Chemosphere 85 (2011) 300–306

Contents lists available at ScienceDirect

Chemosphere

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

Occurrence of PCDD/F, PCB, PBDE, PFAS, and Organotin Compounds in Fish Meal, Fish Oil and Fish Feed

K. Suominen [a,*], A. Hallikainen [a], P. Ruokojärvi [b], R. Airaksinen [b], J. Koponen [b], R. Rannikko [a], H. Kiviranta [b]

[a] Finnish Food Safety Authority Evira, Mustialankatu 3, FI-00790 Helsinki, Finland
[b] National Institute for Health and Welfare, Department of Environmental Health, P.O. Box 95, FI-70701 Kuopio, Finland

ARTICLE INFO

Article history:
Received 6 October 2010
Received in revised form 4 March 2011
Accepted 1 June 2011
Available online 20 July 2011

Keywords:
Fish feed
Polychlorinated dibenzo-*p*-dioxins and furans
Polychlorinated biphenyls
Polybrominated diphenyl ethers
Organotin compounds
Perfluorinated alkyl substances

ABSTRACT

We analysed polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F, dioxins), and polychlorinated biphenyls (PCB) in 13 fish meal, five fish oil, and seven fish feed samples. Polybrominated diphenyl ethers (PBDE), organotin compounds (OTC), and perfluoroalkylated substances (PFAS) were analysed in ten fish meal, two fish oil, and two fish feed samples. All measured TEQ concentrations of PCDD/F and PCB were below the maximum levels set by Directive 2002/32/EC. There was no correlation between concentrations of $WHO_{PCDD/F}$-TEQ and indicator PCB in our samples. The most common congeners among PBDEs were BDE-47 and BDE-100. BDE-209 was present in five fish meals of the ten analysed. Tributyltin (TBT) was the predominant congener in all samples except in three fish meals, where monobutyltin (MBT) was the major congener. Perfluorooctane sulphonate (PFOS) was the predominant congener in six fish meals of the ten analysed. There was large variation in concentrations and congener distributions of the studied compounds between our samples. Our results underline a need to pay special attention to the origin and purity of feed raw material of marine origin.

1. Introduction

Fish has many beneficial properties from a human health perspective and fish consumption is recommended by nutritional authorities worldwide. However, fish is an important source of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F), polychlorinated biphenyls (PCB), polybrominated diphenyl ethers (PBDE), organotin compounds (OTC) and perfluorinated alkyl substances (PFAS) in the human diet (Kiviranta et al., 2004; Berger et al., 2009; Airaksinen et al., 2010).

Fish meal and fish oil are the major components of fish feed, and they may constitute 50–70% of all material in fish feed. Fish meal is a powdery substance prepared from fish and fish trimmings. Typically, the fat content of fish meal is 2–20% and the dry matter content is about 90%. The fish species typically used as raw material for fish meal and fish oil in northern Europe include sprat (*Sprattus sprattus*), small sand eel (*Ammodytes tobianus*), blue whiting (*Micromesistius poutassou*), Norway pout (*Trisopterus esmarkii*), capelin (*Mallotus villosus*), and herring (*Clupea harengus*). In Finland, fish meal and fish oil are used mainly as feed for fish and fur animals. Feed for monogastric animals, such as poultry and pigs, may contain a few percent of fish meal or fish oil. Use of fish meal as cattle feed is forbidden in the EU (European Union, 1994). Methods have been developed to clean PCDD/F and PCB from fish oil and fish meal with activated carbon (Usydus et al., 2009), supercritical CO_2-extraction (Kawashima et al., 2009) or by extraction and enzymatic treatment (Baron et al., 2007). These methods may clean up to 94% of TEQs in fish oil (Kawashima et al., 2009; Usydus et al., 2009).

