# Investigation into levels of dioxins, furans, polychlorinated biphenyls and brominated flame retardants in fishery produce in Ireland.

**January 2007**

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*Marine Environment and Health Series, No.26, 2006*

## Acknowledgements

The authors wish to express their appreciation to An Bord Iascaigh Mhara (BIM) for their financial contribution to this project and for providing some of the samples. Special thanks are due to Helen Cooper (BIM), Emer O'Reilly (FSAI), Conor Duffy, Denise Glynn, Brian Boyle and Jane Kinane (MI) for their assistance.

*This study was sponsored by FSAI, BIM and the Marine Institute.*

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# 1. Summary

The Food Safety Authority of Ireland in collaboration with the Marine Institute and An Board Iascaigh Mhara (Sea Fisheries Board) has carried out a surveillance study of levels of dioxins (PCDDs), furans (PCDFs) polychlorinated biphenyls (PCBs), and brominated flame retardants (BFRs), specifically polybrominated diphenylethers (PBDEs) and hexabromocyclododecane (HBCD), in a variety of fish species and fishery products, including fresh and processed products available on the Irish market. The study was undertaken because of concern about the possible effects on human health of these bio-persistent environmental contaminants, known to be present in a number of foodstuffs, notably meat, fish, eggs and dairy products.

The study showed that levels of PCDDs and PCDFs in Irish fish and fishery products available on the Irish market were well below existing EC legal limits for these contaminants as laid down in Regulation 466/2001. The lowest level was found in a sample of canned tuna (0.012 ng WHO TEQ/kg whole weight) with the highest level found in a farmed salmon sample (0.82 ng WHO TEQ/kg whole weight), compared with the maximum level under the legislation of 4 ng WHO TEQ/kg whole weight.

The levels found were also below the new limits for dioxin-like PCBs (dl-PCBs) and for the sum of WHO-TEQs for PCDDs, PCDFs and dioxin-like PCBs, which were introduced in November, 2006 via Regulation 199/2006. The upper-bound mean levels of PCDDs, PCDFs and dioxin-like PCBs expressed as total WHO-TEQs ranged from 0.05 – 2.15 ng/kg WHO TEQ whole weight, which can be compared with the new maximum level of 8 ng WHO TEQ/kg whole weight for the sum of PCDDs, PCDFs and dioxin-like PCBs.

Results of this study are in line with those from previous FSAI studies on PCDD and PCDF levels in fish and also in meat, milk and eggs, and indicate relatively low levels of these contaminants in fishery produce available in the Irish marketplace. Reductions of PCDD/Fs and dl-PCBs in Irish farmed salmon were observed in comparison to levels measured in a previous FSAI/MI survey in 2001, in which a mean level of 4.02 ng WHO TEQ/kg whole weight was detected compared with 2.15 ng/kg WHO TEQ whole weight in the present study. Similar observations can be made for levels reported in a study carried out by An Board Iascaigh Mhara in 2004, in which a mean level of 1.75 ng WHO TEQ/kg whole weight was reported.

Concentrations of brominated flame retardants were also low. The mean PBDE concentrations ranged from <0.31 to 3.71 µg/kg whole weight in canned tuna to farmed salmon respectively. Although there are no acceptable daily intake (ADI) or maximum limits set for PBDEs or HBCD, the levels of these contaminants found in the study were low, and are very unlikely to present a health risk to Irish consumers.

Although fish is a recognised dietary source of PCDDs, PCDFs and PCBs, the health benefits of eating fish are well established, and on the basis of these results the FSAI considers that there is no need to alter current advice on fish consumption. Current advice is that consumers should eat two portions of fish a week, one of which should be oily. The full study report follows, providing further sampling details, analytical methodologies and discussion of the resulting datasets.

# 2. Background

The Food Safety Authority of Ireland (FSAI) has a statutory responsibility to ensure the safety of food consumed, distributed, produced and sold on the Irish market. In this respect, the FSAI co-ordinates the collation of food safety surveillance information from laboratories run by its official agents, the Health Service Executive (HSE), the Department of Agriculture and Food, the Department of Communication, Marine and Natural Resources, the Marine Institute and the local authorities. The FSAI also conducts targeted food safety surveillance in areas where potential safety issues have been identified and/or on food contaminants for which there are currently no testing facilities in Ireland, such as dioxins.

The nutritional benefits of eating fish, in particular oily fish, are well known. The FSAI advises consumers to eat two portions of fish each week, of which one should be oily. In recent years there has been some public debate concerning the health risks to consumers associated with persistent organic pollutants, such as dioxins, in certain species of fish.

This report provides the results of a targeted surveillance study undertaken in 2004 - 2005 in collaboration with the Marine Institute and An Board Iascaigh Mhara (Sea Fisheries Board) on levels of dioxins (PCDDs), furans (PCDFs), polychlorinated biphenyls (PCBs), and brominated flame retardants (BFRs), specifically polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) isomers in a variety of fishery products available on the Irish market.

The present work builds on previous studies undertaken by FSAI into levels of these environmental contaminants in fish and fish oils (FSAI, 2002a, undertaken jointly with the Marine Institute), meat (FSAI, 2004a), milk (FSAI, 2002b) and eggs (FSAI, 2004b), and was undertaken against the background of increased awareness in the European Union of the possible health risks posed by these substances in the food chain. It also reflects Ireland's participation in the 2004 – 2006 EC monitoring programme for the background presence of dioxins, furans and dioxin-like PCBs in foodstuffs which has been agreed between the European Commission and the Member States via Commission Recommendation 2004/705/EC. The EC monitoring programme has recently been extended for a further 2 years, until 31$^{st}$ December 2008, via Commission Recommendation 2006/794/EC (repealing Recommendation 2004/705).

Monitoring of other residues and environmental contaminants, such as trace metals in fish and shellfish is undertaken by the Marine Institute as part of a service contract with FSAI (e.g. Marine Institute 2004a, 2004b). An Board Iascaigh Mhara have also recently carried out studies into levels of PCDDs, PCDFs and PCBs in Irish farmed salmon (Gruemping *et al*., 2004).

As part of this study, analysis of nutritionally beneficial polyunsaturated fatty acids (PUFAs) was also undertaken. These results will be the subject of a separate report.

## 2.1 Dioxins and furans (PCDDs and PCDFs)

The term 'dioxins' covers a group of 75 polychlorinated dibenzo-p-dioxin (PCDD) and 135 polychlorinated dibenzofuran (PCDF) congeners, 17 of which are of toxicological concern. Exposure to dioxins can result in a wide range of toxic responses, including dermal toxicity (chloracne), immunotoxicity, carcinogenicity, reproductive toxicity and possible neurobehavioral (cognitive) effects (SCF, 2000). Studies on children exposed *in utero* to dioxins are reported to have shown persistent endocrine and developmental changes (SCF, 2000). The toxicological effects of dioxins are thought to arise due to binding to a specific receptor protein within cells, the aryl hydrocarbon (Ah) receptor, present in most tissues of animals and humans. The most toxic dioxin congener is 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD) and is classified by the International Agency for Research on Cancer (IARC) and other international organisations as a known human carcinogen. By analogy other dioxins are therefore considered as presumed carcinogens. The EU Scientific Committee for Food (SCF), in line with the World Health Organisation (WHO), have concluded however that the carcinogenic effect of dioxins does not occur at levels below a certain threshold (SCF, 2000).

Dioxins are chlorinated environmental contaminants and have no known commercial applications, other than in the preparation of analytical standards and research materials. They are formed during combustion processes, for example in the incineration of municipal waste, although natural combustion processes such as forest fires and bonfires may also result in dioxin formation. They can also occur as by-products of industrial processes, for example production and use of pentachlorophenol-containing wood preservatives, production and use of certain herbicides and bleaching of paper pulp using chlorine. Dioxins have been identified in almost all environmental compartments as a result of these emissions. Emissions of dioxins to air may ultimately result in deposition in the terrestrial environment and in aquatic sediments, followed by uptake into the food chain e.g. by ruminants and fish.

Dioxins are highly resistant to degradation processes in the environment and consequently persist in the environmental compartments where they have been deposited. This in part is due to their lipophilic characteristics, which can result in accumulation in the fatty tissues of the primary intake species e.g. cattle or fish. Approximately 90% of human exposure to dioxins and furans results from the consumption of contaminated food. Exposure by other routes, such as inhalation and ingestion of particles from air, ingestion of contaminated soil and dermal absorption normally contributes less than 10% of daily intake.

Humans are considered the ultimate consumers in the food chain, and accumulate dioxins in body tissues primarily as a result of exposure via food. In the case of cows or other lactating species, high levels of dioxins can potentially occur in milk (specifically in milk fat) and consequentially also in cream and in milk products such as cheese, in addition to accumulation within carcass meat. In fish, levels are usually higher in fatty tissues such as the liver and consequently levels can be more elevated in fish liver oils. In Europe, the fraction of the dietary intake of dioxins contributed by these foods is: fish and fish products (2 – 63%),

meat and meat products (6 – 32%); milk and dairy products (16 – 39%). Fruit and vegetables provide only a minor contribution to human intake (European Commission, 2000).

The Belgium dioxin crisis in 1999 triggered an increased awareness in the European Union of the dangers posed by dioxins, furans and polychlorinated biphenyls in the food chain and as a consequence of this crisis, the European Community (EC) established maximum levels for dioxins in furans in foodstuffs, in order to protect the health of consumers.

## 2.2 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls or PCBs are a group of extremely stable aromatic chlorinated compounds which, like dioxins, are relatively resistant to biological degradation and hence persist and accumulate in the environment and in the food chain. There are 209 structurally possible PCB compounds (congeners), with one to ten chlorine atoms per molecule. They have excellent electrical and heat transfer properties, which led to their widespread use in a variety of industrial, commercial and domestic applications. The production and use of PCBs has been discontinued in most countries, due to concern about their toxicity and persistence, but large amounts remain in electrical equipment, plastic products, buildings and the environment. Incorrect disposal of such material can result in continued release to the environment, adding to existing levels present as a consequence of past releases.

