Environmental Protection Agency

Dioxin Levels in the Irish Environment

Third Assessment (Summer 2004)

Based on levels in Cows' Milk

Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

Environmental Protection Agency

AGENCY STATUS

The Environmental Protection Agency (EPA) is an independent public body established in July 1993 under the Environmental Protection Agency Act, 1992. Its sponsor in Government is the Department of the Environment, Heritage and Local Government.

The EPA is managed by a full time Executive Board consisting of a Director General and four Directors. Independence is assured through the selection procedures for the Director General and Directors and the freedom, as provided in the legislation, to act on its own initiative. The assignment, under the legislation, of direct responsibility for a wide range of functions underpins this independence. Under legislation, it is a specific offence to attempt to influence the Agency, or anyone acting on its behalf, in an improper manner.

The Agency is assisted by an Advisory Committee of twelve members, appointed by the Minister for the Environment, Heritage and Local Government.

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- licensing large/complex industrial and other processes with significant polluting potential;
- monitoring environmental quality, including the establishment of databases to which the public have access;
- publishing periodic reports on the state of the environment;
- promoting environmentally sound practices;
- promoting and co-ordinating environmental research;
- licensing all significant waste disposal and recovery activities, including landfills, and the preparation of a national hazardous waste management plan;
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- implementing and enforcing the GMO Regulations for the contained and deliberate release of GMOs into the environment;
- preparing and implementing a national hydrometric programme;
- drafting a National Allocation Plan for greenhouse gas emissions allowance trading; the establishment of a National Competent Authority for the issuing of trading permits and allowances to those covered by the scheme; the monitoring, overseeing and verification of emissions from participating companies; and the establishment of a National Emissions Trading Registry;

and, under the Office of Environmental Enforcement, established in 2003 and dedicated to the implementation and enforcement of environmental legislation in Ireland:

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- raising awareness about the importance of enforcement of environmental protection legislation in Ireland;
- enforcing IPPC licences and Waste licences issued by the EPA;
- auditing and reporting on the performance of local authorities in the discharge of their environmental protection functions, including:
  - enforcement in respect of breaches of waste permits,
  - taking action in relation to illegal dumping,
  - implementation of waste collection permits, and
  - enforcement of producer responsibility initiatives (for example, in the area of packaging waste);
- taking action against local authorities that are not discharging their environmental protection functions in an adequate manner;
- prosecuting, or assisting local authorities to prosecute, significant breaches of environmental protection legislation, in a timely manner; and
- assisting local authorities to improve their environmental protection performance on a case by case basis, through the establishment of an enforcement network to promote information exchange and best practice, and by the provision of appropriate guidance.

Dioxin Levels in the Irish Environment

Third Assessment (Summer 2004) Based on Levels in Cows' Milk

Colman Concannon

October 2005

Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhsaoil
PO Box 3000, Johnstown Castle, Co. Wexford, Ireland

Telephone: +353 53 60600 Fax: +353 53 60699
Email: info@epa.ie Website: www.epa.ie

Lo Call 1890 33 55 99

DIOXIN LEVELS IN THE IRISH ENVIRONMENT

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EXECUTIVE SUMMARY

Background

In line with the Agency's intention to maintain surveillance of dioxins and dioxin-like compounds, it was decided to carry out in Summer 2004 a follow-up survey to the 1995 and 2000 dioxin cow's milk surveys (EPA 1996, EPA 2001).

"Dioxins" is a collective term for the category of 75 polychlorinated dibenzo-para-dioxins (PCDDs) and 135 polychlorinated dibenzofurans (PCDFs) and arise mainly as unintentional by-products of incomplete combustion and from certain chemical processes. Seventeen PCDD and PCDF compounds are likely to be of toxicological significance.[1] The most toxic of these is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). The toxic responses include dermal effects, immunotoxicity and carcinogenicity, as well as reproductive and developmental toxicity.

Given that the primary mechanism for dioxins entering the food chain is through atmospheric deposition, cows' milk is considered to be a particularly suitable matrix for assessing their presence in the environment since cows tend to graze over relatively large areas and these compounds will, if present, concentrate in the fat content of the milk.

In order to conform to current practice, testing for dioxin-like polychlorinated biphenyls (PCBs) was included in this programme.

