Investigation into levels of dioxins, furans, PCBs and PBDEs in food supplements, offal and milk (2005)

Table of Contents

Summary

The Food Safety Authority of Ireland has carried out a surveillance study of levels of dioxins (PCDDs), furans (PCDFs) polychlorinated biphenyls (PCBs) and polybrominated flame retardants (polybrominated diphenylethers, PBDEs) in food supplements, offal and milk available on the Irish market. The study was undertaken because of concern about the possible effects on human health of these biopersistent environmental contaminants, known to be present in a number of foodstuffs, notably meat, fish, eggs and dairy products and to fulfil EC monitoring requirements in this area.

The study showed that levels of PCDDs and PCDFs in Irish milk and offal were below existing legal limits, with the exception of one sample of lamb's liver. All marine and plant oils covered by this survey were also in compliance with existing legislation. Of the substances tested, both the lowest and highest concentrations were observed in food supplements, the lowest being found in a vitamin preparation, while the highest concentration was found in pure cod liver oil.

The total mean upper-bound levels of PCDDs, PCDFs and dioxin-like PCBs expressed as WHO-TEQs ranged from <0.41 - 0.88 ng/kg fat for milk, <0.75 – 8.34 ng/kg fat in offal and <0.25 - 10.15 ng/kg fat in food supplements.

For PBDEs the highest concentrations were found in fish oil containing supplements and the lowest concentrations were found in vitamin E preparations, ranging from <0.82 – 15.5 µg/kg fat for the sum of 16 PBDE congeners included in this survey.

The results found for liver and milk are in line with those from previous FSAI studies on dioxin and furan levels in milk, fish meat and eggs. Although the levels in sheep liver were higher than those in liver from other species or in muscle meat, they were still low compared with the levels found in sheep liver from more industrialised countries in the European Union. Milk levels were also low compared with the European norm. This supports the conclusion that levels in Irish food are relatively low compared with similar products from more industrialised countries in the European Union. The findings indicate that exposure of consumers of Irish food to dioxins and furans is therefore likely to be lower than the European average. In contrast, the levels found in a range of food supplements were broadly similar to those reported for similar products available in other EU countries, reflecting the fact that the raw material for these products may be obtained from a relatively small number of sources, although the products are widely distributed internationally.

Abbreviations

Ah receptor	aryl hydrocarbon (Ah) receptor
b.w.	"body weight"
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 reported below the LOD set at zero
MI	"Marine Institute
ng	"nanogram" (0.000000001 g)
pg	"picogram" (0.000000000001 g)
ppb	"parts per billion" (equal to ng/g or µg/kg)
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 reported below the LOD set at the LOD value
w.w.	"wet weight or whole weight"
PCDDs	"polychlorinated dibenzo-*p*-dioxins"
PCDFs	"polychlorinated dibenzofurans"
PCB	"polychlorinated biphenyl"
PBDEs	"polybrominated diphenylethers"
PCDD/F	abbreviation for PCDDs and PCDFs
dl PCB	"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	"7 marker PCBs"
Σ	"Sum"

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, Fisheries and Food, the Sea Fisheries Protection Agency, 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. This report provides the results of a targeted surveillance study on levels of dioxins (PCDDs), furans (PCDFs), polychlorinated biphenyls (PCBs) and brominated flame retardants (PBDEs) in food supplements, lamb's liver and milk available on the Irish market.

The study builds on previous studies undertaken by FSAI into levels of these environmental contaminants in milk, fish/fish oils, meat and eggs, 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.

Dioxins and furans

The term 'dioxins' covers a group of 75 polychlorinated dibenzo-p-dioxin (PCDD) and 135 polychlorinated dibenzofuran (PCDF) congeners, of which 17 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. Studies on children exposed *in utero* to dioxins are reported to have shown endocrine and developmental changes, persisting for long periods. The toxicological effects of the dioxins are thought to arise due to binding of the dioxins to a specific receptor protein in the cells, the aryl hydrocarbon (Ah) receptor present in most tissues of animals and humans. The most toxic dioxin congener is 2, 3, 7, 8-tetrachlordibenzo-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.

Dioxins and furans are environmental contaminants and have no commercial applications, other than for preparation of analytical standards and research materials. They are formed during combustion processes when the element chlorine is present, for

example in the incineration of municipal waste, although natural combustion processes such as forest fires and bonfires 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 in industrialised countries, as a result of these emissions. Emissions to air result in deposition in the terrestrial environment and in aquatic sediments, followed by uptake into the food chain e.g. by ruminants and by fish. Dioxins are highly resistant to degradation processes in the environment and consequently persist in the environmental compartments where they have been deposited. This is due to their lipophilic characteristics, which also results in accumulation in the fatty tissues of the primary intake species, e.g. cows or fish. Approximately 90% of human exposure to these compounds 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.

Because humans are the ultimate receivers in the food chain, there is a significant potential for accumulation of dioxins in human tissues 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 carcass meat. In fish, high levels may be found in fatty tissues such as liver and consequently 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 [(1)].

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 and furans in foodstuffs.

PCBs

The polychlorinated biphenyls or PCBs are a group of extremely stable aromatic chlorinated compounds which, like the dioxins, are resistant to biological degradation and hence persist and accumulate in the environment and in the food chain. There are 209 possible PCB compounds, 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. Disposal of such material results in continued release to the environment, adding to existing levels present as a consequence of past releases.

As a class, PCBs are generally regarded as having potentially 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 profile 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 in toxicological studies, including developmental effects, immuno- and neurotoxicity, endocrine disrupting effects and tumour promotion. They have been evaluated, *inter alia*, by the International Programme on Chemical Safety (IPCS), who noted that the PCB congener pattern found in food, human tissues and the environment is different from that of commercial PCB mixtures on which the majority of toxicological studies have been carried out. The so-called marker or indicator PCBs (i.e. PCBs 28, 52, 101, 118, 138, 153 and 180) are detected in these media using readily applicable analytical techniques and have been used as indicators of the total PCB content or body burden of environmental biota, food and human tissue.