PCBs are generally regarded as having potential to cause adverse effects on health, with particular concern being expressed about the 12 so-called dioxin-like PCBs. This group of non-ortho (PCBs 77, 81, 126, 169) and mono-ortho (PCBs 105, 114, 118, 123, 156, 157, 167, 189) PCBs are assumed to have essentially the same toxicity potential as the dioxins and furans, since they also bind to the Ah receptor.

Other PCBs (non-dioxin-like PCBs) do not exert their toxicological effects via binding to the Ah receptor but nonetheless are associated with a wide spectrum of toxic responses, including developmental effects, immuno- and neurotoxicity, endocrine disrupting effects and tumour promotion. The so-called marker or indicator PCBs have been used as indicators of the total PCB content or body burden of environmental biota, food and human tissue. The most frequent approach is to use either the total level of six of the most commonly occurring PCBs (6 indicator PCBs, PCBs 28, 52, 101, 138, 153 and 180) or the total level of seven of these (7 indicator PCBs, PCBs 28, 52, 101, 118, 138, 153 and 180), including the dioxin-like PCB 118.

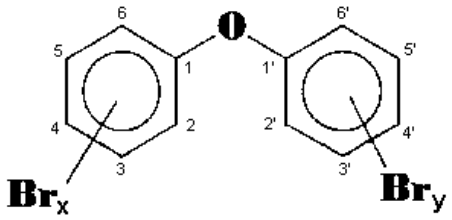
## 2.3 Polybrominated Diphenyl Ethers (PBDEs)

Brominated flame retardants (BFRs) are a group of chemicals which are added to many household products for the purpose of fire prevention. The types of products containing these chemicals include clothing and household textiles, furniture, computers and TVs.

There are five major classes of brominated flame retardants: brominated bisphenols, brominated diphenyl ethers, brominated cyclododecanes, brominated phenols and brominated phthalic acid derivatives. This survey covers polybrominated diphenyl ethers (PBDEs) only.

The term polybrominated diphenyl ethers (PBDEs) refers to three commercial mixtures of decabromodiphenyl ether (DBDE), octabromodiphenyl ether (Octa, OBDE), and pentabromodiphenyl ether (Penta, pentaBDE). The European Union banned production of both pentaBDE and octaBDE in 2004, however decaBDE (DBDE) is still in use.

The general chemical formula of PBDEs is




*(Source: WHO, 1994, BROMINATED DIPHENYL ETHERS, ENVIRONMENTAL HEALTH CRITERIA 162, Geneva)*

PBDEs are similar in structure to PCBs (polychlorinated biphenyls) and also have some similarities to the dioxin family of chemicals. They contain the element bromine rather than the chlorine found in the PCBs. Like the dioxins and PCBs, the PBDEs break down slowly in the environment and in living organisms including the human body. Continuous exposure can result in accumulation of PBDEs in body tissues. Because they show physico-chemical similarities to dioxins and PCBs, they may have some of the health effects of these chemicals, although they appear to be less toxic. Recent toxicological studies have shown that some PBDEs have endocrine or hormone disrupting properties, an effect that is also associated with dioxins and PCBs, and is thought to be associated with changes in fertility, sexual development and possibly certain types of cancer such as breast, testicular and prostate cancer. It has also been reported that PBDEs can have an effect on brain development in mice, slowing the learning process. As with PCBs, exposure to PBDEs may be particularly harmful during a critical window of brain development during pregnancy and early childhood. While the pentabromo compounds appear to be the most toxic, many of these persistent chemicals have not been extensively studied.

PBDEs were first reported in wildlife species, including fish, seals, whales and birds' eggs. In the late 1990's they were reported in the breast milk of mothers in Sweden, and research showed that levels had increased from zero in 1970 to high levels in the 1990's in parallel with the use of PBDEs. Following restrictions on their use in Sweden, followed by the EC-wide ban on Penta and Octa-mixtures, levels in breast milk in European women are now dropping, but in contrast levels in human tissues and breast milk in North America are still rising.

A recent study carried out by Hites and co-workers (Hites *et al*, 2004) has reported PBDEs to be present in both farmed and wild salmon. Although the levels of the contaminants were generally higher in farmed fish than wild fish, one species of wild salmon contained the highest level of PBDE found in the study.

There is only very limited information on the presence of PBDEs in other foods. The EC is currently considering the establishment of maximum limits for these chemicals in food and is encouraging Member States to carry out measurements to assist in this process.

## 2.4 Hexabromocyclododecane (HBCD)

Hexabromocyclododecane (HBCD) has primarily been used to improve flame retardant characteristics of extruded and expanded polystyrene products. Technical HBCD comprises three diasteroisomers (α, β and γ), with γ-HBCD contributing approximately 80% to the technical formulation. Although the evidence for the widespread environmental presence of HBCD is small, its detection in a wide range of matrices is a potential environmental and consumer food safety concern. Furthermore, its usage may increase as alternative BFRs (such as PentaBDE) are phased out.

## 2.5 Toxic equivalence factors for dioxins and dioxin-like PCBs

The toxicity of PCDDs, PCDFs and the dioxin-like PCB congeners are expressed using toxic equivalence factors (TEFs) (see Tables 1 and 2) representing the relative toxicity of the compound being measured to the most toxic dioxin congener, TCDD. This in turn reflects the relative strength of binding to the Ah receptor. It should be noted however that the toxicity of many of these substances, both dioxins and PCBs, has not been extensively evaluated.

An arbitrary TEF of 1 is assigned to TCDD, and by multiplying the analytically determined concentrations of each congener in a sample by its corresponding TEF, individual toxicity equivalents (TEQs) are determined. Summing the contribution from each congener, the total TEQ value of the sample can be obtained using the following equation:

TEQ = (PCDDi × TEFi) + (PCDFi × TEFi) + (*dioxin-like* PCBi × TEFi)

Several different TEF schemes have been proposed. For many years the most widely used schemes were that of NATO/CCMS (NATO/CCMS, 1988), giving the so-called International TEFs (I-TEFs) for PCDDs and PCDFs and the WHO-ECEH (European Centre for Environment and Health of the World Health Organization) scheme for PCBs. In 1998, WHO-ECEH proposed a new scheme of WHO-TEFs for PCDDs, PCDFs and dl-PCBs, which to date has been the most commonly used scheme (van den Berg *et al*, 1998). Dioxin TEQ values for food and human samples based on WHO-TEFs are approximately 10-20% higher than those obtained by using the I-TEFs of NATO/CCMS. WHO has recently re-evaluated the WHO-TEFs

proposed in 1998 (van den Berg *et al*, 2006) and has adjusted the TEFs for a number of compounds. The results provided in this report are however based on the 1998 scheme for WHO-TEFs.

**Table 1 Toxic Equivalence Factors (TEFs) for Dioxins and Dioxin-like PCBs**

| **PCDDs and PCDFs** | **I-TEF** (NATO/CCMS, 1988) | **WHO-TEF** (van den Berg *et al*, 1998) |
|---|---|---|
| 2,3,7,8-TCDD | 1 | 1 |
| 1,2,3,7,8-PnCDD | 0.5 | 1 |
| 1,2,3,4,7,8-HxCDD | 0.1 | 0.1 |
| 1,2,3,6,7,8-HxCDD | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDD | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCDD | 0.01 | 0.01 |
| OCDD | 0.001 | 0.0001 |
| 2,3,7,8-TCDF | 0.1 | 0.1 |
| 1,2,3,7,8-PnCDF | 0.05 | 0.05 |
| 2,3,4,7,8-PnCDF | 0.5 | 0.5 |
| 1,2,3,4,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,6,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDF | 0.1 | 0.1 |
| 2,3,4,6,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCDF | 0.01 | 0.01 |
| 1,2,3,4,7,8,9-HpCDF | 0.01 | 0.01 |
| OCDF | 0.001 | 0.0001 |
| **PCBs (IUPAC No. in parenthesis)** | **I-TEF** (NATO/CCMS, 1988) | **WHO-TEF** (van den Berg *et al*, 1998) |
| ***Non-ortho PCBs*** | | |
| 3,3',4,4'-TCB (77) | 0.0005 | 0.0001 |
| 3,4,4',5-TCB (81) | - | 0.0001 |
| 3,3',4,4',5-PnCB (126) | 0.1 | 0.1 |
| 3,3',4,4',5,5'-HxCB (169) | 0.01 | 0.01 |
| ***Mono-ortho PCBs*** | | |
| 2,3,3',4,4'-PnCB (105) | 0.0001 | 0.0001 |
| 2,3,4,4',5-PnCB (114) | 0.0005 | 0.0005 |
| 2,3',4,4',5-PnCB (118) | 0.0001 | 0.0001 |
| 2,3,4,4'5-PnCB (123) | 0.0001 | 0.0001 |
| 2,3,3',4,4',5-HxCB (156) | 0.0005 | 0.0005 |
| 2,3,3',4,4',5'-HxCB (157) | 0.0005 | 0.0005 |
| 2,3',4,4',5,5'-HxCB (167) | 0.00001 | 0.00001 |
| 2,3,3',4,4',5,5'-HpCB (189) | 0.0001 | 0.0001 |
| ***Di-ortho PCBs*** | | |
| 2,2',3,3',4,4',5-HpCB (170) | 0.0001 | 0.0001 |
| 2,2',3,4,4',5,5'-HpCB (180) | 0.00001 | 0.00001 |

*PnCDD, pentachlorodibenzo-p-dioxin; HxCDD, hexachlorodibenzo-p-dioxin; HpCDD, heptachlorodibenzo-p-dioxin; OCDD, octachlorodibenzo-p-dioxin; PnCDF, pentachlorodibenzofuran; HxCDF, hexachlorodibenzofuran; HpCDF, heptachlorodibenzofuran; OCDF, octachlorodibenzofuran. TCB, tetrachlorobiphenyl; PnCB, pentachlorobiphenyl; HxCB, hexachlorobiphenyl; HpCB, heptachlorobiphenyl.*

## 2.6 Risk assessment of dioxins, furans and PCBs in food

The SCF have carried out a risk assessment of dioxins and dioxin-like PCBs in food (SCF, 2000, SCF, 2001), as a consequence of which they concluded that the Tolerable Weekly Intake (TWI) for PCDDs, PCDFs and dl-PCBs should be no more than 14 pg WHO-TEQ/kg body weight (b.w.). This is very similar to the Provisional Tolerable Monthly Intake (PTMI) of 70 pg/kg b.w. per month derived by the FAO/WHO Joint Expert Committee on Food Additives and Contaminants (JECFA) (JECFA, 2002). It has been stated that the European average dietary intake is 1.2 to 3.0 pg WHO-TEQ/kg b.w./day, which translates into a weekly intake of between 8.4 and 21 pg WHO-TEQ/kg b.w. The upper end of this range exceeds the TWI as established by the SCF.