Dioxins have never been commercially manufactured, but they are found almost everywhere in the environment, as a result of decades of release from various industrial and incineration processes (Estrellan and Iino, 2010). PCB have been used as lubricants and in the electric industry, as well as in oils, paints, adhesives, plastics, etc. PCB production was banned globally by the Stockholm Convention on Persistent Organic Pollutants in 2001. PBDE have been used as fire retardants in the textile, electronic, and plastics industries. Manufacture, use, and import of technical mixtures of penta- and octa-BDE has been banned in the EU (European Union, 2003a), and the use of PBDE in electronic equipments has been restricted (European Union, 2002a). The production and use of tetra-, penta-, hexa-, and heptabromodiphenyl ethers (congeners in commercial penta and octa BDE flame retardants) have been globally restricted by Stockholm Convention in 2009. Plastics and textile industry in Europe and North America has committed voluntarily to decrease emissions of BDE-209 and other brominated flame retardants into the environment (VECAP, 2008).

Trisubstituted OTC such as tributyltin (TBT) and triphenyltin (TPhT) have been used extensively as biocides in wood

* Corresponding author.
E-mail address: kimmo.suominen@evira.fi (K. Suominen).

0045-6535/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2011.06.010

preservatives, antifouling paints, and pesticides. Mono- and disubstituted OTC (e.g. monomethyltin (MMT), dimethyltin (DMT), dibutyltin (DBT), mono-*n*-octyltin (MOT) and di-*n*-octyltin (DOT)) are generally used in mixtures as polyvinyl chloride (PVC) stabilizers, and dialkyltins have been approved as PVC stabilizers for food contact materials (Hoch, 2001). For fishery products, the main source of OTC, especially TBT and TPhT, are antifouling paints applied on ship hulls and underwater structures. Antifouling paints containing OTC have been banned in the EU since the beginning of 2008 (European Union, 2003b).

PFAS is a collective name for a vast group of fluorinated compounds which consist of an alkyl carbon chain with a hydrophilic functional group. The most commonly studied PFAS are the perfluorinated sulfonates and carboxylates. PFAS have been used for instance in industrial and consumer applications including stain- and water resistant coatings for fabrics, oil-resistant coatings for paper products approved for food contacts, fire-fighting foams, and many other purposes. Directive 2006/122/EC (European Union, 2006) sets restrictions on the marketing and use of perfluorooctane sulphonate (PFOS) in the EU, and also expresses concern about other PFAS with similar risk profile to PFOS. The production and use of PFOS, its salts, and perfluorooctane sulfonyl fluoride (PFOS-F) have been severely restricted by Stockholm Convention in 2009.

Concentrations of environmental contaminants in farmed fish and fish feed have been widely studied. There is less information on the occurrence of these compounds in raw materials of fish feed. In this study we analysed the occurrence of PCDD/F, PCB, PBDE, OTC, and PFAS in fish meal, fish oil, and fish feed in the EU market (Denmark, Poland, Germany, Norway, Iceland, and Finland).

2. Materials and methods

2.1. Sampling and pre-treatment

In total, 25 samples were collected during 2002 and 2007–2008, of which 13 were fish meal, 7 were fish feed and 5 were fish oil samples (Table 1). Ten of the fish meal samples, two of the fish feed samples, and two of the fish oil samples were analysed for PCDD/F, PCB, PBDE, PFAS, and OTC. The rest of the samples were analysed only for PCDD/F and PCB. Samples were collected according to Directive 76/371/EEC (European Union, 1976). Each final sample was an aggregate of 32 incremental samples. Fish meal and fish oil were sampled during the unloading of the ship vessel or the container. Fish feeds were sampled at the feed factory during production. Fish meals were imported to Finland from Denmark, Germany, Poland, Norway, and Iceland. However, the area of origin of the raw material of these products remained uncertain. The raw material for Finnish fish feed is imported from other, mainly European countries. Prior to chemical analysis, the fish oil samples were homogenised, and fish meal and fish feed samples were freeze dried and homogenised.

2.2. Chemical analysis

Concentrations of all contaminants in the present study were analysed at the National Institute for Health and Welfare (THL), Chemical Exposure Unit, which is an accredited testing laboratory (Code T077, EN ISO/IEC 17025) and a national reference laboratory for PCDD/F and PCB in food and feed. The scope of accreditation includes analyses of persistent organic pollutants (POP) in environmental samples.