Toxic Equivalence Factors and Tolerable Intakes for dioxins and dioxin-like PCBs

The toxicity of PCDD, PCDF 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 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 amounts of each congener in a sample by the corresponding TEF and summing the contribution from each congener the total TEQ value of the sample can be obtained using the following equation:

$$TEQ = (PCDDi \times TEFi) + (PCDFi \times TEFi) + (\textit{dioxin-like}\ PCBi \times TEFi)$$

Several different TEF schemes have been proposed. For many years the most widely used schemes were that of NATO/CCMS (2), 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 (3). 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 (4) 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 TEFS FOR DIOXINS

PCDDs and PCDFs	Toxic Equivalency Factor (TEF)		
	I-TEF	WHO-TEF 1998	WHO-TEF 2005
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PnCDD	0.5	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01
OCDD	0.001	0.0001	0.0003
2,3,7,8-TCDF	0.1	0.1	0.1
1,2,3,7,8-PnCDF	0.05	0.05	0.03
2,3,4,7,8-PnCDF	0.5	0.5	0.3
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
OCDF	0.001	0.0001	0.0003

Table 2 TEFS FOR DIOXIN-LIKE PCBS

PCBs (IUPAC No. in parenthesis)	Toxic Equivalency Factor (TEF)		
	I-TEF	WHO-TEF 1998	WHO-TEF 2005
Non-*ortho* PCBs			
3,3',4,4'-TCB (77)	0.0005	0.0001	0.0001
3,4,4',5-TCB (81)	-	0.0001	0.0003
3,3',4,4',5-PnCB (126)	0.1	0.1	0.1
3,3',4,4',5,5'-HxCB (169)	0.01	0.01	0.03
Mono-*ortho* PCBs			
2,3,3',4,4'-PnCB (105)	0.0001	0.0001	0.00003
2,3,4,4',5-PnCB (114)	0.0005	0.0005	0.00003
2,3',4,4',5-PnCB (118)	0.0001	0.0001	0.00003
2,3,4,4'5-PnCB (123)	0.0001	0.0001	0.00003
2,3,3',4,4',5-HxCB (156)	0.0005	0.0005	0.00003
2,3,3',4,4',5'-HxCB (157)	0.0005	0.0005	0.00003
2,3',4,4',5,5'-HxCB (167)	0.00001	0.00001	0.00003
2,3,3',4,4',5,5'-HpCB (189)	0.0001	0.0001	0.00003
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	-

Risk assessment of dioxins and PCBs in food

The SCF have carried out a risk assessment of dioxins and dioxin-like PCBs in food, as a consequence of which they concluded that the Tolerable Weekly Intake (TWI) for PCDDs, PCDFs and dioxin-like PCBs should be no more than 14pg WHO-TEQ/kg body weight (b.w.) [(5)] This is very similar to the Provisional Tolerable Monthly Intake (PTMI) of 70pg/kg b.w. per month, as calculated by the FAO/WHO Joint Expert Committee on Food Additives and Contaminants (JECFA) [(6)]. It has been stated that the European average dietary intake is 1.2 to 3.0pg WHO-TEQ/kg b.w./day, which translates into a weekly intake of between 8.4 and 21pg WHO-TEQ/kg b.w. This exceeds the TWI established by the SCF.

However, several studies carried out by the Food Safety Authority of Ireland (FSAI) have shown that levels of dioxins in Irish food are relatively low. Hence, it is likely that the exposure of the Irish population to dioxins in food is less than the European average.

This conclusion is supported by the results of a recent study carried out by FSAI on levels of PCDDs, PCDFs and dioxin-like PCBs in breast milk from Irish mothers. This study was part of an international WHO and results can be found elsewhere ([7])

A risk assessment for the non-dioxin-like PCBs (ndl-PCBs) in food has also been carried out recently at European level by the Panel on contaminants in the food chain (CONTAM) 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.

[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).

Poly Brominated Diphenyl Ethers (PBDEs)

Brominated flame retardants 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 has banned production of both pentaBDE and octaBDE in 2004, however decaBDE (DBDE) is still in use.

The PBDEs are similar in structure to the PCBs (polychlorinated biphenyls) and also have some similarities to the dioxin family of chemicals. They contain the element bromine rather than the chlorine element 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 to them leads to build-up in the body. Because they have similarities to dioxins and PCBs, they may have some of the same effects on health as these chemicals, although they appear to be less toxic. Recent toxicological studies have shown that some of them are endocrine or hormone disruptors, an effect that is also associated with the 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 they 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-BDE, levels in breast milk in European women are now dropping, but levels in human tissues and breast milk in North America are still rising rapidly.

A recent study carried out by Hites et al [8] has reported PBDEs to be present in both farmed and wild salmon.

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.

The FSAI has recently carried out a study looking for the presence of 16 of the PBDEs in Irish eggs (free range and battery), as part of its wider survey of dioxin and PCB levels in eggs. Traces of 4 of these compounds were found, PBDE-99, PBDE-100, PBDE-153 and PBDE-47. PBDE-47 and PBDE-99 are the predominant congeners found in environmental samples, including human specimens.

Levels in Irish eggs were approximately 0.1 parts per billion (ppb) in total egg. The approximate level expressed in ppb per kg egg fat was 1 ppb, and this may be compared with levels ranging between 17 to 460 ppb body fat in women in San Francisco, and an average level of 16 ppb for 6 species of fish taken from San Francisco Bay in 2002[9]. Levels in retail farmed salmon reported by Hites et al. [10] range between 0.6 to 3.9 ppb w.w. and all confirmed farmed fish 1.25 to 3.9 ppb w.w. In 2004 the Marine Institute in Ireland[10] measured PBDEs in Irish farmed fish and found levels ranging from 2.28 to 4.61 (mean 3.05) ppb w.w. and 0.7 to 1.8 (mean 1.17) ppb w.w. for the sum of the 17 individual PBDEs and for total HBCD respectively. However, there are differences in the number of congeners determined in the various studies listed and therefore direct comparisons of the datasets cannot be made.

FSAI is currently carrying out another study to determine the levels pf PBDEs and other flame retardants in farm milk, carcass fat, eggs and offal, the results of which are expected in 2008.

Risk assessment of PBDEs in food

A Tolerable Intake Level (Tolerable Daily or Weekly Intake, TDI/TWI) has not been determined for the PBDEs by expert bodies such as the European Food Safety Authority, because there is as yet insufficient information available on their toxicity and their occurrence in food. Because of the lack of information, FSAI considers that exposure to them should be kept to a minimum.

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. 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 feedingstuffs 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. in 2001 introduced Maximum Levels for PCDDs and PCDFs in foodstuffs. Maximum levels for the sum of dioxins and dioxin-like PCBs have been set in 2006 as this is the most appropriate approach from a toxicological point of view. In order to ensure a smooth transition, the levels for dioxins continue to apply for a transitional period in addition to the levels for the sum of dioxins and dioxin-like PCBs. Foodstuffs must comply during that transitional period with the maximum levels for dioxins and with the maximum levels for the sum of dioxins and dioxin-like PCBs. Consideration will be given by 31 December 2008 to dispensing with the separate maximum levels for dioxins.