However, several studies carried out by the Food Safety Authority of Ireland (FSAI) have indicated that levels of dioxins in Irish food are relatively low. The 2002 collaborative study between County Council Cork and FSAI on dioxins, furans and PCBs in milk (FSAI, 2002b) showed dioxin levels ranging from 0.28 to 0.42 pg WHO-PCDD/F-TEQ/g fat over the period 1995 to 2001, compared with a regulatory Maximum Limit (ML) of 3 pg WHO-TEQ/g fat (Table 2). A study conducted on meat (carcass fat) from cattle, sheep, pigs and poultry in 2004 showed levels ranging from 0.08 – 0.62 pg WHO-PCDD/F-TEQ/g fat, which are well below the established regulatory maximum limits for the various animal species (FSAI, 2004a).

Similarly, the FSAI/Marine Institute (MI) study on levels of dioxins and dioxin-like PCBs in farmed fish and fish oil supplements (FSAI, 2002a) showed levels of PCDD/Fs in wild salmon ranging from 0.14 to 0.62 ng WHO-TEQ/kg whole weight, in farmed salmon from 0.59 to 1.50 ng WHO-TEQ/kg and in farmed trout from 0.17 to 0.55 ng WHO-TEQ/kg, compared with a regulatory Maximum Limit (ML) of 4 ng WHO-TEQ/kg for fish muscle meat on a whole weight basis (Table 2). Levels of total TEQ (Sum PCDD/Fs and dl-PCBs) were determined as follows: wild salmon 0.68 to 1.8 ng WHO-TEQ/kg whole weight; farmed salmon 2.3 to 6.3 ng WHO-TEQ/kg whole weight; and farmed trout 0.7 to 2.0 ng WHO-TEQ/kg whole weight. This confirmed previous findings that the contribution of dl-PCBs to the total TEQ is greater than PCDD/Fs for these fish in European waters (European Commission 2000). In the 2004 study of An Board Iascaigh Mhara, a mean level of 0.41 ng WHO TEQ/kg whole weight was reported for PCDD/Fs in farmed Irish salmon (Gruemping *et al*., 2004).

These studies indicate that levels of dioxins, furans and dioxin-like PCBs found in Irish milk, fish and meat are lower than those found in comparable foodstuffs from the more industrialised EC countries. Hence, it is likely that the exposure of the Irish population to dioxins in food is less than the European average.

A risk assessment for the non-dioxin-like PCBs (ndl-PCBs) in food has also been carried out recently at European level by the Scientific Panel on Contaminants of the European Food Safety Authority (EFSA), to include identification of the most relevant/sensitive toxicological endpoints for the PCB-congener patterns usually found in food (EFSA, 2005a). The panel concluded that the current toxicological database on health effects is not suitable for the separate assessment of ndl-PCBs. Also the human data on exposure did not

enable a distinction between the effects of ndl-PCB and PCDD/F to be made, due to co-occurrence of PCDDs and PCDFs, and therefore the assessment was based on individual ndl-PCB congeners. Due to the absence of mutagenicity the establishment of a health-based guidance value for levels of ndl-PCBs in food was considered possible, however, the panel considered the toxicological database too limited and hence a "Margin of Exposure" (MoE)[1] approach was used. This approach, which can be used to assess the risks to human health of exposure to a substance in absence of a tolerable daily intake or similar guidance value, has recently been endorsed by the EFSA Scientific Committee (EFSA, 2005b) and the WHO/FAO Joint Expert Committee on Food Additives and Contaminants (WHO/FAO, 2005). A rather small margin of exposure of 10 was calculated, however, the panel stressed that the endpoints considered in the evaluation of individual ndl-PCB congeners can also be observed with PCDD/F and dl-PCB. Overall, the panel concluded that further research and additional data is needed to better evaluate adverse effects from ndl-PCBs and a continuing effort to lower the levels of ndl-PCB in food is warranted.

## 2.7 Legislation on dioxins, furans and PCBs in food

Given that the weekly average dietary intake of dioxins by at least some of the European population exceeds the TWI established by the SCF, on a European scale it is desirable to reduce the exposure of the population to dioxins. In 2001, the European Commission published its Community strategy for dioxins, furans and polychlorinated biphenyls, aimed at achieving a reduction in human exposure to dioxins and PCBs (European Commission, 2001). Environmental legislation designed to limit dioxin emissions is in the process of discussion at European level. Other source-directed measures have been introduced to reduce the contamination of feeding stuffs for animal nutrition (Council Directive 2001/102/EC amending Directive 1999/29/EC on the undesirable substances and products in animal nutrition).

In addition, as part of its reduction strategy the E.C. has also introduced maximum levels for PCDDs, PCDFs and dioxin-like PCBs in foodstuffs, via Council Regulation (EC) No. 1881/2006[2] which sets maximum levels for certain contaminants in foodstuffs. Table 2 shows the maximum levels established in this Regulation for dioxins (sum of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), expressed in World Health Organisation (WHO) toxic equivalents using the WHO-TEFs (toxic equivalency factors (van den Berg *et al*, 1998), and sum of dioxins and dioxin-like PCBs, sum of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs), expressed in World Health Organisation toxic equivalents using the WHO-TEFs.

[1]The margin of exposure is defined as the reference point on the dose-response curve (usually based on animal experiments in the absence of human data) divided by the estimated intake by humans. (EFSA 2005b).

[2]This Regulation consolidates all legislation on contaminants and replaces Commission Regulation 466/2001 and all its amendments. The new legislation applies from 1st March, 2007, and until this date the limits laid down in Commission Regulation 466/2001 (which are identical to those in the new Regulation) remain in force.

The legislation also imposes an obligation on Member States to monitor the levels of dioxins in foodstuffs and report results to the E.C. Under this obligation, Ireland is required to carry out monitoring for a range of contaminants in a variety of foodstuffs. Results for previous monitoring surveys have been published and reports are available on the FSAI website (FSAI, 2002a, 2002b, 2004a, 2004b). Such data will ultimately be used to review the maximum limits and gauge the effectiveness of the reduction strategy.

**Table 2 Maximum Levels for dioxins, furans and dioxin-like PCBs in food**

| FOOD | Maximum levels Sum of dioxins and furans (WHO-PCDD/F-TEQ) (2) | Maximum levels Sum of dioxins, furans and dioxin-like PCBs (WHO-PCDD/F-PCB-TEQ) (1) (2) |
|---|---|---|
| 5.1.1 Meat and meat products (3)<br>- of ruminants (bovine animals, sheep)<br>- of poultry and farmed game<br>- of pigs<br>5.1.2 Liver and derived products of terrestrial animals | <br>3 pg/g fat(4)<br>2 pg/g fat (4)<br>1 pg/g fat (4)<br>6 pg/g fat (4) | <br>4.5 pg/g fat(4)<br>4 pg/g fat(4)<br>1.50 pg/g fat(4)<br>12 pg/g fat(4) |
| 5.2 Muscle meat of fish and fishery products and products thereof with the exception of eel(5) (6)<br>- Muscle meat of eel (*Anguilla anguilla)* and products thereof | 4 pg/g whole weight<br>4 pg/g whole weight | 8 pg/g whole weight<br>12 pg/g whole weight |
| 5.3 Milk(7) and milk products, including butter fat | 3 pg/g fat(4) | 6 pg/g fat(4) |
| 5.4 Hen eggs and egg products (8) | 3 pg/g fat(4) | 6 pg/g fat(4) |
| 5.5 Oils and fats<br>- Animal fat<br>- of ruminants<br>- of poultry and farmed game<br>- of pigs<br>- mixed animal fats<br>- Vegetable oil and fats<br>- marine oil (fish body oil, fish liver oil and oils of other marine organisms intended for human consumption ) | <br><br>3 pg/g fat<br>2 pg/g fat<br>1 pg/g fat<br>2 pg/g fat<br>0.75 pg/g fat<br>2 pg/g fat | <br><br>4.5 pg/g fat<br>4 pg/g fat<br>1.5 pg/g fat<br>3 pg/g fat<br>1.5 pg/g fat<br>10 pg/g fat |

(1) Applicable from 4th November, 2006.

(2) Upperbound concentrations: Upperbound concentrations are calculated on the assumption that the values of the different congeners below the limit of quantification are equal to the limit of quantification.

(3) Meat of bovine animals, sheep, pig, poultry and farmed game as defined in Annex I to Regulation (EC) No 853/2004 of the European Parliament and of the Council (OJ L 139, 30.4.2004. Corrected version in OJ L 226, 25.6.2004, p. 22) but not including edible offal as defined in that Annex.

(4) The maximum levels are not applicable for food products containing < 1 % fat.

(5) Muscle meat of fish and fishery products as defined in categories (a), (b), (c), (e) and (f) of the list in Article 1 of Council Regulation (EC) No 104/2000 (OJ L 17, 21.1.2000, p. 22. Regulation as amended by the 2003 Act of Accession). The maximum level applies to crustaceans, excluding the brown meat of crab and excluding head and thorax meat of lobster and similar large crustaceans (Nephropidae and Palinuridae) and to cephalopods without viscera.

(6) Where fish are intended to be eaten whole, the maximum level applies to the whole fish.

(7) Milk (raw milk, milk for the manufacture of milk-based products and heat-treated milk as defined in Annex I to Regulation (EC) No 853/2004.

(8) Hen eggs and egg products as defined in Annex I to Regulation (EC) No 853/2004.

