Environment International 114 (2018) 219–230

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Occurrence and spatial distribution of chemical contaminants in edible fish species collected from UK and proximate marine waters

A.R. Fernandes[a,*], D. Mortimer[b], M. Holmes[c], M. Rose[a,1], L. Zhihua[c,d], X. Huang[c,d], F. Smith[a], S. Panton[a], L. Marshall[c]

[a] Fera Science Ltd, Sand Hutton, York YO41 1LZ, UK
[b] Food Standards Agency, Aviation House, 125 Kingsway, London WC2B 6NH, UK
[c] School of Food Science and Nutrition, University of Leeds, Leeds LS2 9JT, UK
[d] School of Food and Biological Engineering, Jiangsu University, Zhenjiang 212013, China

ARTICLE INFO

Editor: Adrian Covaci

Keywords:
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

* Corresponding author at: School of Env. Sciences, University of East Anglia, Norwich NR4 7TJ, UK.
E-mail address: Alwyn.Fernandes@uea.ac.uk (A.R. Fernandes).
[1] Current address: Manchester Institute of Biotechnology, University of Manchester, UK.

https://doi.org/10.1016/j.envint.2018.02.047
Received 12 December 2017; Received in revised form 13 February 2018; Accepted 26 February 2018

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., 2009a, 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 are subject to EU regulations (European Commission, 2011). Earlier studies (Fernandes et al., 2004a, 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., 2009a, 2014a, 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 (Esion, 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, 2006a, 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, 2009a; 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, 2014a, 2014b; Zacs 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; Picó 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