A recent overhaul of the contaminants legislation led to consolidation of existing contaminant legislation and was published in 2006. Regulation 1881/2006/EC as amended by Regulation 1126/2007/EC contains maximum levels for certain contaminants in foodstuffs. The currently applicable maximum levels for PCDDs, PCDFs and sum of PCDD/Fs&DL-PCBs in food are shown in Table 3.

Table 3 Maximum Levels for dioxins, furans and dioxin-like PCBs in food

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

(1) 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.

(2) 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.

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

(4) 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.

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

(6) 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.

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

Legislation to cover Non dioxin-like PCBs is currently being discussed at EC level and is likely to be adopted in 2009.

There are also currently 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.

Current legislation also carries with it an obligation for Member States to monitor the levels of dioxins in foodstuffs and report these to the E.C. Under this obligation, Ireland is required to carry out monitoring in a variety of foodstuffs. The dioxin monitoring program for previous years included food supplements, meat, offal, fruit, vegetables, fish and eggs. The results for have been published previously are available on the FSAI website [11, 12].

This report provides updated results for food supplements and adds onto previously reported results for milk and offal. These data will ultimately be used to review the maximum limits and gauge the effectiveness of the reduction strategy.

Materials and Methods

Study outline

The present study was undertaken to investigate the current levels of dioxins, furans, PCBs and PBDEs and HBCD in food supplements, offal and milk and thereby increase the available data on the occurrence of these contaminants in these foodstuffs.

For this survey the following types of food samples were collected (see table 4):

1. Food supplements
2. Offal (Lamb's Liver)
3. Farm Milk

Group 1 was partly provided by industry via the Irish Health Trade Association and partly purchased at retail outlets. Group 2 was obtained from supermarkets and Butchers and Group 3 was supplied partly by officers of the Department of Agriculture, Fisheries and Food at production level and the remainder taken by officers of the Food Safety Authority of Ireland at retail level.

In particular samples included cod liver oil containing food supplements (15 samples), omega-3 containing food supplements (8 samples), other marine oils containing food supplements (12 samples), Vitamin containing food supplements (2 samples), lambs liver (11 samples), pork liver (1 sample), retail milk (4 samples), goat milk (1 sample) and farm milk (5 samples). Samples were mostly capsules or liquid samples with an approx. sample weight of 10 - 350g or 100 – 250 ml in case of food supplements, 200 - 500 g (fresh sample) in case of liver samples and 1-2 L fresh weight in case of the milk samples.

Analysis of the samples was undertaken by Eurofins GfA/Muenster, under contract to FSAI.

Food Supplements

Oil	Brand	Quantity	BB Date	Identifier	Source
Cod liver oil & evening primrose oil with vits A, D & E	Seven Seas	150 ml	Oct-07	342693	Tesco, Clare Hall
Cod liver oil & evening primrose oil	Tesco	1200 mg~ capsules, 90	Feb-07	B/N2038	Tesco, Clare Hall
Pure cod liver oil	Seven Seas	170 ml	Jan-08	350547	Tesco, Clare Hall
Pure cod liver oil enriched with triomega fish oil with vits A, D & E and glucosamine	Seven Seas	1000 mg~ capsules, 30	Jul-07	350390	Tesco, Clare Hall
Pure cod liver oil with vitamin E, plus A & D	Seven Seas	1000 mg~ capsules, 30	Aug-06	342170	Tesco, Clare Hall
Cod liver oil	Holland & Barrett	1000 mg capsules, 60 x 2	Aug-07	36034201	IHTA
Cod liver oil	Tesco	300 ml	Feb-07	90076290591	Tesco, Clare Hall
Cod liver oil	Boots	500 ml	Nov-06	5118 2	Boots, Pavilions
Cod liver oil	Sona	30 x 4	Jan-07	1340	IHTA
Cod liver oil	Kordel's	1000 mg capsules, 90 x 2	Jun-05	765761	IHTA
Pure cod liver oil	Lifeplan	550 mg, 120 x 2	Jan-08	05/13/105	IHTA
cod liver oil	Beeline	400 mg~ capsules, 120	Mar-06	BN Co2940	Tesco, Clare Hall
Omega-3 fish oil orange flavour syrup for kids with vits A C D & E	Haliborange	150 ml	Nov-06	351085	Tesco, Clare Hall
Omega-3 fish oil	Higher Nature	1000 mg capsules, 90 x 2	Jan-08	10205	IHTA
Pulse Pure fish oils Omega 3 with Vit. E	Seven Seas	600 mg~ capsules, 60	Oct-06	342657	IHTA
IQ 3 Pure fish oils Omega 3 with Vit. E	Biomedical Labs, UK	1000 mg~ capsules, 200	Oct-07	311007	IHTA
Boots super strength concentrated fish oils	Boots	1000 mg capsules, 60	Nov-07	5C57	Boots, Pavilions
Efamarine Marine fish oil, EPO and vit. E	Efamol	500 mg~ capsules, 90	Dec-07	31260	
Omega-3	Sona	1000 mg~ capsules, 30 x 2	Dec-07	2532	IHTA
Omega-3	Solgar	700 mg capsules, 60 x 2	Sep-07	83093	IHTA
Omega-3 + vit E	Lifeplan	30 capsules x 2	Apr-08	05/17/53	IHTA
Omega-3/6 sachets	Smartfish	28 capsules	Nov-06	503EO1	IHTA
Omega-3/6	Eskimo Kids	210 ml	Oct-07	322010 15k712	IHTA
Omega-3/6	Eskimo Kids	210 ml	Mar-08	12401015K474	IHTA
Omega-3/6	Eskimo 3	210 ml	Jan-07	137457 2050156	IHTA
Omega-3/6	Eskimo 3	210 ml	Dec-06	019383 042109	IHTA

