton, S., Garcia-Lopez, M. 2016. Bromine
636 content and brominated flame retardants in food and animal feed in the UK. Chemosphere, 150, 472-
637 478

638 Fernandes A., Rose, M., Falandysz J. 2017. PCNs in Food and Humans. Environ Int. 104, 1-13
639
640 Food Standards Agency, 2006. Brominated chemicals in farmed and wild fish and shellfish and fish oil
641 dietary supplements Food Survey Information Sheet 04/06 Available at:
642 http://www.food.gov.uk/news/ science/surveillance/fsisbranch2006/fsis0406
643
644 Food Standards Agency, 2006B. Fluorinated chemicals: UK dietary intakes. . Food Surveillance
645 Information Sheet 10/06 available at http://www.food.gov.uk/multimedia/pdfs/fsis1106.pdf
646
647 Jarv, L., Kiviranta, H., Koponen, J., Rantakokko,P., Ruokojarvi, P., Radin, M., Roots, O., Simm, M.
648 2017. Persistent organic pollutants in selected fishes of the Gulf of Finland. J. Marine Systems. 171,
649 129

650 Martellini, T., Diletti, G., Scortichini, G., Lolini, M., Lanciotti, E., Katsoyiannis, A., Cincinelli A. 2016.
651 Occurrence of polybrominated diphenyl ethers (PBDEs) in foodstuffs in Italy and implications for
652 human exposure. Food Chem. Toxicol., 89 (2016), pp. 32-38,

653 Noorlander, C., van Leeuwen, S., Te Biesebeek, J., Mengelers, M., Zeilmaker, M. 2011. Levels of
654 perfluorinated compounds in food and dietary intake of PFOS and PFOA in the Netherlands. J Agric.
655 Food Chem. 59(13), 7496-505.

656 Ohta, S., Tokusawa, H., Nakao, T., Aozasa, O., Miyata, H., Alaee, M. 2008. Global contamination of
657 coplanar PBCBs in the market fishes from Japan. *Chemosphere*, **2008**, *73*, 531-538.

658 Perelló, G., Díaz-Ferrero, J., Llobet, J., Castell, V., Vicente, E., Nadal, M., Domingo, J. 2015. Human
659 exposure to PCDD/Fs and PCBs through consumption of fish and seafood in Catalonia (Spain):
660 Temporal trend. Food Chem. Toxicol, 81, 28-33.
661
662 Picó, Y., Farré, M., Llorca, M., Barceló, D. 2011. Perfluorinated compounds in food: a global
663 perspective. Crit. Rev. Food Sci. Nutr. 51(7), 605-25
664

Prefecture de la Seine-Maritime. 2010. Arrêté n°10-20 du 8 février 2010 portant interdiction de la pêche des sardines (sardina pilchardus) dans certaines eaux maritimes littorales des départements de la Seine-Maritime, du Calvados et de la Manche en vue de la consommation et de la commercialisation. Recueil spécial n° 6 - Février 2010 du 9 février 2010

Rose, M. and Fernandes, A. 2012. in "Chemical contaminants and residues in food". Ed. Schrenk, D. ISBN 0 85709 058 5. Woodhead Publishing Ltd. Cambridge, UK.

Schecter, A., Haffner, D., Colacino, J., Patel, K., Päpke, O., Opel M., Birnbaum L. 2010. Polybrominated diphenyl ethers (PBDEs) and hexabromocyclodecane (HBCD) in composite U.S. food samples. Environ. Health Perspect. 118(3), 357-62

Stahl, L., Snyder, B., Olsen, A., Kincaid, T., Wathen, J., McCarty, H. 2014. Perfluorinated compounds in fish from U.S. urban rivers and the Great Lakes. Sci. Tot. Environ. 499,185-95

Van den Berg, M., Birnbaum, L., Denison, M., De Vito, M., Farland, W., Feeley, M., Fiedler, H., Hakansson, H., Hanberg, A. et al. 2006. The 2005 World Health Organization Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds. Toxicol. Sci. 93, 223–241.

Vassiliadou, I., Costopoulou, D., Kalogeropoulos, N., Karavoltsos, S., Sakellari, A., Zafeiraki, E., Dassenakis, M., Leondiadis, L. 2015. Levels of perfluorinated compounds in raw and cooked Mediterranean finfish and shellfish. Chemosphere, 127, 117-126

Vuorinen, P., Roots, O., Kein, M. 2017. Review of Organohalogen toxicants in fish from the Gulf of Finland. J. Marine Systems. 171, 141

Wall, R., Fernandes, A., Rose, M., Rowlands, C., Bell, D., Mellor, I. 2015. Characterisation of mixed halogenated ligands as potent and as partial agonists of the aryl hydrocarbon receptor. Environ. Int., 76, 49-56,

Zacs, D., Rjabova, J., Bartkevics, V. 2013. Occurrence of Brominated Persistent Organic Pollutants (PBDD/DFs, PXDD/DFs, and PBDEs) in Baltic Wild Salmon (Salmo salar) and Correlation with PCDD/DFs and PCBs. Environ. Sci. Technol., 2013, 47 (16), 9478–9486

Zacs, D., Rjabova, J., Fernandes A., Bartkevics, V. 2016 Brominated, chlorinated and mixed brominated/chlorinated persistent organic pollutants in European eels (Anquilla anquilla) from Latvian lakes. Food Addit. Contam: Part A, 33(3), 460-472.