There are currently no maximum levels for non-dioxin like PCBs set by the EC, however, a number of EC Member-States have set national levels for individual or sum of the 7 indicator PCBs. The most stringent level has been set in Belgium for the sum of 7 indicator PCBs with a maximum level of 75 µg/kg product for "Fish, including shellfish and crustaceans and foodstuffs derived thereof" (EU Working Document, 2005). The European Commission is currently considering the regulation of non-dioxin like PCBs, possibly via setting maximum levels for the 6 indicator PCBs.

There are also no EU maximum limits for BFRs in food. Tolerable daily intakes (TDIs) have not been derived, primarily due to limited toxicological data for BFRs and the associated uncertainties with such studies. Considerably more work is required internationally on the toxicology and risk assessment of BFRs.

# 3. Study Outline

The present study was undertaken to investigate the current levels of dioxins, furans, PCBs and PBDEs in fishery produce available on the Irish market and thereby increase the available data on the occurrence of these contaminants in such produce.

## 3.1 Materials and Methods

For this survey a total of 70 samples were collected in the 2$^{nd}$ half of 2004, comprising the following species and retail groupings: (1) Farmed Atlantic salmon, (2) Wild Atlantic salmon, (3) Fresh herring, (4) Fresh mackerel, (5) Fresh tuna, (6) Fresh shellfish, (7) Smoked farmed salmon, (8) Canned salmon, (9) Canned tuna, (10) Canned herring, (11) Canned sardines and (12) Canned mackerel.

Groups 1 to 6 were collected by staff of the Marine Institute from landings at Irish ports and production level (farmed salmon), group 7 was provided by An Board Iascaigh Mhara and the remainder were sampled by officers of the Food Safety Authority of Ireland at retail level. Fresh tuna and wild salmon samples were analysed individually, all other groupings composed a number of pooled sub-samples (see Table 3). Capture locations and retail batch origin details were collected as appropriate.

**Table 3 Sample Details**

| Common Name | Species | N | sub-N | Origin | Details | | |
|---|---|---|---|---|---|---|---|
| Oysters | *Crassostrea gigas* | 5 | 25 | Ireland | Cultivated pacific oysters | raw | shelled |
| Herring | *Clupea harengus* | 4 | 20 | Ireland | fresh herring | raw | skin off |
| Mackerel | *Scomber scombrus* | 5 | 20 | Ireland | fresh mackerel | raw | skin off |
| Albacore Tuna | *Thunnus alunga* | 5 | 1 | Ireland | fresh tuna | raw | skin off |
| Atlantic Salmon | *Salmo salar* | 10 | 1 | Ireland | wild salmon | raw | skin off |
| Atlantic Salmon | *Salmo salar* | 15 | 5 | Ireland | farmed salmon | raw | skin off |
| Atlantic Salmon | *Salmo salar* | 10 | 5 | Ireland | smoked salmon | smoked | skin off |
| Herring | *Clupea harengus* | 2 | 5 | Retail | Tinned herring (kippers) | tinned | skin on |
| Mackerel | *Scomber scombrus* | 2 | 5 | Retail | Tinned mackerel (brine) | tinned | skin on |
| Pink & red Salmon | n.a. | 5 | 5 | Retail | tinned salmon | tinned | skin off |
| Sardines | n.a. | 1 | 5 | Retail | tinned sardines (oil) | tinned | skin on |
| Skipjack Tuna | n.a. | 5 | 5 | Retail | tinned tuna | tinned | skin off |

N = number of pooled (individuals) analysed.
Sub-N = number of individuals in a pooled sample.
n.a. = exact species information not available

## 3.2 Analytes included in the survey

### 3.2.1 PCDDs/PCDFs and PCBs

The 17 PCDD/PCDF congeners of toxicological concern are shown in Table 1. The following PCB congeners, including the 12 dioxin-like PCBs[3] and the 7 indicator PCBs[4] were also analysed in this study.

- PCB 18
- PCB 28
- PCB 31
- PCB 33
- PCB 37
- PCB 41
- PCB 44
- PCB 47
- PCB 49
- PCB 51
- PCB 52
- PCB 60
- PCB 66
- PCB 74
- PCB 77
- PCB 81
- PCB 87
- PCB 99
- PCB 101
- PCB 105
- PCB 110
- PCB 114
- PCB 118
- PCB 123
- PCB 126
- PCB 138
- PCB 141
- PCB 151
- PCB 153
- PCB 156
- PCB 157
- PCB 167
- PCB 169
- PCB 180
- PCB 183
- PCB 185
- PCB 187
- PCB 189
- PCB 191
- PCB 193
- PCB 194
- PCB 201
- PCB 203
- PCB 206

[3] (PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189)
[4] (PCBs 28, 52, 101, 118, 138, 153 and 180)

### 3.2.2 Brominated flame retardants

The following 16 PBDE congeners were analysed in this study:

- BDE-17
- BDE-28
- BDE-47
- BDE-49
- BDE-66
- BDE-71
- BDE-77
- BDE-85
- BDE-99
- BDE-100
- BDE-119
- BDE-126
- BDE138
- BDE153
- BDE 154
- BDE-183

The isomers of hexabromocyclododecane (α-HBCD, β-HBCD and γ-HBCD) were analysed in a subset of samples in this study. Isomer specific analysis was completed on 4 farmed salmon, 1 smoked salmon, 2 tinned tuna, 1 wild tuna (albacore) and 1 tinned mackerel sample.

## 3.3 Methodology

Sample preparation

All samples were prepared in the Marine Institute. Skin was removed from all samples with the exception of tinned samples. Subcutaneous lipid was removed from skin, added back to samples and samples were aggregated as appropriate (see Table 3). Muscle tissue samples were then homogenised. Total lipid content was determined by the Marine Institute using the Smedes method (Smedes, 1999). Frozen homogenates were analysed for PCDD/F, PCBs and PBDEs by Eurofins Europe (GfA), Germany, and for HBCD at the Central Science Laboratory (CSL), York England, under contract to FSAI. Moisture content determination was carried out at the Marine Institute.

Sample Analysis

Analysis of PCDD/Fs and PCBs was performed according to the EN ISO 17025 accredited methods GfA QMA 504-191/203/205. The analytical methodology is in compliance with the requirement for the HRGC/HRMS confirmatory analysis of food for PCDD/Fs and PCBs as laid down by EU Directive 2002/69 (European Commission, 2002). For the analysis of PBDEs, a GfA-established GC/MS method was used while HBCD isomers were analysed by CSL using LC-MS/MS. Further details on analytical methodology and quality assurance are reported in the Appendix.

# 4. Results

## 4.1 Dioxins, furans and PCBs

Table 4 presents summary information on the levels of PCDD/Fs, dioxin-like PCBs and indicator PCBs measured in fishery products available in Ireland sampled during this study.

Results are expressed as total WHO-TEQs in ng/kg whole (fresh) weight for PCDD/Fs and dioxin-like PCBs, additionally the sum of PCDD/Fs and dioxin-like PCBs are reported. The sum of the 7 indicator PCBs are reported in µg/kg whole weight. In each case results are presented as upper-bound values.

**Table 4 Upper-bound levels (<LOQ = LOQ) of PCDD/Fs, dioxin-like PCBs and total TEQs and sum of 7 Indicator PCBs in fishery products (whole weight)**

| Sample | N (subN) | Statistics | *Σdl- PCBs&PCDD/F* | *PCDD/F* | *dl-PCBs* | *7 Indicator PCBs* |
|---|---|---|---|---|---|---|
| | | | WHO TEQs ng/kg | | | µg/kg |
| Wild Atlantic salmon | 10(1) | Mean | 0.80 | 0.34 | 0.46 | 5.49 |
| | | Median | 0.76 | 0.32 | 0.45 | 5.67 |
| | | Std.Dev. | 0.26 | 0.14 | 0.12 | 1.10 |
| | | Minimum | 0.41 | 0.13 | 0.28 | 3.25 |
| | | Maximum | 1.30 | 0.61 | 0.69 | 6.85 |
| Farmed Atlantic salmon* | 15(5) | Mean | 2.15 | 0.54 | 1.61 | 17.1 |
| | | Median | 2.14 | 0.49 | 1.66 | 16.8 |
| | | Std. Dev. | 0.46 | 0.17 | 0.30 | 3.64 |
| | | Minimum | 1.22 | 0.25 | 0.97 | 8.34 |
| | | Maximum | 2.86 | 0.82 | 2.04 | 23.9 |
| Fresh tuna (albacore) | 5(1) | Mean | 0.90 | 0.16 | 0.74 | 8.70 |
| | | Median | 0.99 | 0.16 | 0.81 | 9.30 |
| | | Std. Dev. | 0.21 | 0.05 | 0.20 | 2.72 |
| | | Minimum | 0.61 | 0.11 | 0.50 | 5.65 |
| | | Maximum | 1.12 | 0.23 | 0.96 | 12.3 |
| Fresh herring | 4(10) | Mean | 1.02 | 0.42 | 0.60 | 7.68 |
| | | Median | 1.03 | 0.42 | 0.60 | 7.56 |
| | | Std. Dev. | 0.07 | 0.03 | 0.04 | 0.57 |
| | | Minimum | 0.93 | 0.38 | 0.55 | 7.14 |
| | | Maximum | 1.09 | 0.44 | 0.65 | 8.44 |
| Fresh mackerel | 4(10) | Mean | 1.24 | 0.28 | 0.96 | 8.04 |
| | | Median | 1.20 | 0.30 | 0.91 | 7.75 |
| | | Std. Dev. | 0.28 | 0.05 | 0.24 | 2.77 |
| | | Minimum | 0.97 | 0.21 | 0.76 | 5.22 |
| | | Maximum | 1.58 | 0.32 | 1.26 | 11.5 |
| Oysters (*C.gigas*) | 5(25) | Mean | 0.37 | 0.21 | 0.16 | 11.6 |
| | | Median | 0.24 | 0.13 | 0.14 | 13.3 |
| | | Std. Dev. | 0.20 | 0.14 | 0.07 | 0.53 |
| | | Minimum | 0.22 | 0.09 | 0.10 | 0.55 |
| | | Maximum | 0.63 | 0.43 | 0.26 | 1.80 |
| Smoked Atlantic salmon | 11(5) | Mean | 1.27 | 0.28 | 0.99 | 10. 6 |
| | | Median | 1.27 | 0.26 | 1.01 | 10.8 |
| | | Std. Dev. | 0.21 | 0.07 | 0.14 | 2.11 |
| | | Minimum | 0.97 | 0.19 | 0.79 | 6.90 |
| | | Maximum | 1.76 | 0.47 | 1.29 | 13.2 |