Sources of Dioxins

Although PCDDs and PCDFs are not produced intentionally except for research and analysis purposes their formation is often a by-product of many anthropogenic and natural activities. Some significant sources internationally are:

- Accidental fires
- Backyard burning of household waste and bonfires
- Cement kilns (especially where hazardous waste is co-incinerated)
- Chlorine bleaching of wood pulp
- Coal fired power plants
- Copper production
- Forest fires and other natural fires
- Incineration of medical waste
- Incineration of municipal or hazardous waste
- Production of steel
- Residential combustion (especially where wood is used)
- Sinter plants
- Traffic

Survey and Results

Two types of sampling stations were chosen:

Type A	background stations covering the entire country (24 samples)
Type B	potential impact stations in areas of perceived potential risk (13 samples)

[1] Those 17 compounds with chlorine atoms at the 2,3,7 and 8 positions

The levels for dioxins expressed as milk fat ranged from 0.06 to 0.45 pg WHO-TEQ/g , with a mean of 0.195 pg WHO-TEQ/g using the newer system of World Health Organisation Toxic Equivalents (WHO-TEQ) for comparing dioxin toxicities of different samples. These concentrations were uniformly low by international standards. The highest level found was more than six times lower that the EU limit for dioxins in milk and milk products of 3.0 pg WHO-TEQ/g. There were no unusually high values meriting particular attention in any of the type A or type B samples. There was a tendency towards slightly higher values in the East Coast samples just as in the 2000 survey but even these levels were low by comparison with similar studies in other countries. In line with other studies including the 2000 survey, the PCB levels account for around half the total dioxin figure.

The concentrations found in the 2004 survey were also significantly lower than the 1995 and 2000 surveys. Notwithstanding the usual difficulties in comparing historical data, there is little doubt that the temporal reduction in levels represents a real decrease. This reflects the pattern shown in similar surveys across Europe which have been attributed to a number of regulatory measures and various technological advances. Examples of measures that were taken in Ireland and which may have had an impact on dioxin levels were the virtual abolition of leaded petrol and the shutting down of all hospital incinerators as they were found to be inadequate and could not meet the high standards required under IPC licensing. The shutting down of the iron smelting facility in Cork may also have had an effect (sample B1 Carrigtwohill/ Cobh/Great Island in Figure 2).

The results from the study confirm the uniformly low levels of dioxins and dioxin-like PCBs in the Irish environment.

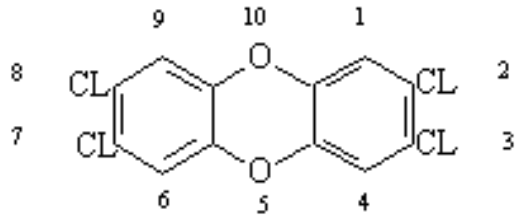
1. INTRODUCTION

Background

In line with the Agency's intention to maintain surveillance of dioxins and dioxin-like compounds, it was decided to carry out a follow-up survey to the 1995 and 2000 dioxin cow's milk surveys (EPA 1996, EPA 2001) in Summer 2004. 37 samples were taken and with a few exceptions, the sample locations were nominally the same for this survey as the 2000 survey. However, in some instances, because of the recent rationalisation of the dairy industry it was not possible to sample in exactly the same location as previously, so that direct comparison of individual sampling points should be made with care. In the 2000 survey, 37 samples were taken as opposed to 33 for the 1995 survey. As in 2000 but unlike 1995 and in order to conform to current practice, testing for dioxin-like PCBs was included in this programme.

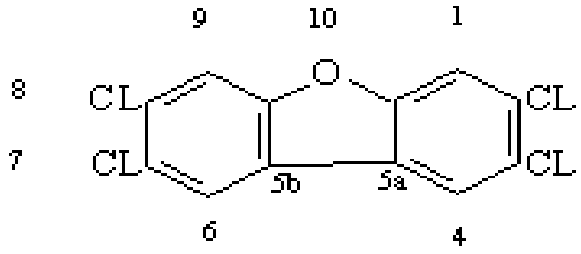
Dioxins

"Dioxins" is a collective term for the category of 75 polychlorinated dibenzo-para-dioxins (PCDDs) and 135 polychlorinated dibenzofurans (PCDFs). These substances arise mainly as unintentional by-products of incomplete or poorly controlled combustion and from certain chemical processes. The toxicity of individual dioxin and dibenzofuran compounds (or congeners) varies considerably. PCDDs have two benzene rings connected by two oxygen atoms; in the PCDFs the two rings are connected by one oxygen atom. The PCDD and PCDF congeners which are likely to be of toxicological significance are those 17 congeners with chlorine atoms at the 2,3,7 and 8 positions. The most toxic dioxin is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD).