Food Supplements continued

Omega + EPO	Equazen mum (P)	30 x 3 capsules	Sep-07	50802	IHTA
Omega + EPO	Equazen mum (P)	30 capsules	Sep-07	50801	IHTA
Omega + EPO	Equazen mum (I)	30 capsules	Sep-07	50851	IHTA
Omega + EPO	Equazen mum (I)	30 capsules	Sep-07	50852	IHTA
Marine fish oil+ EPO	Equazen eye q	500 mg, 60 capsules	Nov-06	505518	IHTA
Marine fish oil+ EPO	Equazen eye q	500 mg, 60x2 capsules	Sep-07	505533	IHTA
Marine fish oil+ EPO	Equazen eye q	500 mg, 60x2 capsules	May-07	505531	IHTA
Marine fish oil+ EPO	Equazen eye q	500 mg, 180	Mar-07	505523	IHTA
Marine fish oil+ EPO vanilla	Equazen eye q	200 ml	Apr-06	505711	IHTA
Marine fish oil+ EPO citrus	Equazen eye q	200 ml	Apr-06	505620	IHTA
Marine fish oil+ EPO citrus	Equazen eye q	200 ml	May-06	505624	IHTA
Marine fish oil+ EPO citrus	Equazen eye q	200 ml	Jul-06	505627	IHTA
Marine fish oil+ EPO citrus	Equazen eye q	200 ml	Oct-06	505634	IHTA
Glucosamine + CLO	Healthcrafts	30 capsules x 2	Mar-06	90727	IHTA
EPO + Starflower oil	Tesco	1000 mg~ capsules, 60	Jan-08	B/N2015	Tesco, Clare Hall
Starflower oil	Holland & Barrett	1000 mg capsules, 50	Apr-08	A05160	H & B, Clare Hall
Evening primrose oil with vit. E	Beeline	1000 mg~ capsules, 30	Dec-06	B/N Co4440	IHTA
Evening primrose oil	Holland & Barrett	1000 mg capsules, 60	Mar-07	A05139	H & B, Clare Hall
Vit E 200 iu	Seven Seas	130 mg~ capsules, 90	Oct-06	332698	Tesco, Clare Hall
Vitamin E400iu	Biohealth	130 mg~ capsules, 30	Jul-07	820673	IHTA
PUFA Flax oil	Flora (FMD)	250 ml	Oct-05	50406	IHTA
Skin Hair & Nails	Healthcrafts	30 capsules x 2	Mar-06	90728	IHTA
PUFA F factor	Nutri	90 capsules x 2	Mar-08	4004125	IHTA
Balanced Oil Blend 3+6+9	Organic Choice	250 ml	Aug-05	545	Cleary's Pharmacy
Salmon Oil	Holland & Barrett	1000 mg~ capsules, 120	Sep-06	58578 05	H & B, Clare Hall
Bio-Fish Oil	Pharm Nord	1000 mg~ capsules, 80	Sep-06	4003304	McCabes Pharmacy, Swords

OFFAL

Product	Supplier	Quantity	BB
Lambs liver	Dunnes Stores	Approx 1 Pound	Jul-14-05 and Jul-26-05 Only 2 samples
Lambs liver	Superquinn	Approx 1 Pound	Jul-11-05, Jul-18-05 and Jul-23-05
Lambs liver	J C's, Swords	Approx 1 Pound	Jul-12-05, Jul-19-05 and Jul-24-05
Pork liver	J C's, Swords	Approx 1 Pound	Jul-15-05, Jul-22-05 and Jul-27-05
Lambs liver	Des Byrne Butchers, Skerries	Loose sample approx 1 Pound	
Lambs liver	Supervalu, Skerries	Approx 1 Pound	Jul-23-05 foodtrace code: 052020697
Lambs liver	Gerry's Supermarket, Skerries	Approx 1 Pound	Jul-26-05,
Lambs liver	Aidan O'Brien Butchers, Skerries	Loose sample approx 1 Pound	
Lambs liver	Buckleys, Talbot St.	Loose sample approx 1 Pound	
Lambs liver	Buckleys, Moore St.	Loose sample approx 1 Pound	
Lambs liver	Troys Butchers, Moore St	Loose sample approx 1 Pound	
Lambs liver	Cousins Butchers, Moore Street	Loose sample approx 1 Pound	

MILK

Product	**Brand**	**Quantity**	**BB Date**	**Identifier**	**Source**
Milk	Tesco full fat	1 litre	Jul-13 18.09		Tesco, Clare Hall
Milk	Avonmore full fat	2 litre	Jul-15 16.21 1405 116		Tesco, Clare Hall
Milk	Premier full fat	3 litre	Jul-15 15.30 1405 116		Tesco, Clare Hall
Milk	Dawn Omega Low fat plus vit A, D, E	1 Litre	Jul-09	15.21 K 3	Tesco, Clare Hall
Milk (Goat)	Glenisk fresh goats	I litre	Jul-12	13.02 A2 1084	Tesco, Clare Hall
Farmmilk Seal 1836		2L		22/7/05 taken	Dep. Agriculture
Farmmilk Seal 17560		2L		25/7/05 taken	Dep. Agriculture
Farmmilk Seal 1836		2L		21/7/05 taken	Dep. Agriculture
Farmmilk Seal 13391		2L		26/7/05 taken	Dep. Agriculture
Farmmilk Seal 13391		2L		26/7/05 taken	Dep. Agriculture

Analytes included in the survey

PCDDs/PCDFs and PCBs

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

PCB 18	PCB 60	PCB 126	PCB 183
PCB 20	PCB 63	PCB 128	PCB 185
PCB 28	PCB 66	PCB 129	PCB 187
PCB 31	PCB 70	PCB 138	PCB 189
PCB 32	PCB 74	PCB 141	PCB 191
PCB 33	PCB 77	PCB 149	PCB 193
PCB 37	PCB 81	PCB 151	PCB 194
PCB 41	PCB 87	PCB 153	PCB 201
PCB 44	PCB 99	PCB 156	PCB 202
PCB 47	PCB 101	PCB 157	PCB 203
PCB 49	PCB 105	PCB 167	PCB 206
PCB 51	PCB 110	PCB 169	PCB 208
PCB 52	PCB 114	PCB 170	PCB 209
PCB 56	PCB 118	PCB 174	
PCB 59	PCB 123	PCB 180	

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

Analytical methods

Sample preparation

The samples were provided as frozen composites by the Food Safety Authority of Ireland, Abbey Court, Lower Abbey Street, Dublin 1 and sent to Eurofins Scientific Ltd, Dundalk, Co Louth, Ireland. From there they were sent to Eurofins / GfA mbH, Münster, Germany for analysis. The frozen samples were shipped in several insulated boxes on August 03, 2005 and arrived on August 05, 2005.
The homogenates of the offal and milk samples were freeze-dried and further homogenized by means of grinding.

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

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.

The fat content of the offal and milk sample was determined gravimetrically after fat extraction.