* 15 farmed salmon samples were collected from separate sites. Each sample contains 5 fish from one cage

**Table 4 (cont'd) Upper-bound levels (<LOQ = LOQ) of PCDD/Fs, dioxin-like PCBs and total TEQs and sum of 7 Indicator PCBs in fishery products (whole weight)**

| Sample | N (subN) | Statistic | *Σdl PCBs&PCDD/F* | *PCDD/F* | *Dl PCBs* | *7 Indicator PCBs* |
|---|---|---|---|---|---|---|
| | | | WHO TEQs ng/kg | | | µg/kg |
| Tinned pink salmon | 3(5) | Mean | 0.08 | 0.02 | 0.06 | 0.67 |
| | | Median | 0.08 | 0.02 | 0.06 | 0.64 |
| | | Minimum | 0.07 | 0.02 | 0.05 | 0.56 |
| | | Maximum | 0.10 | 0.03 | 0.07 | 0.80 |
| Tinned red salmon | 2(5) | Mean | 0.48 | 0.19 | 0.29 | 2.67 |
| | | Median | 0.48 | 0.19 | 0.29 | 2.67 |
| | | Minimum | 0.34 | 0.14 | 0.20 | 1.99 |
| | | Maximum | 0.61 | 0.24 | 0.37 | 3.35 |
| Tinned tuna skipjack | 5(5) | Mean | 0.05 | 0.02 | 0.03 | 0.08 |
| | | Median | 0.05 | 0.02 | 0.03 | 0.08 |
| | | Std. Dev. | 0.01 | 0.003 | 0.01 | 0.02 |
| | | Minimum | 0.04 | 0.01 | 0.03 | 0.06 |
| | | Maximum | 0.06 | 0.02 | 0.04 | 0.12 |
| Tinned mackerel | 2(5) | Mean | 1.04 | 0.31 | 0.73 | 5.87 |
| | | Median | 1.04 | 0.31 | 0.73 | 5.87 |
| | | Minimum | 1.02 | 0.29 | 0.72 | 5.77 |
| | | Maximum | 1.06 | 0.33 | 0.73 | 5.97 |
| Tinned herring | 2(5) | Mean | 0.82 | 0.38 | 0.44 | 5.17 |
| | | Median | 0.82 | 0.38 | 0.44 | 5.17 |
| | | Minimum | 0.81 | 0.38 | 0.43 | 5.09 |
| | | Maximum | 0.82 | 0.38 | 0.44 | 5.25 |
| Tinned sardines | 1(5) | Mean | 2.12 | 0.56 | 1.56 | 2.84 |

As reported in Table 4 the highest total TEQ (sum PCDD/F & dl-PCB) was observed in farmed salmon, at a mean concentration of 2.15 ng/kg whole weight, followed by tinned sardines (1 sample) with a mean TEQ level (sum PCDD/F & dl-PCB) of 2.12 ng/kg whole weight. The lowest level was observed in tinned tuna, with a mean concentration of 0.05 TEQ ng/kg whole weight. Fresh and tinned herring and mackerel showed levels within similar ranges, whereas tinned salmon and tuna generally showed lower levels of contamination, which may be attributed to differences in species, origin and fat content of the fish compared to their fresh counterparts. Significant differences ($p<0.003$) in dioxin concentrations were observed between wild and farmed salmon samples in this study, with wild salmon on average showing 40% lower dioxin levels than its farmed counterpart. Even larger differences were observed for dl-PCBs with levels being on average about 70% lower in wild salmon.

The data are also presented in graphical form in

Figure **1**, while Figure 2 provides an overview of mean concentrations of indicator PCBs in the fish species covered by this survey.

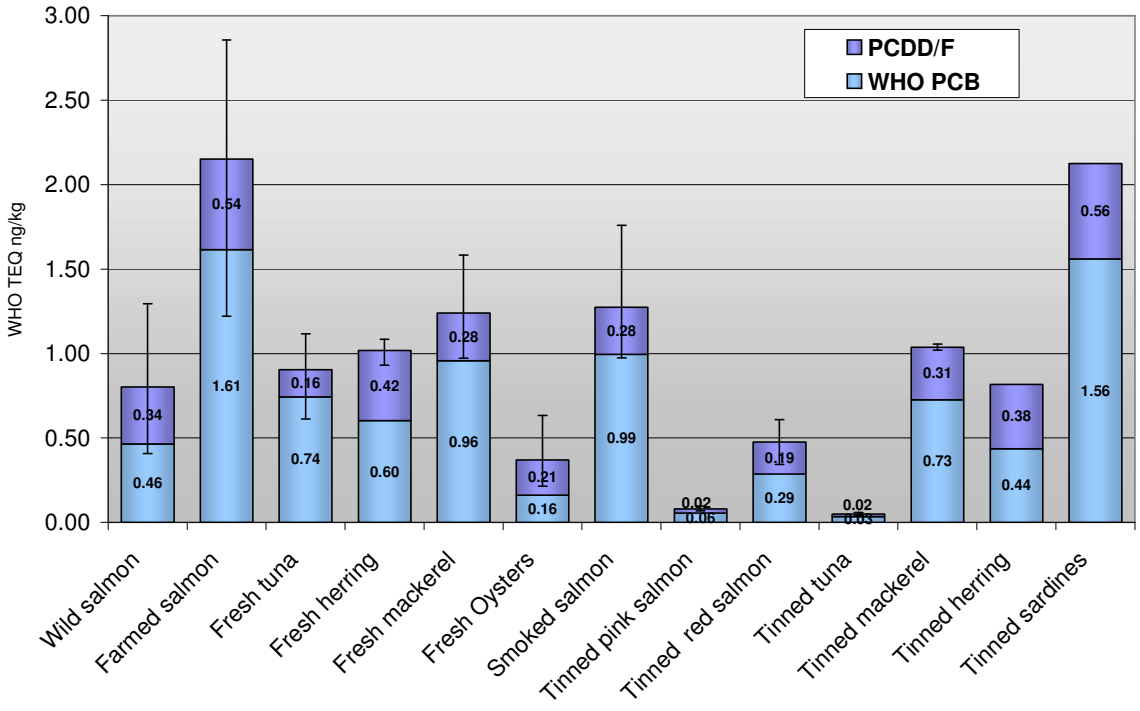



**Figure 1** **Mean upper-bound WHO TEQ PCDD/F & dl-PCB ng/kg whole weight in fish species (bars represent min and max levels)**

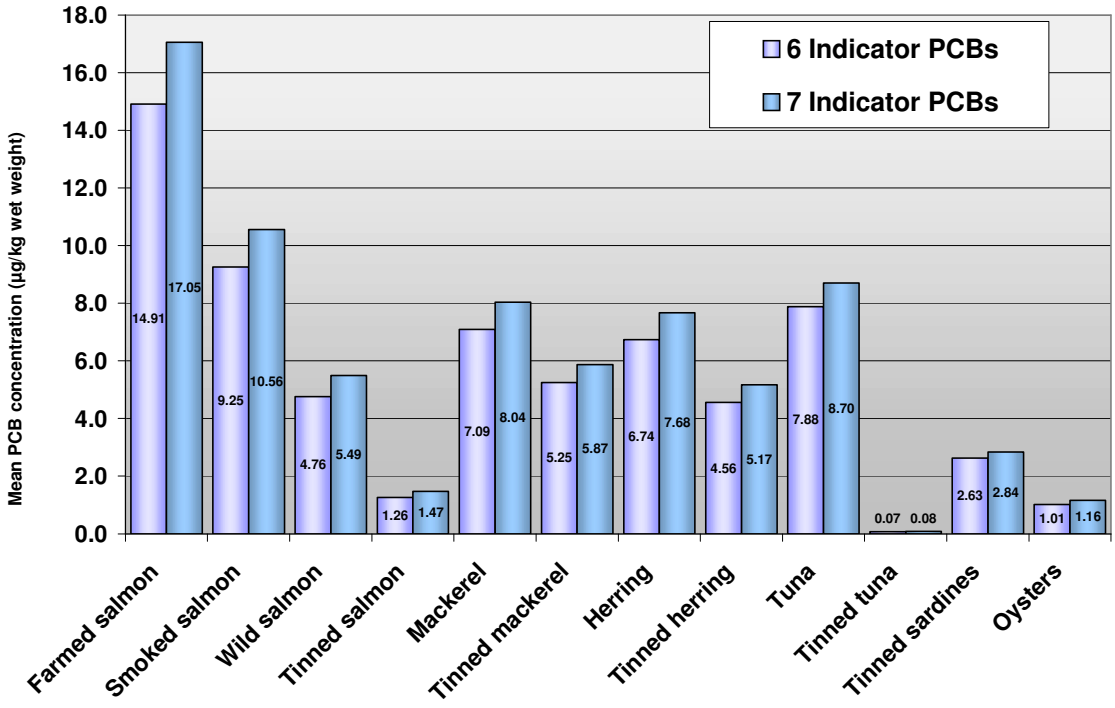



**Figure 2** **Mean concentration of Σ 7 Indicator PCBs and Σ 6 Indicator PCBs (µg/kg fresh weight, upper-bound)**

Levels of lipophilic contaminants such as PCDDs/PCDFs and PCBs are generally recognised to increase in fish species as the lipid content of the sample increases, supporting the contention that oily fish tend to accumulate lipophilic contaminants to a higher degree than non-oily fish.

Table 5 summarises the mean lipid data analysed by the Marine Institute for all the species groupings covered in this survey. Comparison of the lipid content with the contaminant data shows that levels of contaminants were somewhat higher in the oily fish examined in this survey, such as farmed salmon and herring, than in the low fat products such as shellfish, tinned and fresh tuna, supporting this contention.