2,3,7,8-TCDD

The most toxic dibenzofuran is 2,3,7,8-tetrachloro-dibenzofuran (2,3,7,8-TCDF) which is similar in toxicity to 2,3,7,8-TCDD.



2,3,7,8-TCDF

The toxic responses include dermal effects, immunotoxicity and carcinogenicity, as well as reproductive and developmental toxicity.

Sources of Dioxins

Although PCDDs and PCDFs are not produced intentionally except for research and analysis purposes, their formation is often a by-product of many anthropogenic activities. The manufacture of some chlorinated compounds is known to result in the formation of PCDDs and PCDFs as unwanted by-products. However the manufacture and usage of many of such substances, mainly pesticides such as pentachlorophenol, where dioxins tended to be present as significant contaminants, is now banned. Internationally the main sources of dioxins in recent years have been identified as a wide range of combustion processes where they may be formed in small quantities when organic materials and chlorine compounds are burned together. Such sources can include incineration of all types of wastes, metallurgical operations such as smelting and scrap metal recovery furnaces and the burning of fuels such as coal, wood (especially where the wood contains preservatives) and petroleum products. Other sources are believed to be motor vehicle emissions (although as they arise mainly from leaded fuels, this source is expected to decrease) and emissions from both accidental and natural fires and volcanoes. Sources such as bonfires and illegal or uncontrolled incineration of domestic waste, according to research conducted in the UK (Dyke and Coleman, 1994) and by USEPA (Gullett et al,. 2000) are also believed to be significant although obviously are difficult to quantify.

For many countries in Europe the main source of dioxins previously was emissions from poorly controlled municipal solid waste (MSW) incinerators. However, the introduction of strict controls on emissions has resulted in the closure of many old incinerators which could not be upgraded. In the UK for example, emissions from MSW incineration plants which was the major source of dioxin emissions in 1990 at 600 g I-TEQ, was reduced to around 2 g I-TEQ by 1999 corresponding to less than 1% of all UK releases (DEFRA 2001).

Dioxin emissions from domestic fires are also believed to be a relatively significant source, particularly when wood, plastic or domestic waste is used on these fires. Dioxins are also found in paper products arising from the bleaching with chlorine of naturally occurring phenols present in wood pulp and in the manufacture of some chlorinated compounds.

A well known example of an accident involving release of dioxins was the explosion in 1976 at Seveso, Italy where some of the contents of a 2,4,5-trichlorophenol manufacturing plant were released into the atmosphere causing severe local contamination with trichlorophenol and 2,3,7,8- TCDD. Dioxins also attracted particular attention during the Vietnam War where they were found to be present as a contaminant in the defoliant Agent Orange, a mixture of 2,4,5-T and 2,4-D. High levels of dioxins were found in poultry and eggs from Belgium in 1999. The cause of the contamination is thought to be contamination of feeding stuff.

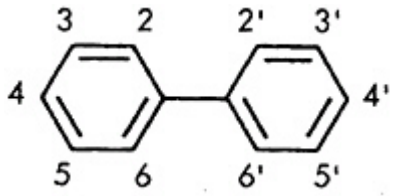
Dioxin compounds have no commercial value and have never been intentionally synthesised other than for laboratory use. Monitoring data for dioxins date only from the 1970s as the analytical capabilities for their detection did not exist before then due to the extremely low concentrations at which they were present in the

environment. However, there can be little doubt that dioxins from anthropogenic activities have existed at least to some extent since the discovery of fire.

Until recently very little firm information on dioxin emission sources existed for Ireland. Accordingly the EPA commissioned a desk study to provide an estimate of dioxin emissions to air, land and water during the calendar year 2000 and also an estimate of projected emissions in 2010 (Hayes & Murmane 2002). The study also attempted to quantify significant dioxin sources in Ireland. The report estimated that in 2000, not withstanding the inherent uncertainties of the calculations, more than half of all air emissions could attributed to domestic burning of waste. Building fires, household heating, cooking with fossil fuel and iron and steel production were the main other sources of dioxin emissions in 2000. The sole iron and steel production facility in the State has since closed.