Further details on analytical methodology and quality assurance are given in the Appendix (see p. 27)

Results

Dioxins, furans and PCBs

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

Results are expressed as total WHO-TEQs in ng/kg fat weight for PCDD/Fs and dioxin-like PCBs separately and for the sum of PCDD/Fs and dioxin-like PCBs together, and as the sum total in µg/kg fat weight for the sum of 7 and sum of 6 indicator PCBs. 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 and sum of 6 Indicator PCBs

Sample	N	Statistics	*ΣdI-PCBs& PCDD/F*	*PCDD/F*	*dI- PCBs*	*ΣPCB 7*	ΣPCB 6
			WHO TEQs ng/kg fat weight			µg/kg fat weight	
Farm Milk	5	Mean	0.57	0.35	0.23	1.03	0.91
		Median	0.47	0.29	0.18	1.07	0.94
		Std. Dev.	0.20	0.11	0.09	0.30	0.29
		Minimum	0.41	0.25	0.16	0.61	0.49
		Maximum	0.88	0.49	0.39	1.43	1.31
		P97.5	0.86	0.49	0.37	1.40	1.28
Retail Milk	4	Mean	0.61	0.34	0.28	1.23	1.03
		Median	0.62	0.30	0.26	0.87	0.71
		Std. Dev.	0.14	0.10	0.09	0.95	0.84
		Minimum	0.45	0.26	0.19	0.55	0.44
		Maximum	0.74	0.48	0.40	2.63	2.28
		P97.5	0.74	0.46	0.39	2.50	2.16
Goat's Milk	1		0.85	0.55	0.29	1.50	1.23
Lamb's Liver	11	Mean	4.23	3.43	0.80	1.85	1.78
		Median	4.62	3.68	0.79	1.81	1.74
		Std. Dev.	2.58	2.15	0.46	0.91	0.89
		Minimum	0.75	0.50	0.15	0.50	0.48
		Maximum	8.34	6.76	1.58	3.53	3.42
		P97.5	8.06	6.53	1.53	3.30	3.19
Porcine Liver	1		1.67	1.44	0.22	0.77	0.70
Food Supplements	46	Mean	2.27	0.40	1.85	2.27	22.73
		Median	1.26	0.27	0.95	1.26	7.92
		Std. Dev.	2.27	0.32	2.04	2.27	32.19
		Minimum	0.25	0.04	0.11	0.25	0.24
		Maximum	10.15	1.51	9.31	10.15	131.79
		P97.5	8.61	1.28	7.18	8.61	105.31

MILK

No significant difference (p=0.4) can be observed between samples taken at retail and samples taken at the farm. Total TEQ (sum PCDD/F & dl-PCB) range from 0.41 – 0.88 ng/kg fat and are well below current legislative limits

of 6 ng/kg fat. 1 sample of goat's milk was found to fall within the range of concentrations observed in cow's milk. Sum-6 Marker PCBs concentration range from 0.44 – 2.28 µg/kg fat and are also well below currently discussed maximum levels for non-dioxin like PCBs.

OFFAL

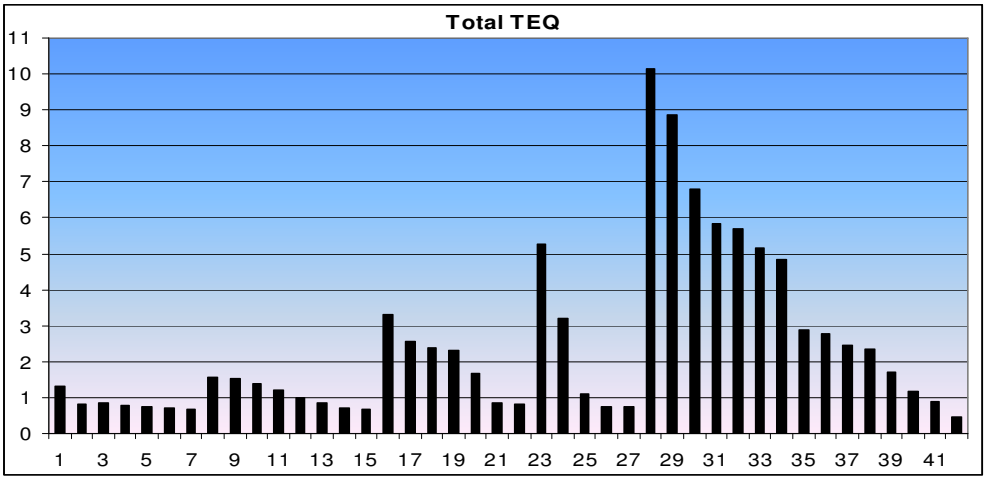
A wide distribution of occurrence of Total TEQ was found in lamb's liver, ranging from 0.75 - 8.34 ng/kg fat. PCDD/F is the major contributor to this Total TEQ, showing that Dioxins and Furans accumulate in the ovine liver and the wide distribution therefore appears to be age and feed related. The same cannot be observed in cows and appears to be due to particular metabolism occurring in the sheep. Due to the latter reason, discussions have commenced in the EC to regulate Dioxins and PCBs on a whole weight basis rather than a fat weight basis in ovine liver. Based on whole weight, the Total TEQ ranges from 0.04 - 0.6 ng/kg.

FOOD SUPPLEMENTS

As reported in Table 4 the highest level of Total TEQ was observed in food supplements. The two highest concentrations were found in cod liver oil, at 10.15 ng/kg fat weight and 8.87 ng/kg fat respectively.

Figure 1 provides an overview of the different type of food supplements covered by this survey and the range of concentration of Total TEQ observed. Lowest levels were found in vitamin preparations only, followed by pure plant oils. Preparations containing fish oil and vitamins and/or plant oils contained somewhat higher concentrations with pure fish oils showing the highest concentration of Total TEQ. Taking into account measurement of uncertainty, none of the pure marine oil samples exceeded the maximum limit of 10 ng/kg fat and none of the pure plant oils exceeded the maximum limit of 1.5 ng/kg fat.

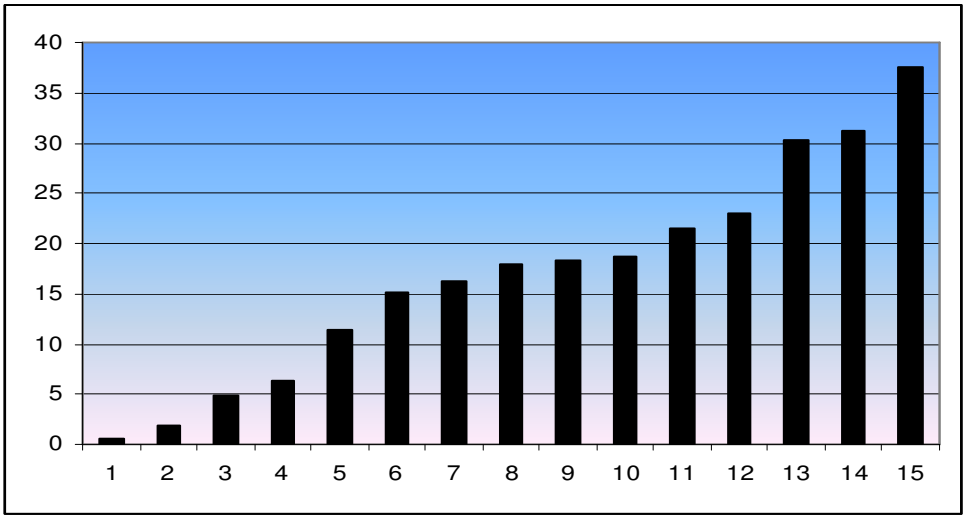
Figure 1 Upper-bound levels (<LOQ = LOQ) of TOTAL TEQS