**Table 5 Mean total lipid levels (%) determined in fish species covered in this survey**

| Fish product | Average Lipid (%) | Range (%) |
|---|---|---|
| Wild salmon | 10.7 | (5.8 - 12.7) |
| Tinned red salmon | 6.7 | (4.7 - 8.0) |
| Tined tuna | 5.3 | (0.7 - 12.5) |
| Smoked salmon | 10.3 | (9.2 - 11.6) |
| Tuna | 10.1 | (5.6 - 15.8) |
| Herring | 13.0 | (11.5 - 14.4) |
| Farmed salmon | 14.5 | (10.4 - 18.4) |
| Mackerel | 10.1 | (7.0 - 13.0) |
| Tinned sardines | 29.5 | NA |
| Tinned mackerel | 30.1 | (28.6 - 31.6) |
| Tinned herring | 16.0 | (15.1 - 16.9) |
| Oysters | 2.5 | (2.0 - 3.3) |

NA =not applicable as n=1.

## 4.2 Brominated Flame Retardants

### 4.2.1 PBDEs

Of the 16 PBDE congeners analysed, only 7 congeners (BDEs 47, 49, 99, 100, 154, 66 and 28) were found to predominate. The most abundant congeners determined in all samples were BDEs-47, 49, 99, 100, 66, 28 and 154. BDEs-17, 153 and 119 were frequently below or close to the Limit of Quantification (LOQ) (0.01, 0.03, 0.02 µg/kg whole (wet) weight respectively) except for farmed and smoked salmon with average BDE-153 levels of 0.07 and 0.05 µg/kg whole weight respectively. No sample showed levels of BDE-71, BDE-85, BDE-77, BDE-126, BDE-138, BDE-183 above the LOQ (0.01, 0.02, 0.01, 0.02, 0.03, 0.05 µg/kg whole weight respectively), with the exception of one shellfish sample (BDE 71 and 85). Table 7 presents an overview of the percentage of the individual BDEs quantified in all 70 samples analysed.

Table 6 presents calculated mean, minimum, median and maximum upper-bound levels for the sum of total PBDE congeners (16 congeners). Results are expressed on a whole weight basis.

**Table 6 Upper-bound levels (<LOQ = LOQ) of Σ16PBDEs in fishery products (µg/kg whole weight)**

| Sample | N (sub-N)* | Statistics | ΣPBDE | Sample | N (sub-N) | Statistics | Σ PBDE |
|---|---|---|---|---|---|---|---|
| Wild salmon | 10(1) | Mean | 0.86 | Tinned pink salmon | 3(5) | Mean | 0.33 |
| | | Median | 0.85 | | | Median | 0.33 |
| | | Minimum | 0.70 | | | Minimum | 0.33 |
| | | Maximum | 1.01 | | | Maximum | 0.34 |
| Farmed salmon | 15(5) | Mean | 3.71 | Tinned red salmon | 2(5) | Mean | 0.34 |
| | | Median | 3.91 | | | Median | 0.34 |
| | | Minimum | 2.42 | | | Minimum | 0.33 |
| | | Maximum | 5.05 | | | Maximum | 0.35 |
| Fresh tuna | 5(1) | Mean | 0.96 | Tinned tuna | 5(5) | Mean | 0.31 |
| | | Median | 0.97 | | | Median | 0.31 |
| | | Minimum | 0.57 | | | Minimum | 0.31 |
| | | Maximum | 1.36 | | | Maximum | 0.31 |
| Fresh herring | 4(10) | Mean | 1.67 | Tinned mackerel | 2(5) | Mean | 1.56 |
| | | Median | 1.65 | | | Minimum | 1.26 |
| | | Minimum | 1.61 | | | Maximum | 1.86 |
| | | Maximum | 1.77 | | | | |
| Fresh mackerel | 5(10) | Mean | 1.35 | Tinned herring | 2(5) | Mean | 1.50 |
| | | Median | 1.33 | | | Minimum | 1.46 |
| | | Minimum | 0.93 | | | Maximum | 1.53 |
| | | Maximum | 1.70 | | | | |
| Shellfish (C.*gigas*) | 5(25) | Mean | 1.75 | Tinned sardines | 1(5) | Mean | 0.34 |
| | | Median | 1.45 | | | | |
| | | Minimum | 0.69 | | | | |
| | | Maximum | 4.21 | | | | |
| Smoked salmon | 11(5) | Mean | 2.39 | | | | |
| | | Median | 2.44 | | | | |
| | | Minimum | 1.69 | | | | |
| | | Maximum | 3.58 | | | | |

*Sub-N = denotes the number of individual samples aggregated to provide a single analytical sample

**Table 7 Overview of BDE congener occurrence above the quantifiable level in fish samples**

| BDE No | No Samples >LOQ | Species | % |
|---|---|---|---|
| 47 | 65 | all except tinned tuna | 92.9 |
| 49, 99, 100 | 59 | all except tinned tuna, tinned salmon | 84.3 |
| 66, 28, 154 | 57 | all except tinned tuna, tinned salmon, shellfish | 81.4 |
| 153 | 30 | mostly farmed salmon & smoked salmon | 42.9 |
| 17 | 18 | mostly in smoked salmon, farmed salmon, tinned mackerel at LOQ, shellfish ~0.03 | 25.7 |
| 119 | 5 | mostly farmed and smoked salmon | 7.1 |
| 71, 85 | 1 | in shellfish | 1.4 |
| 77, 126, 138, 183 | 0 | not quantified in any sample | 0 |

The highest concentrations of total PBDE (sum 16) were observed in farmed and smoked (farmed) Atlantic salmon (3.71 and 2.39 µg/kg whole weight respectively). Fresh mackerel, fresh herring and shellfish showed lower levels (1.35, 1.67 and 1.75, µg/kg whole weight upper-bound means respectively) as did

fresh tuna and wild salmon (0.96 and 0.86 µg/kg whole weight respectively) which showed the lowest levels in all fresh fish included in this survey. Levels in canned tuna were all below the limit of quantification.

Comparable contaminant concentrations were observed for canned fish (herring or mackerel) and their corresponding fresh samples. Results for canned sardines were also comparably low. The data are also presented in graphical form in Figure 3 below.

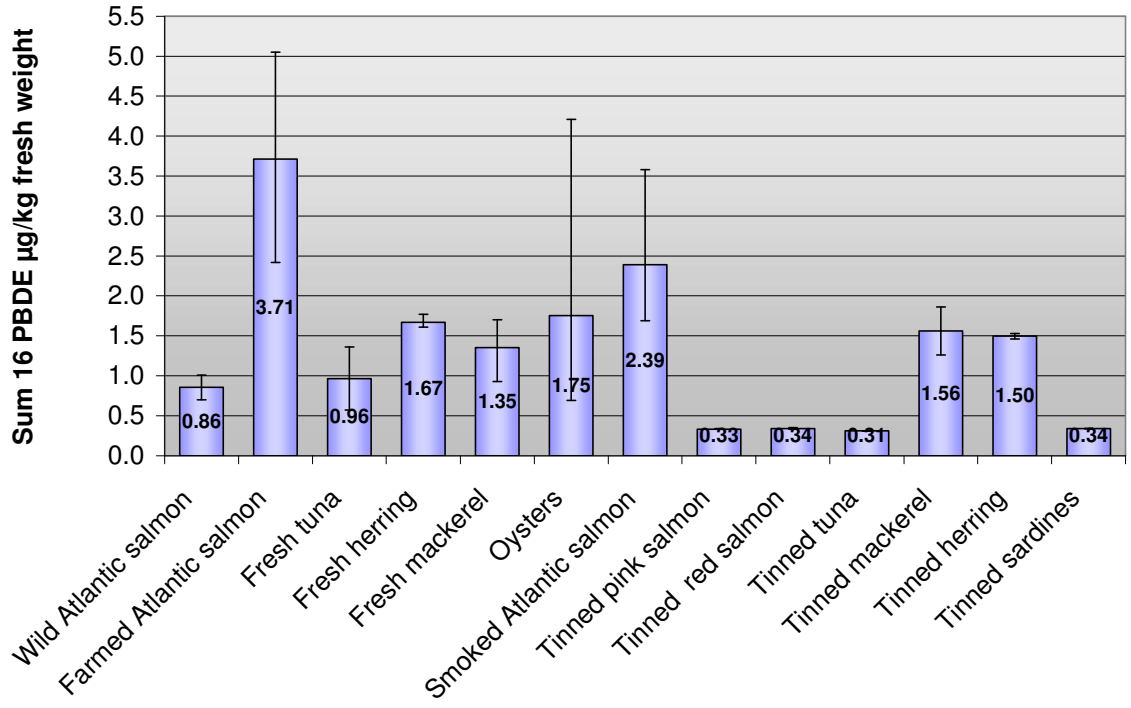



**Figure 3 Mean Upperbound concentration Σ16 PBDE in fish samples expressed in µg/kg whole weight (bars represent min and max levels)**

### 4.2.2 HBCD

Total and isomer specific HBCD levels in 10 samples are presented in Table 8.

**Table 8 Levels of α β and γ-HBCD isomers and total (upperbound) HBCD in individual samples of fishery produce on the Irish marketplace (µg/kg wet weight)**

| Sample Ref. | Matrix | αHBCD | βHBCD | γHBCD | Total |
|---|---|---|---|---|---|
| MSC/04/1120 | Tinned salmon | <0.073 | <0.014 | <0.016 | <0.10 |
| MSC/04/1129 | Farmed salmon | 1.20 | <0.049 | <0.068 | 1.32 |
| MSC/04/1141 | Farmed salmon | 0.88 | <0.043 | 0.16 | 1.08 |
| MSC/04/1124 | Tinned tuna | <0.073 | <0.014 | <0.016 | <0.10 |
| MSC/04/1128 | Tinned tuna | <0.073 | <0.014 | <0.016 | <0.10 |
| MSC/04/1147 | Smoked salmon | 0.55 | 0.044 | <0.084 | 0.68 |
| MSC/04/1132 | Farmed salmon | 2.30 | 0.10 | 0.27 | 2.67 |
| MSC/04/1137 | Farmed salmon | 1.30 | <0.053 | <0.016 | 1.37 |
| MSC/05/0003 | Tinned mackerel | 0.87 | <0.014 | 0.13 | 1.01 |
| MSC/04/1176 | Tuna | 0.28 | <0.014 | <0.016 | 0.31 |

# 5. Discussion

The results of this study, undertaken to investigate levels of dioxins (PCDDs), furans (PCDFs), PCBs, PBDEs and HBCD in fish and fishery products available on the Irish market place, show that levels in the food commodities analysed were generally low, and were well below the maximum limits laid down for PCDDs/PCDFs and dioxin-like PCBs in Council Regulation 1881/2006 .