PCBs

Polychlorinated biphenyls (PCBs) are chlorinated hydrocarbons which were synthesised by direct chlorination of biphenyl but whose production has now been discontinued. PCBs consist of a biphenyl (two benzene rings with a carbon to carbon bond between carbon 1 on one ring and carbon 1' on the second ring) with a varying number of chlorine atoms substituting for hydrogen atoms on the biphenyl rings.



Basic PCB structure

Depending on the number and location of the chlorine atom substituents, there are 209 possible PCB congeners. Some PCB congeners have a “coplanar” structure with the two biphenyl rings lying in the same plane. Of these, there are 12 mono-ortho (chlorine in 2 or 6 position in structure above) and non-ortho substituted PCBs which show similar toxicological properties to dioxins and are often termed “dioxin-like PCBs”.

Unlike dioxins, PCBs have found widespread use in a number of commercial open and closed applications, due to their physical and chemical properties, such as non-flammability, chemical inertia, high boiling points and high dielectric constants. Typical open applications have been their use in pigments, sealants, rubber products and carbonless copy paper. Closed applications have included use of PCBs in hydraulic and heat transfer systems, transformers and capacitors. The production and use of PCBs has been discontinued for some years but because of their persistent qualities they remain in electrical equipment, buildings and the environment. Dioxins and furans are often found in appreciable quantities as contaminants in PCBs.
In conformity with current practice this survey included analysis of the 12 dioxin-like PCBs.

Mechanism of Toxicological Action

A broad variety of data, primarily on TCDD but also on other members of the class of dioxin-like compounds, has shown the importance of the Aryl hydrocarbon Ah (dioxin) receptor in mediating the biological effects of dioxin. These data have been collected using many experimental models in multiple species and also from studies on human exposure. The precise chain of molecular events by which the ligand-activated receptor elicits these effects is not yet fully understood.

Toxic Equivalency Factors (TEFs) for Assessing Mixtures of Dioxins and Dioxin-like Compounds

Because real samples containing dioxins are made up of complex mixtures, a system of Toxic Equivalents has been developed in order to address the problem of differing toxicities and environmental behaviour of these substances. This procedure uses a scheme of weighting factors which expresses the toxicity of each individual PCDD and PCDF in terms of an equivalent amount of 2,3,7,8-TCDD. This weighting factor, called a toxic equivalent factor (TEF), is multiplied by the concentration of the individual compounds in a mixture to give a 2,3,7,8-TCDD toxic equivalent, (TEQ) which is the sum of the concentrations of the individual congeners multiplied by their TEFs.

A number of different systems for establishing toxic equivalent factors now exist. The NATO/CCMS (North Atlantic Treaty Organisation's Committee on Challenges of Modern Society) I-TEQ system which was used in the EPA 1996 report, defines most of the older data. The newer system devised by the World Health Organisation (WHO) in 1998 also incorporates PCBs. The WHO have also suggested that the TEQ scheme be re-evaluated every five years and that TEFs be reanalysed in the light of any new scientific information. Clearly it is important when comparing data to define correctly the TEQ units and also whether PCBs are being considered. Usually I-TEQ concentrations will be a little lower than WHO-TEQs as some of TEFs have been revised upwards by the WHO. The TEF values for both systems are tabulated in the Appendix (Tab 03 for dioxins and Tab 05 for PCBs). In general, it can be safely assumed that older data will have been calculated according to the I-TEQ system.

In calculating TEQs for compounds which are not found in concentrations above the limit of detection, the conventional approach up to recently was to use one half of the detection level for non-detects. A recent EC Directive which set maximum levels for dioxins in foodstuffs stipulated that limits of quantification (LOQs)[1] be used instead of limits of detection (LODs)[1] and also that the full LOQ should be taken in the calculation of non-detects (EC 2001). Since limits of quantification are invariably higher than limits of detection this totally conservative approach to estimating TEQs at trace levels, the full detection level can result in significantly higher estimates than

[1]Limit of detection as used in analytical chemistry is commonly defined as:

*The limit of detection is the smallest concentration of unknown that can reliably be **detected** by the instrumental method. The accepted limit is that concentration of analyte, which produces an instrumental response that is three times as large as the standard deviation S of the instrumental noise level (L.O.D. = 3 x S/N)*