1-2	Supplements, Vitamin preparation
3-7	Supplements, Plant oils
8-15	Supplements, Omega3 and/or Omega6 Preparations
16-22	Supplements, Fish oil/Vitamin Preparations
23-27	Supplements, Fish oil/Plant oil Preparations
28-42	Supplements, Fish oils

Much progress has been made to reduce occurrence of Dioxins and PCBs in marine oils. A survey conducted by the Food Safety Authority of Ireland in 2002 showed concentrations of Total TEQ in 15 fish oil supplement samples ranging up to 38 ng/kg ([13]) (see Figure 2).

Figure 2 Total TEQ (upperbound) in ng/kg fat weight in fish oil supplements (2002)



Brominated Flame Retardants

Of the 16 PBDE congeners analysed, BDEs 47 and 49 were quantified in all samples. Overall the most abundant congeners determined in all samples were BDEs-47, 49, 99, 100, and 153, however the pattern of occurrence varied between the different matrices analysed (see Figure 3). No sample showed levels of BDE-71, BDE-126, BDE-138, above the LOQ.

Table 5 presents a statistical overview of the sum of 16PBDEs found in the samples. Fish Oil containing supplements showed the highest levels, ranging from 0.2 – 15.5 µg/kg fat weight, whereas plant oils and vitamin preparations showed the lowest levels ranging from 0.2-0.5 µg/kg fat weight.

Table 5 UPPER-BOUND LEVELS (<LOQ = LOQ) OF Σ 16PBDES IN MILK, OFFAL AND FOOD SUPPLEMENTS (µG/KG FAT WEIGHT)

Sample	Statistics	N	ΣPBDE	Sample	Statistics	N	ΣPBDE
Milk	Mean	10	0.622	Supplements, Fish oil/Vitamin Prep	Mean	8	5.556
	Std		0.293		Std		5.193
	Med		0.558		Med		2.500
	Min		0.304		Min		0.330
	Max		1.520		Max		13.410
	P97.5		1.251		P97.5		13.122
Liver	Mean	12	0.873	Supplements, Omega3 and/or Omega6	Mean	5	0.716
	Std		0.460		Std		0.310
	Med		0.735		Med		0.660
	Min		0.390		Min		0.260
	Max		2.130		Max		1.209
	P97.5		1.896		P97.5		1.171
Supplements, Fish oil	Mean	15	7.467	Supplements, Plant oil	Mean		0.276
	Std		6.270		Std		0.148
	Med		4.190		Med		0.210
	Min		0.200		Min		0.200
	Max		15.460		Max		0.540
	P97.5		15.278		P97.5		0.509
Supplements, Fish oil/Plant oil	Mean	12	4.106	Supplements, Vitamin preparation	Mean	2	0.391
	Std		4.471		Std		
	Med		1.760		Med		
	Min		0.420		Min		0.360
	Max		10.030		Max		0.420
	P97.5		9.802		P97.5		

Figure 3 % Occurrence of PBDE congeners in samples from different matrices

Milk	**47**	**99**	**100**	**153**	**49**	**66**	**183**	**28**	**154**	**17**	**85**
% Occurrence	100	100	88	88	81	56	50	44	31	6	6

Liver	**47**	**99**	**100**	**153**	**28**	**49**	**154**
% Occurrence	100	100	58	58	42	17	17

Fish Oil	**47**	**99**	**100**	**49**	**154**	**28**	**66**	**153**	**17**	**119**	**77**
% Occurrence	93	93	93	93	87	80	80	80	53	53	7

Fish Oil/Vitamins	**47**	**99**	**100**	**49**	**28**	**154**	**66**	**153**	**17**	**119**	**183**
% Occurrence	100	100	100	100	83	67	67	58	42	42	8

Omega	**47**	**99**	**100**	**153**	**154**	**49**	**66**	**28**	**119**	**17**
% Occurrence	100	100	75	63	63	50	50	25	25	13

Plant Oil	**47**	**99**	**100**	**153**
% Occurrence	80	40	20	20

vitamins	**47**	**99**
% Occurrence	50	50

Conclusions

This study has demonstrated that levels of dioxins, furans and PCBs in milk, offal and food supplements available on the Irish market are below the relevant legislative limits for these contaminants with the exception of one ovine liver sample. 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, meat, milk, and eggs, and with studies on the individual foodstuffs carried out in other EU countries. The levels found in the food supplements surveyed in this study, which contained a high proportion of fish oil-based products, vary widely and were similar to those found in similar products surveyed in other EU countries. A survey conducted in the UK in 2001 showed concentrations of dioxins and dioxin-like PCBs in fish oil supplements in the range 1.9 - 46 ng WHO-TEQ/kg oil[14], surveys in Denmark in 2000 and 2002 showed levels in the range 0.3 – 38 ng WHO-TEQ/kg oil[15] and a survey conducted in Germany in 2002 showed concentrations of 0.07 – 1.5 ng/kg fat WHO TEQ PCDD/F[16] which also compares well with figures reported in this survey (WHO TEQ PCCD/F 0.04 – 1.51 pg/g fat).
This can be predicted, since these products are produced for transnational markets, and hence have a wide distribution, although the raw materials may be obtained from a relatively limited number of sources. Thus, contaminant levels can be anticipated to be similar wherever the product is purchased, e.g. Ireland, United Kingdom, France, etc

Recent studies carried out on levels of dioxins, furans and PCBs in sheep liver by the United Kingdom has shown comparatively high levels of these contaminants compared with liver from other species, and levels in liver are generally higher than in e.g. muscle meat. This has been attributed to particular metabolism of these compounds occurring in the sheep liver compared with other species. The levels in Irish sheep liver, while higher than the levels previously found by FSAI in foodstuffs such as fish, (muscle) meat, milk, and eggs, are still relatively low compared with data for sheep liver from more industrialised countries in the European Union. Similarly, the most recent results for levels of dioxins, furans and PCBs in Irish milk show that these levels are low compared with those found in milk from many other European countries. 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.