PCDD/F, PCB and PBDE samples were extracted with toluene: ethanol using an ASE Accelerated solvent extractor, ASE 350. The fat extract was purified using multiple column chromatography, and quantification of PCDD/F, PCB and PBDE congeners was performed by selective ion recording using a high resolution mass spectrometer. For PCDD/F and PCB toxic equivalents (WHO-TEQs) were calculated with a set of toxic equivalency factors (TEFs) recommended by WHO in 1997 (van den Berg et al., 1998) and 2005 (van den Berg et al., 2006). OTC-samples were extracted with tropolone as a complexing agent and ethylated with sodium tetraethylborate. Quantification of OTC was performed by selective ion recording using a high resolution mass spectrometer. Details of the analytical method for OTC have been described previously (Rantakokko et al., 2008). For PFAS, the samples were extracted with an ion-pair extraction method described by Hansen et al. (2001) with some modifications. PFAS was quantified using liquid chromatography negative ion electrospray tandem mass spectrometry (LC–ESI-MS/MS). The details of the analysis procedure are shown in the supplementary information. We report TEQ concentrations of PCDD/F and non-*ortho*-PCB as ng kg^{-1} material with a moisture content of 12% or as ng kg^{-1} fat. The concentrations of other PCB, PBDE and organotin cations are reported as μg kg^{-1} material with a moisture content of 12% or as μg kg^{-1} fat. Concentrations of PFAS are reported as μg kg^{-1} material with a moisture content of 12%.

2.3. Quality assurance

In all analyte groups, laboratory blank samples were analysed within each batch of samples, and the results were corrected accordingly. With PCDD/F, PCB, and PBDE, an in-house control sample was used to ensure the repeatability of analyses from batch to batch. With OTC, a certified mussel tissue CRM 477 was used as the control sample. The CRM 477 has certified concentrations for monobutyltin (MBT), DBT, and TBT, and indicative concentrations for MPhT, DPhT, and TPhT, respectively (Pellegrino et al., 2000).

The recoveries of labelled PCDD/F, PCB, PBDE and perdeuterated butyltin congeners were mainly between 60% and 110%. High recoveries (up to 140%) of some PCDD/F, PCB and PBDE congeners (mainly OCDD, OCDF and BDE-183) were accepted due to very low concentrations of these compounds in part of our samples. For perdeuterated phenyltins a strong matrix induced gas chromatographic response enhancement resulted in recoveries up to 500%. However, the use of own perdeuterated analogue for each phenyltin congener corrects for this response enhancement and produces correct final result (Erney et al., 1993).

3. Results

3.1. PCDD/F and PCB

Upper bound TEQ (1998) concentration of PCDD/F in fish meals ranged from 0.1 to 0.9 ng kg^{-1} 12% moisture (Table 1). Highest concentrations of PCDD/F were detected in four fish meals from Denmark (#1, #2, #3, #4). $WHO_{PCDD/F}$-TEQ concentrations in fish feed ranged from 0.5 to 1.4 ng kg^{-1} 12% moisture. In fish oils, concentrations ranged from 2.8 to 4.5 ng $WHO_{PCDD/F}$-TEQ kg^{-1} fat.

Upper bound TEQ (1998) concentrations of PCB in fish meals ranged from 0.3 to 1.3 ng kg^{-1} 12% moisture. The highest concentrations of DL-PCB were detected in fish meals from Denmark (#1, #4) and from Germany (#8). The lowest concentrations were detected in fish meals from Norway (#12) and from Iceland (#13). Concentrations of PCB in fish feed ranged from 0.6 to 1.4 ng WHO_{PCB}-TEQ kg^{-1} 12% moisture. Concentrations of WHO_{PCB}-TEQs in fish oil ranged from 4.3 to 13 ng kg^{-1} fat. Fish liver oil from Norway (#25) showed the highest TEQ concentration of PCB. Congener distribution and upper bound TEQ (1998, 2005) concentrations of PCDD/F and PCB per fat are displayed in supplementary material.