[1]Limit of quantification is commonly defined as:

*The limit of quantification is the smallest concentration of unknown that can reliably be **quantified** by the instrumental method. The accepted limit is that concentration of analyte, which produces an instrumental response that is ten times as large as the standard deviation S of the instrumental noise level (L.O.Q. = 10 x S/N)*

the use of zero values in low level samples. This approach, which was generally introduced in 2002, has been used in the calculations below and should be borne in mind when making comparisons with older low level studies. For comparison purposes the TEQ values assigning zero values for non-detects has also been calculated and it can be seen that there is little or no difference between the two values except at extremely low concentrations. (Attached GfA report). As not all reported data consider non-detects it is important to clarify this issue when comparing low level data.

2. NATIONAL DIOXIN SURVEY

Background

It is generally accepted that the principal mechanism of environmental release of dioxins in this country is by low level emission from multiple sources to the atmosphere. Due to their physical and chemical properties, dioxins tend to be adsorbed onto dust and soot particles which in turn are deposited by atmospheric sedimentation on soil and vegetation such as grass which is directly ingested by grazing cows. Due to their lipophilic and persistent properties, PCDD/F are transferred into the milk fat of the lactating cow. Therefore, milk constitutes an efficient and rapid elimination pathway of these contaminants. If milk production is exclusively based on grazing, the resulting PCDD/F levels in cow's milk reflect the atmospheric PCDD/F deposition on the pasture. Therefore, dioxin levels in milk samples taken during the grazing season can be used as indicators for the actual average local dioxin exposure by atmospheric deposition.

This survey was planned as a follow-up to the national surveys carried out in 1995 and 2000. As far as possible the same approach was adopted in terms of time of year and location of samples. However, unlike the 1995 survey, the analyses included the 12 dioxin-like PCBs.

Samples were taken in June and July 2004 when the cows could be expected to be found grazing outdoors. Details are given in Tables 1-4.

Sampling strategy

Two types of sampling stations were chosen:

Type A	background stations covering the entire country (24 samples)
Type B	potential impact stations in areas of perceived potential risk (13 samples)

Type A samples were normally taken from full milk silos in regional dairies. The typical volume of these silos is 30,000 to 50,000 gallons and they are equipped with an agitator to keep the milk mixed. However there were a number of instances where sampling from silos was not possible and the samples were taken instead from road tankers representative of the area to be covered. These instances are noted in the tables. Type B samples were taken from road tankers representing the "potential impact" areas.

Sampling procedure

Samples were taken in thick walled pyrex glass bottles of one litre capacity which had been washed with detergent and acetone. The sample volume was 800 ml. Duplicate samples were taken with the intention of submitting one sample for analysis and retaining the other sample in the event of a repeat analysis being required.

The samples were taken by EPA personnel while the milk was still in its raw state. The samples were then taken to the nearest EPA regional laboratory where they were frozen at –20° C. Shipment of samples was by overnight courier in ice boxes to the laboratory. (see below).

Analysis

The analysis of very low concentrations of dioxins, such as were found in this survey require dedicated facilities which do not yet exist in this country. The State Laboratory which has recently relocated to Celbridge has made provision for a dioxin laboratory at its new premises but this is as yet not operational. The laboratory chosen for the analyses was the same one used for the 2000 survey, Gesellschaft für Arbeitsplatz und Umweltanalytik (GfA) laboratory in Münster, Germany. This laboratory is very experienced in the analysis of dioxins in milk and other food matrices and has undertaken analyses for clients in many countries. The laboratory is fully accredited for the analysis of PCDDs, PCDFs and PCBs in food matrices, including milk.

Analyses were carried out following pre-treatment and extraction using high resolution gas chromatography and high resolution mass spectrometry with ^{13}C-labelled isomers as internal standards. This method is considered to be the most suitable for low-level dioxin measurements.
Further analytical details are contained in the Appendix which contains extracts from the GfA report to the Agency. It is not reproduced here in full for reasons of space and since a number of sections largely overlap with the EPA report (see below).

Results and Tables

The data showing I-TEQs and WHO TEQs are shown in Tables 1-4. The detailed analytical results showing the levels for the individual congeners along with further analytical details are not given here due to space considerations. These are, however, available on the EPA web site.
The fat content was measured separately and TEQs were determined in fat and then back-calculated to give corresponding levels in the original whole milk sample.