There were marked differences in dioxin levels between wild and farmed salmon samples in this study, with wild salmon on average showing 40% lower dioxin levels than its farmed counterpart. Even larger differences were observed for dl-PCBs, with levels being on average about 70% lower in wild salmon. A general reduction in dioxin and PCB contamination in farmed fish can, however, be observed, when comparing levels to a previous survey (FSAI, 2002a).

This previous study, carried out in 2001, investigated levels of PCDD/F and dl-PCBs in wild and farmed salmon. Direct comparison with this previous survey is difficult due to differences in analytical limits of detection between the two surveys, however for a number of congeners determined above the limit of detection in both studies some comparisons can be made. For 2,3,7,8 TCDD, the most toxic of the dioxin congeners, a significant reduction ($p<0.002$) could be observed. Table 9 provides an overview of the percentage reduction observed for the congeners detected above LOQs in both surveys. Taking the above mentioned limitations into account an overall reduction of 38% ($p<0.001$) can be calculated for Sum WHO TEQ PCDD/F in the 2004 farmed salmon samples versus the 2001 farmed salmon samples.

**Table 9 Percentage (%) reduction in levels of specific PCDD and PCDF congeners in 15 farmed salmon samples analysed in 2004 compared to 15 farmed salmon samples analysed in 2001.**

| Congener | Reduction from 2001 survey (%) |
|---|---|
| 2,3,7,8-Tetra-CDD | 37.6 |
| 1,2,3,7,8-Penta-CDD | 40.5 |
| 1,2,3,6,7,8-Hexa-CDD | 35.4 |
| 2,3,7,8-Tetra-CDF | 45.0 |
| 1,2,3,7,8-Penta-CDF | 42.1 |
| 2,3,4,7,8-Penta-CDF | 27.3 |

Significant ($P<0.001$) reductions of approximately 50% could also be observed for dl-PCBs. These figures indicate a general reduction in dioxin and dl-PCB contamination in Irish farmed salmon, which may in part be attributable to source-directed measures adopted by the industry in the intervening period, such as changes in sources or species of fish oils in fish feeds or changes in feeding management regimes, amongst other possibilities.

In relation to the non-dioxin-like PCBs, the concentrations found in Irish farmed salmon in this survey are substantially below maximum levels for the so-called indicator PCBs (either sum of 6 or sum of 7) currently set in some EU Member States. Results concur with results of routine monitoring of indicator PCBs in

farmed and wild fish carried out by the Marine Institute. As with the PCDD/F and dl-PCBs, a reduction of 48% in the levels of the indicator PCBs in farmed salmon was observed between the study carried out in 2001 and this study ($p<0.001$), again indicative of risk management measures adopted by the industry, such as changes in sources or species of fish oils in fish feeds or changes in feeding management regimes.

Comparison of the fat content with the contaminant data shows that levels of contaminants were somewhat higher in the oily fish examined in this survey, such as farmed salmon and herring compared with the low fat products such as shellfish, tinned tuna and salmon. However, there are particular health benefits associated with consuming oily fish due to their high contents of polyunsaturated fatty acids (PUFAs). The FSAI will report separately on the levels of PUFAs found in the various species examined in this study and the risks and benefits of consumption of oily fish including farmed salmon.

PBDE results in farmed salmon were similar to those recorded in a smaller Marine Institute study completed in 2004 (Marine Institute, 2004c), in which results ranged from 2.28 to 4.61 (mean 3.05) µg/kg whole weight for the sum of 17 individual PBDEs. Levels reported by Hites and co-workers (Hites *et al,* 2004) in retail farmed salmon range between 0.6 to 3.9 µg /kg whole weight and the range was 1.25 to 3.9 µg/kg in all confirmed farmed fish. These are comparable to the levels found in the present study. However, differences exist in the number of congeners determined in the various studies listed and therefore direct comparisons of the datasets cannot be made.

The higher PBDE concentrations observed in farmed Atlantic salmon versus wild Atlantic salmon may in part be attributable to differences in feed regime and sources. Differences observed in fresh salmon and fresh tuna versus canned salmon and canned tuna may in part be due to differences in species types sampled, for example skipjack tuna is the dominant species used for canning and albacore tuna is the most widely marketed fresh species in Ireland. Fish processing practices may also result in such differences.

The size/age, diet, lipid content and trophic status of the fish are also likely to be contributing factors. Furthermore, the majority of canned samples available on the Irish market differ in geographic origin from the fresh samples analysed, with canned samples mainly being imported/originating from countries bordering the Indian Ocean and the North Pacific Ocean.

Total HBCD levels were low in all samples and levels in farmed salmon are in agreement with those of a previous Marine Institute survey (1.17 ± 0.26) (Marine Institute, 2004c).

A study of BFR-contaminated trout and eel from the Skerne-Tees river system was carried out by the UK Food Standards Agency (Food Standards Agency, 2004). Levels in the fish from the UK study were much higher than those determined in this present study and the study completed by the Marine Institute in 2004. In the UK study, however, the observed contamination was linked to a specific source, a BFR manufacturing facility located on the River Skerne which closed in December 2003.

The Independent Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) UK concluded that the estimated dietary intakes of PBDEs and HBCD from the consumption of a weekly single portion of fish from the Skerne-Tees river system were unlikely to represent a risk to health. The results of this present study have shown that levels of PBDEs and HBCD are over one and three orders of magnitude lower respectively than the levels at which COT assessed dietary intake. This would suggest that there is a correspondingly greater safety margin for consumers of farmed salmon and other fishery produce as determined in both this study and the MI study in 2004[5].

A more recent survey conducted in the UK (Food Standards Agency, 2006) showed levels of PBDE congeners in tinned and farmed salmon, tinned herring and mackerel and oysters comparable to those found in this present survey, whereas fresh Irish herring and mackerel and wild Atlantic salmon showed lower levels in this survey compared with the UK survey. Fresh tuna samples, originating from the waters south west of Ireland, displayed higher levels than those found in the UK survey.

# 6. Conclusions

This study has demonstrated that levels of dioxins, furans, PCBs in Irish seafood are in general well below the relevant legislative limits for these contaminants. Levels of the indicator PCBs 28, 52, 101, 118, 138, 153, and 180 are similarly low, as are levels of those brominated flame retardants measured in the study.

The results of the study are in line with those from previous FSAI studies on dioxin levels in fish and also studies on meat, milk, and eggs, and confirm that dioxin levels in these foods are relatively low compared with data for similar products from more industrialised countries in the European Union. FSAI is pleased to report these results and to note that Irish produce readily complies with legislation in this area. These findings support the interpretation that exposure of consumers of Irish food to dioxins is likely to be lower than the European average, a conclusion which should be reassuring to Irish consumers.

On the basis of these results, the FSAI considers that there is no need to amend existing advice on fish consumption, namely that consumers should consume two portions of fish per week, one of which should be oily (e.g. salmon, herring or mackerel).

[5] It should be noted that COT's conclusions were tentative due to uncertainties surrounding the toxicological database and exposure assessment. Additionally, the MI study only tested a limited number of samples.

# 7. Abbreviations

| | |
|---|---|
| **Ah receptor** | aryl hydrocarbon (Ah) receptor |
| **b.w.** | body weight |
| **congener** | term referring to one of many configurations of a common chemical structure |
| **DCMNR** | Department of Communication, Marine and Natural Resources |
| **EC** | European Community |
| **EFSA** | European Food Safety Authority |
| **FSAI** | Food Safety Authority of Ireland |
| **HSE** | Health Service Executive (formerly the Health Boards) |
| **JECFA** | FAO/WHO Joint Expert Committee Food Additives and Contaminants |
| **LOD** | Limit of Detection |
| **LOQ** | Limit of Quantification/Quantitation |
| **Lower-bound** | Analytical results below the LOD are set at zero for calculation purposes |
| **MI** | Marine Institute |
| **ng** | nanogram (0.000000001 g) |
| **pg** | picogram (0.000000000001 g) |
| **ppb** | parts per billion (equal to ng/g or µg/kg) |
| **PUFA** | poly unsaturated fatty acids |
| **TEF** | toxic equivalency factor |
| **TEQ** | toxicity equivalent |
| **PTMI** | Provisional Tolerable Monthly Intake |
| **SCF** | Scientific Committee of Food |
| **TWI** | Tolerable Weekly Intake |
| **TDI** | Tolerable Daily Intake |
| **µg** | microgram (0.000001 g) |
| **Upper-bound** | Analytical results below the LOQ are set at the LOQ value for calculation purposes |
| **w.w.** | wet weight or whole weight |
| **BFRs** | Brominated flame retardants |
| **HBCD** | Hexabromocyclododecane |
| **PCDDs** | polychlorinated dibenzo-*p*-dioxins |
| **PCDFs** | polychlorinated dibenzofurans |
| **PCBs** | polychlorinated biphenyls |
| **PBDEs** | polybrominated diphenylethers |
| **PCDD/F** | abbreviation for PCDDs and PCDFs |
| **dl-PCB** | dioxin-like PCB |
| **ndl-PCB** | non-dioxin-like PCB |
| **TCB** | tetrachlorobiphenyl |
| **PnCB** | pentachlorobiphenyl |
| **HxCB** | hexachlorobiphenyl |
| **HpCB** | heptachlorobiphenyl |
| **PnCDD** | pentachlorodibenzo-*p*-dioxin |
| **HxCDD** | hexachlorodibenzo-*p*-dioxin |
| **HpCDD** | heptachlorodibenzo-*p*-dioxin |
| **OCDD** | octachlorodibenzo-*p*-dioxin |
| **PnCDF** | pentachlorodibenzofuran |
| **HxCDF** | hexachlorodibenzofuran |
| **HpCDF** | heptachlorodibenzofuran |
| **OCDF** | octachlorodibenzofuran |
| **Σ7PCB** | Sum of 7 indicator PCBs (28, 52, 101, 118, 138, 153 and 180) |
| **Σ6PCB** | Sum of 6 indicator PCBs(28, 52, 101,138, 153 and 180) |
| **Σ** | Sum |
| **BB** | body burden |

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# 9. Appendix

## 9.1 Methods of Analysis

Fat extraction

Tissue homogenates of the fish samples were freeze-dried and further homogenized by means of grinding. The fat extraction was performed by means of Accelerated Solvent Extraction (ASE) using an ASE 300 instrument of Dionex Corp., Sunnyvale, CA, USA. For fat extraction, 20 g of the freeze-dried sample material was mixed with about 15 g of diatomaceous earth and filled into the ASE extraction cartridge. Prior to the start of the extraction, a surrogate standard (50 pg $^{13}$C12-labelled 1,2,3,4-TetraCDD) was added to the sample material in order to control the extraction efficiency. After ASE extraction the solvents were removed from the fat extract by means of a rotary evaporator which was operated under defined conditions. The fat fraction finally was determined gravimetrically.