FSAI is pleased to report these results and to note that Irish produce (milk and offal) complies with legislation in this area. On the basis of these results, the FSAI considers that there is no need to advise consumers to restrict intake of any of the commodities tested in this survey.

APPENDIX

Analytical methods

Sample preparation and fat extraction

The homogenates of the offal and milk 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, 15 g (Liver samples) to 20 g (milk samples) of the freeze-dried sample material was mixed with about 15 g of diatomic earth and filled into the ASE extraction cartridge. Prior to the start of the extraction, a surrogate standard (50 pg 13C12-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.
In case of the capsules and the liquid food supplement samples the liquid (2 to 3,5 g fat) has been separated, solved in hexane and cleaned-up by the Power-Prep System. All other food supplements which were not solvable in hexane have been solved in water and have been further treated by liquid-liquid extraction and normal clean-up.

Analysis of food 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 13C12-labelled PCDD/F congeners were added to the fat extract of each sample as internal standards. Table 03 shows, for nearly each native PCDD/F congener to be determined, the added corresponding 13C12-labelled PCDD/F standard (isotope dilution). For separation of the PCDF/Ds from the milk fat, the total fat extract was dissolved in 14 ml of hexane and subsequently injected into an automated clean-up system, called 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-orto PCBs and other PCBs was achieved by means of a carbon column.
Prior to the instrumental analysis, two further PCDD standards (13C6-1,2,3,4-TetraCDD and 13C12-1,2,3,7,8,9-HexaCDD) were added to the PCDD/F

fraction to determine the recovery of the 13C12-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. The operation parameters of the instruments are listed in Table 04. Before starting an analysis sequence, a HRMS tune was carried out to adjust the instrumental performance (at least once per analysis day, 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 13C12-labelled standards and the seventeen native standards was 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 lock masses.
The limits of quantification (LOQs) for the determination of individual PCDD/Fs in the food supplement samples were in general between 0.01 pg/g fresh weight (for 2,3,7,8-TetraCDD) and 0.5 pg/g fresh weight for OctaCDD/F. In case of the offal samples the LOQs were in general between 0.03 pg/g fat weight (for 2,3,7,8-TetraCDD) and 1.29 pg/g fat weight for OctaCDD/F and in case of the milk samples between 0.02 pg/g fat weight (for 2,3,7,8-TetraCDD) and 0.91 pg/g fat weight for OctaCDD/F. Limits of detection (LODs) are usually a factor of three lower. However, only LOQs are reported.

Analysis of food samples for PCBs

The PCB 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 marker PCBs and further 29 PCB congeners as specified in the FSAI request.
Similar to the dioxin analysis, for each native dioxin-like or marker PCB congener to be determined the corresponding 13C12-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 13C-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, VG-AutoSpec) was also used. The procedures for the instrument tuning, the determination of relative retention times and

§ Retention time relative to the corresponding $^{13}C_{12}$-labelled internal standard
** Response factor relative to the internal $^{13}C_{12}$-labelled standard which was used for the quantification of the native DF/Ds

response factors, and the lock mass check were basically the same as described for the PCDD/Fs, however, adjusted to the PCB determination. The eighteen 13C12-labelled internal PCB standards used for the identification and quantitative determination of native PCB congeners are listed in Table 05.
On the basis of the GC/MS system used for the PCB detection co-elution of the following PCB congeners is observed:

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

Consequently, the concentrations determined for these 6 PCB congeners have to be considered as maximum values.

The limits of quantification (LOQs) were in general in case of the food supplement samples in the range of 1.7 and 20 pg/g fresh weights for the non-ortho PCBs 77, 81, 126 and 169. For the marker and the other PCB congeners LOQs between 5 and 200 pg/g fresh weights were generally achieved. In case of the offal samples the LOQs were in general between 0.05 - 2.6 pg/g fat weight for the non-ortho PCBs 77, 81, 126 and 169 and for the marker and the other PCB congeners between 0.2 - 70 pg/g fat weight. In case of the milk samples the LOQs were in general between 0.9 – 6.6 pg/g fat weight for the non-ortho PCBs 77, 81, 126 and 169 and for the marker and the other PCB congeners between 2.0 - 32 pg/g fat weight. Detection limits are lower; however, the limits of quantification are reported.

Analysis of food samples for PBDEs
For the analysis of brominated flame retardant compounds in the food samples, a GfA-established GC/MS method was used.
For the determination of PBDEs four 13C12-labeled PBDE congeners were added to an aliquot of the fat extract of the sample as internal standard. The extract aliquots were treated with sulfuric acid and further cleaned up by liquid/solid chromatography. A recovery standard is added prior to the instrumental analysis using capillary gas chromatography (HRGC) coupled with low resolution mass spectrometry (LRMS). The gaschromatographic separation was performed on a 30 m non-polar DB-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.
The limits of quantification (LOQs) were in general in case of the food supplement samples in the range of 0.01 ng/g - 0.02 ng/g fresh weight for the Tri- to HeptaBDE congeners. In case of the offal samples the LOQs were in general between 0.01 – 0.70 pg/g fat weight and case of the milk samples the

LOQs were in general between 0.02 – 0.15 pg/g fat weight. Detection limits are lower; however, the limits of quantification are reported.

Quality assurance

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, a mean to verify the precision of the quantification of analytes in a specific matrix, were performed with a set of six samples from this investigation program (see Table 15/1 – 15/6) for PCDD/Fs and with a set of five samples from this investigation program PCBs (see Table 16/1 – 16/5). In all cases, the repeated analyses confirmed the first result. The results of the mean values of the duplicate analyses are reported within the final data. The relative deviation of the mean from the single values is between 1,9 -26,3 % for WHO-PCDD/F-TEQ (incl. LOQ) with a mean value of 11,7 % and 2,2 - 18 % WHO-PCB-TEQ with a mean value of 9,6% (incl. LOQ).

Accuracy of PBDE, HBCD, PCDD/F and PCB analysis was verified by analysing a certified "contaminated fish reference material" (CIL EDF-2525) within this project. The results of these analyses are summarized in Table 17 to 19. The relative deviation of the analytically determined TEQ from the assigned value is between 2,8 – 15,6 % for the Tetra- to Hepta-PBDE, 9,6 % for WHO-PCDD/F-TEQ (incl. LOQ) and 0,1 % WHO-PCB-TEQ (incl. LOQ). In case of the 2,4,4'-TriBDE our measurements show a RSD value of 8,7%. Therefore we assume that the assigned value is not anymore correct and our value looks more reasonable.