Whole milk TEQ levels are reported in Tables 1 and 3 and fat levels in Tables 2 and 4.

Table 1

Survey on the whole milk related PCDD/F and PCB-TEQ values determined in the background samples A1 - A 25

Sample	Milk supply area	Dioxins		PCBs	Dioxins and PCBs
		I-TEQ incl. LOQ	WHO-TEQ incl. LOQ	WHO-TEQ incl. LOQ	Total WHO-TEQ incl. LOQ
	Unit	*pg/kg whole milk*	*pg/kg whole milk*	*pg/kg whole milk*	*pg/kg whole milk*
A 1	Mitchelstown Area (T)	4.9	6.0	5.1	11.1
A 2	Co. Waterford	4.9	5.8	5.2	11.0
A 3	Dublin South.County/North Wicklow Area (T)	9.1	10.7	10.5	21.2
A 4	North Co. Wexford	7.7	8.9	14.1	23.0
A 5	Charleville, Co Cork Area	4.2	5.1	5.1	10.2
A 6	Ballyragget, Co Kilkenny Area	6.3	7.4	5.8	13.2
A 7	Renmore, Co Galway Area	5.3	6.2	5.6	11.8
A 8	Moate, Co Westmeath Area	5.1	6.1	5.3	11.4
A 9	Tipperary Town/Thurles Areas	6.6	7.3	7.1	14.4
A 10	Nenagh, Co. Tipperary Area	5.5	6.4	6.0	12.4
A 11	Cavan/Longford/Leitrim	7.0	8.6	7.0	15.6
A 12	Drinagh, Co Cork (T)	3.3	4.2	1.6	5.8
A 13	Bandon Area (T)	2.3	2.7	5.6	8.3
A 14	North Kerry Area	4.2	5.1	5.0	10.1
A 15	Co Sligo (T)	5.3	6.4	4.9	11.3
A 16	Roscommon/East Galway (T)	4.4	5.3	5.3	10.6
A 18	Kiltoghert , Co Leitrim	6.1	7.5	5.6	13.1
A 19	Co Monaghan	6.7	7.8	7.7	15.5
A 20	Co Louth	13.3	15.4	10.8	26.2
A 21	North Kildare/West Dublin (T)	9.4	11.1	11.4	22.5
A 22	South Kerry (Cahirciveen area) (T)	1.7	1.9	3.4	5.3
A 23	South Wexford	5.8	6.9	6.6	13.5
A 24	SE Co.Mayo	4.2	5.2	4.3	9.5
A 25	Co.Donegal (T)	9.4	11.5	7.6	19.1

Sample corresponding to A17 in the 1995 survey was not taken in 2000 or 2004

(T) Denotes sampling from a road tanker. All other A samples were taken from bulk silos.

Table 2

Survey on the milk fat related PCDD/F and PCB-TEQ values determined in the background samples A 1 - A 25

Sample	Milk supply area	Dioxins		PCBs	Dioxins and PCBs
		I-TEQ incl. LOQ	**WHO-TEQ incl. LOQ**	**WHO-TEQ incl. LOQ**	**Total WHO-TEQ incl. LOQ**
	Unit	*pg/g milk fat*	*pg/g milk fat*	*pg/g milk fat*	*pg/g milk fat*
A1	Mitchelstown Area (T)	0.119	0.146	0.122	0.268
A2	Co. Waterford	0.138	0.163	0.147	0.310
A3	Dublin South.Co./North Wicklow Area (T)	0.264	0.312	0.306	0.618
A4	North Co. Wexford	0.213	0.245	0.389	0.634
A5	Charleville, Co Cork Area	0.144	0.139	0.138	0.277
A6	Ballyragget, Co Kilkenny Area	0.166	0.197	0.154	0.351
A7	Renmore, Co Galway Area	0.114	0.169	0.152	0.321
A8	Moate, Co Westmeath Area	0.126	0.151	0.133	0.284
A9	Tipperary Town/Thurles Areas	0.163	0.181	0.176	0.357
A10	Nenagh, Co. Tipperary Area	0.152	0.178	0.167	0.345
A11	Cavan/Longford/Leitrim	0.189	0.232	0.188	0.420
A12	Drinagh, Co Cork (T)	0.094	0.118	0.045	0.163
A13	Bandon Area (T)	0.069	0.079	0.165	0.244
A14	North Kerry Area	0.127	0.154	0.150	0.304
A15	Co Sligo (T)	0.128	0.157	0.119	0.276
A16	Roscommon/East Galway (T)	0.103	0.126	0.124	0.250
A18	Kiltoghert , Co Leitrim	0.156	0.190	0.141	0.331
A19	Co Monaghan	0.196	0.231	0.225	0.456
A20	Co Louth	0.334	0.387	0.270	0.654
A21	North Kildare/West Dublin (T)	0.255	0.303	0.311	0.614
A22	So Kerry Cahirciveen area) (T)	0.051	0.056	0.101	0.157
A23	South Wexford	0.154	0.183	0.175	0.358
A24	SE Co.Mayo	0.123	0.152	0.124	0.276
A25	Co.Donegal (T)	0.246	0.301	0.198	0.499