Analysis of fish samples for PCDD/Fs PCDD/F

Analysis was performed according to the EN ISO 17025 accredited methods GfA QMA 504-191/203/205. The analytical methodology is in compliance with the requirement for the HRGC/HRMS confirmatory analysis of food for PCDD/Fs and PCBs as laid down by the EU directive 2002/69 and its amendment 2004/44 from April 2004. Each analysis included the determination of the seventeen PCDD/F congeners with 2,3,7,8-chloro-substitution. For PCDD/F analysis, sixteen $^{13}$C12-labelled PCDD/F congeners were added to the fat extract of each sample as internal standards.

For separation of the PCDF/Ds from the fish lipid, the total fat extract was dissolved in 14 ml of hexane and subsequently injected into an automated clean-up system, (Power-Prep FMS, Fluid Management Systems Inc., Waltham, MA, USA). PCB-free Power-Prep Columns were used for the automated clean-up. The hexane solution was percolated through a high capacity disposable silica column, a multilayer silica column and a basic alumina column. Final separation of PCDF/Ds / non-ortho PCBs and other PCBs was achieved by means of a carbon column. Prior to the instrumental analysis, two further PCDD standards ($^{13}$C6-1,2,3,4-TetraCDD and $^{13}$C12-1,2,3,7,8,9-HexaCDD) were added to the PCDD/F fraction to determine the recovery of the $^{13}$C12-labelled internal PCDD/F standards through the clean-up. For the PCDD/F determination, a capillary gas chromatograph (HRGC, HP 5890) equipped with a PTV injector and connected to a high resolution mass spectrometer (HRMS, VG-AutoSpec) was used.

Prior to starting analysis, a HRMS tune was carried out to adjust the instrumental performance (at least once per analysis batch, including mass axis calibration, adjustment of mass resolution and sensitivity). The instrument sensitivity was then checked by means of native PCDD/F standards. A mixture of the sixteen $^{13}$C12-labelled standards mentioned above and the seventeen native standards were always injected to determine the relative retention times and the relative response factors for identification and quantification.

During sample analysis, the stability of the mass focus was assured by means of perfluorokerosene locked masses.

The limits of quantification (LOQs) for the determination of individual PCDD/Fs in the fish samples were in general between 0.002 pg/g whole weight (for 2,3,7,8-TetraCDD) and 0.2 pg/g whole weight for OctaCDD/F. Limits of detection (LODs) are usually a factor of three lower. However, only LOQs are reported.

Analysis of fish samples for PCBs

Analyses were performed by application of the EN ISO 17025 accredited methods QMA 504-191/203/251. The analytical procedure is in compliance with the requirements for the PCDD/F and PCB analysis of food by means of HRGC/HRMS laid down in the EU directive 2002/69 and it's amendment 2004/44 from April 2004. The analyses covered the determination of the twelve dioxin-like PCB congeners for which TEFs were established by the WHO in 1998 plus seven indicator PCBs and further 29 PCB congeners as specified in the FSAI request.

Similar to the dioxin analysis, for each native dioxin-like or indicator PCB congener to be determined the corresponding $^{13}$C12-labelled PCB was added as internal standard to the extract (isotope dilution). The remaining PCB congeners are also quantified by means of these and other internal $^{13}$C-labelled PCB standards using response factors relative to an internal standard with the same degree of chlorination. After fat and matrix separation by means of the silica and alumina columns as described above, non-ortho PCBs and PCDD/Fs were separated from the other PCBs by means of a carbon column. The fractions containing the non-ortho PCBs and the other PCBs were analysed in separate GC/MS runs. For PCB detection, a capillary gas chromatograph (HRGC, HP 5890) equipped with a split/splitless injector and connected to a high-resolution mass spectrometer (HRMS, VGAutoSpec) was also used. The procedures for the instrument tuning, the determination of relative retention times and response factors, and the locked mass check were basically the same as described for the PCDD/Fs, however, adjusted to the PCB determination. On the basis of the GC/MS system used for the PCB detection co-elution of the following PCB congeners is observed:

| PCB analyte | PCB co-eluting |
|---|---|
| PCB 33 | PCB 20 |
| PCB 41 | PCB 71 |
| PCB 66 | PCB 81 |
| PCB 123 | PCB 106 |
| PCB 180 | PCB 193 |
| PCB 187 | PCB 182 |

Consequently, concentrations determined for these 6 PCB congeners can be considered as maximum values. The limits of quantification (LOQs) were in general in the range of 0.2 and 0.8 pg/g whole weight for the non-ortho PCBs 77, 81, 126 and 169. For the indicator and the other PCB congeners LOQs between 0.2 and 10 pg/g whole weight were generally achieved. Detection limits are lower; however, the limits of quantification are reported.

Analysis of fish samples for PBDEs

For the analysis of brominated flame retardant compounds in the fish samples, a GfA established GC/MS method was used. For the determination of PBDEs four $^{13}$C12-labeled PBDE congeners were added to an aliquot of the fat extract of the sample as internal standard.

Extract aliquots were treated with sulphuric acid and further cleaned-up by liquid/solid chromatography. A recovery standard was added prior to the instrumental analysis using capillary gas chromatography (HRGC) coupled with low resolution mass spectrometry (LRMS). The gas chromatographic separation was performed on a 30m HP-5 column with 0.32 mm inner diameter and 0.1 mm film thickness.

The native PBDE congeners were quantified via the internal isotope labelled PBDE standards. Relative response factors of native to isotope labelled PBDEs were determined by means of calibration mixtures analyzed within each analysis sequence. LOQs were in the range of 0.01 ng/g and 0.05 ng/g whole weight for the Tri- to HeptaBDE congeners. The limits of detection (LODs) are lower however, the limits of quantification are reported.

Analysis of fish samples for HBCD:

Samples were spiked with deuterated internal standards and with the analytes of interest. Each sample was then mixed with anhydrous sodium sulphate, hexane:dichloromethane and acid modified silica was added. The filtrate and washings were collected reduced in volume and then quantitatively transferred to a glass vial and evaporated to dryness. Methanol and water was added and the solution was transferred to a HPLC-MS/MS vial for analysis using a Sunfire C-18 150 x 2.1 mm, particle size 3.5 µm HPLC column Detection was carried out by MS/MS in multiple reaction monitoring mode (MRM) mode. Quantification was completed by means of internal standard recovery correction.

## 9.2 Quality assurance/control

The method implemented quality assurance and quality control followed the basic requirements of international standards for the analysis of Dioxins and PCBs at low concentration levels by using isotope dilution and high resolution mass spectrometry (e.g. EC directive 2002/69, EN 1948, EPA 1613). Furthermore, a series of additional tests and analyses were performed to assure quality within this project.

Duplicate analyses, to verify precision of analyte quantification were performed with a set of five samples for PCDD/Fs and PCBs. In all cases, repeat analyses confirmed the first result.

Accuracy of PCDD/F and PCB analysis was verified by analysing a certified “contaminated fish reference material” (CIL EDF-2525) within this project. To assess the performance of the BFR analysis, an in-house reference material (Fish oil from Quasimeme Laboratory Proficiency Test, Round 33 BFR DE8, July 2003) was used.

The relative deviation of the analytically determined TEQ from the assigned value was 11 % for WHO-PCDD/F-TEQ (incl. LOQ) and 0.1 % WHO-PCB-TEQ (incl. LOQ).

The recoveries of the internal $^{13}$C12-labelled PCDD/F, PCB and PBDE standards are in general in the range of 70 to 120 % for the measurements of this study, demonstrating the appropriateness of the applied methods for the analysis of Dioxins/Furans and PCBs in fish.

Expanded measurement uncertainties were derived for the determination of PCDD/F and PCB in fatty food. Uncertainties were calculated on the basis of the "Guide to the expression of uncertainty in measurement (GUM)"12 and the EURACHEM/CITAC Guide "Quantifying uncertainty in analytical Measurement (QUAM)"13. The expanded uncertainties calculated here using a coverage factor of 2 (level of confidence of approximately 95 %).

For PCDD/F TEQs relative expanded uncertainties were calculated to be 12 % and for the PCB TEQs 13%. The Eurofins / GfA laboratory, Münster is accredited according to DIN EN ISO/IEC 17025:2000 and its quality management system complies with the requirements of the DIN EN ISO 9002:1994.

Further to these QA procedures the Eurofins / GfA laboratory has been performing Dioxin and PCB analyses in various matrices for nearly 20 years and has steadily and regularly taken part in external proficiency tests and interlaboratory comparisons.

No certified reference materials available for HBCD analysis in food matrices so an in-house reference material (IHRM) was prepared and analysed in duplicate in each batch. The values obtained are in close agreement with those expected and the relative standard deviations are all less than 2%. Each batch contained two procedural blanks, two IHRMs, a blank and a spiked sunflower oil to allow recovery correction calculations for the IHRM. Analytical recoveries were within the following ranges: 74 - 117% for αHBCD, 84 - 115% for βHBCD and 70 - 120% for γHBCD. The limits of detection (LODs) were calculated as the highest level of the analytes detected in the procedural blank samples.

The Marine Institute is ISO17025 accredited for total lipid determination (Smedes) method and moisture content in marine biota.