Together with the samples 8 PCDD/F, 8 PCB and 4 PBDE blanks were performed. Blanks have been related to the different extraction/clean-up procedures for food supplement, offal samples, Vitamin samples and milk samples and related to their sample fat amount for a better comparison to the values of the real sample. PCDD/F and PCB blanks show only for a few congeners results at a very low level, resulting in WHO-PCDD/F-TEQ (incl. LOQ) and WHO-PCB-TEQ (incl. LOQ) significantly below the lowest sample values and significantly below 1/5th of the EU-guideline levels. Some other PCB blanks are observed at very low levels. The recoveries of the internal 13C12-labelled PCDD/F, PCB and PBDE standards are in general in the range of 60 to 120 % for the measurements of this study, demonstrating well 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. The uncertainties were calculated on the

†† EC directive 2002/69 of July 26, 2002 laying down the sampling methods and methods of analysis for the official control of dioxins and the determination of dioxin-like PCBs in foodstuffs; July 2002

‡‡ EN 1948, Stationary source emissions: Determination of the mass concentration of PCDDs/PCDFs, CEN: European Committee for Standardisation, Rue de Strassart 36, 1050 Brussel, Belgium, December 1996

§§ EPA 1613, US EPA, Water engineering and analysis division (4303) 401 M Street S.W. Washington, D.C. 20460, October 1994

basis of the "Guide to the expression of uncertainty in measurement (GUM)"*** and the EURACHEM/CITAC Guide "Quantifying uncertainty in analytical Measurement (QUAM)"†††. The expanded uncertainties calculated here using a coverage factor of 2 which gives a 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.

*** Guide to the expression of uncertainty in measurement, International Organisation for Standardization (ISO), Geneva, Switzerland, 1993, (ISBN 92-67-10188-9), amended in 1995 by ISO

††† Ellison, L.S.R., Rosslein, M., Williams, A. (Editors), Quantifying uncertainty in analytical measurement, EURACHEM/CITAC Guide, 2nd Edition, EURACHEM Laboratory of the Government Chemist, London, 2000

REFERENCES

1 European Commission (2000) Reports on tasks for scientific cooperation: Report of experts participating in Task 3.2.5. Assessment of dietary intake of dioxins and related PCBs by the population of EU Member States http://europa.eu.int/comm/dgs/health_consumer/library/pub/pub08_en.pdf

2 NATO/CCMS (1988), International Toxicity Equivalency Factor (I-TEF) Method of Risk Assessment for Complex Mixtures of Dioxins and Related Compounds. Pilot Study on International Information Exchange on Dioxins and Related Compounds, Report Number 176, August 1988, North Atlantic Treaty Organization, Committee on Challenges of Modern Society

3 Van den Berg, M. , Birnbaum, L.S., Bosveld, A.T.C., Brunström, B., Cook, Ph., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R., Kennedy, S.W., Kubiak, T., Larsen, J.C., van Leeuwen, F.X.R., Liem, A.K.D., Nolt, C., Peterson, R.E., Poellinger, L., Safe, S., Schrenk, D., Tillitt, D., Tysklind, M., Younes, M., Wærn, F., and Zacharewski, T. (1998). Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Env. Health Persp., 106, 775-792.

4 Van den Berg, M, Birnbaum, L S, Denison, M., De Vito, M, Farland, W, Feeley, M, Fiedler, H, Hakansson, H, Hanberg, A, Haws, L, Rose, M, Safe, S, Schrenk, D, Tohyama, C, Tritscher, A, Tuomisto, J, Tysklind, M, Walker, N and Peterson, R E (2005) The 2005 World Health Organization Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds. Toxicol Sci. 2006 Oct;93(2):223-41. Epub 2006 Jul 7 (http://toxsci.oxfordjournals.org/cgi/content/full/93/2/223)

5 Opinion on the risk assessment of dioxins and dioxins-like PCBs in food (update based on the new scientific information available since the adoption of the SCF opinion of 22 November 2000) (adopted by the SCF on 30 May 2001) http://europa.eu.int/comm/food/fs/sc/scf/out90_en.pdf

6 JECFA (2002) Safety Evaluation of certain food additives and contaminants: Polychlorinated dibenzodioxins, plychlorinated dibenzofurans and coplanar polychlorinated biphenyls; http://www.inchem.org/documents/jecfa/jecmono/v48je20.htm

7 Food Safety Authority of Ireland (2005) Investigation into levels of dioxins, furans, PCBs and PBDEs in Irish food 2004. http://www.fsai.ie/publications/reports/dioxins.pdf

8 Hites et al., 2004. Global Assessment of polybrominated diphenyl ethers in farmed and wild salmon. Environment Science and Technology, 38:4945-4949. (http://pubs.acs.org/journals/esthag)

9 Oros, D.R., Hoover D., Rodigari F., Crane D. and Sericano J. (2005) Levels and Distribution of Polybrominated Diphenyl Ethers in Water, Surface Sediments, and Bivalves from the San Francisco Estuary. Environ. Sci. Technol.; *39*(1) pp 33 - 41;

10 Marine Institute (2004) Analysis of Brominated Flame Retardants in farmed salmon. Unpublished.

11 Food Safety Authority of Ireland (2004). Investigation into Levels of Dioxins, Furans, PCBs and some elements in Battery, Free-Range, Barn and Organic Eggs. Report published and available on the FSAI Website, www.fsai.ie

12 Tlustos C, McHugh B, Pratt I, Tyrrell L and E McGovern (2007) Investigation into levels of dioxins, furans, polychlorinated biphenyls and brominated flame retardants in fishery produce in Ireland. Marine Environment and Health Series, No.26, 2006 Available at http://www.fsai.ie/surveillance/food_safety/chemical/fish_POPs.pdf

13 Food Safety Authority of Ireland (2002) Summary of the investigation of dioxins, furans and PCBs in farmed salmon, wild salmon, farmed trout and fish oil capsules - March 2002. Available at http://www.fsai.ie/surveillance/food_safety/chemical/surveillance_food_summarydioxins.asp

14 Food Standards Agency (2002) Food Surveillance Sheet 26/02 DIOXINS AND DIOXIN-LIKE PCBs IN FISH OIL SUPPLEMENTS http://www.food.gov.uk/multimedia/pdfs/26diox.pdf

15 Fødevaredirektoratet (2003) Helhedssyn på fisk og fiskevarer. FødevareRapport 2003:17 Available at http://www.2gangeomugen.dk/fileadmin/downloads/diverse/Helhedssyn_p__fisk_og_fiskevarer.pdf

16 Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit (2004) Fischoelkapseln. Available at http://www.lgl.bayern.de/lebensmittel/fischoelkapseln.htm#Untersuchungsergebnisse%20des%20LGL