Sample corresponding to A17 in the 1995 survey was not taken in 2000 or 2004

(T) Denotes sampling from a road tanker. All other A samples were taken from bulk silos.

Table 3

Survey on the whole milk related PCDD/F and PCB-TEQ values determined in the potential impact samples B1 - B 17

Sample No.	Milk supply area	Dioxins		PCBs	Dioxins and PCBs
		I-TEQ incl. LOQ *pg/kg whole milk*	**WHO-TEQ incl. LOQ** *pg/kg whole milk*	**WHO-TEQ incl. LOQ** *pg/kg whole milk*	**Total WHO-TEQ incl. LOQ** *pg/kg whole milk*
B1	Carrigtwohill/ Cobh/Great Island	5.5	6.5	6.4	12.9
B2	Ahgada/East Cork Harbour	5.9	6.5	6.4	12.9
B3	Askeaton area	5.7	6.9	7.2	14.1
B4	Tarbert Co. Kerry	3.7	4.2	4.3	8.5
B5	Clarecastle Co.Clare	3.7	4.5	4.9	9.4
B6	Cooraclare Co.Clare	5.7	6.9	6.4	13.3
B7	Ballydine, So. Tipperary	4.4	5.0	6.0	11.0
B8	Castleknock/ Mulhuddart. Co.Dublin	13.4	16.2	21.8	38.0
B9	Grannagh. So.Kilkenny	8.4	10.3	8.6	18.9
B13	Kinsale (Dunderow) Co.Cork	6.0	8.2	6.5	14.7
B14	Ringaskiddy area. Co.Cork	7.8	9.4	8.4	17.8
B15	Crossakiel (nr Kells). Co.Meath	5.6	4.7	6.7	11.4
B17	Carranstown Co.Meath	7.1	8.1	7.1	15.2

Samples corresponding to B10, B11 and B12 in the 1995 survey were not taken in 2000 or 2004.

Sample corresponding to B16 in the 2000 survey was not taken in 1995 or 2004

All “B” samples were taken from road tankers

Table 4
Survey on the milk fat related PCDD/F and PCB-TEQ values determined in the potential impact samples B1 - B 17

Sample No.[a]	Milk supply area	Dioxins		PCBs	Dioxins and PCBs
		I-TEQ incl. LOQ	WHO-TEQ incl. LOQ	WHO-TEQ incl. LOQ	Total WHO-TEQ incl. LOQ
		pg/g milk fat	*pg/g milk fat*	*pg/g milk fat*	*pg/g milk fat*
B1	Carrigtwohill/Cobh/Great Island	0.143	0.168	0.166	0.334
B2	Ahgada/East Cork Harbour	0.154	0.168	0.167	0.335
B3	Askeaton area	0.118	0.143	0.149	0.292
B4	Tarbert, Co. Kerry	0.097	0.111	0.113	0.224
B5	Clarecastle Co.Clare	0.104	0.127	0.137	0.264
B6	Cooraclare Co.Clare	0.151	0.181	0.168	0.349
B7	Ballydine, So. Tipperary	0.117	0.134	0.160	0.294
B8	Castleknock/ Mulhuddart. Co.Dublin	0.373	0.452	0.608	1.06
B9	Grannagh. So.Kilkenny	0.212	0.259	0.218	0.477
B13	Kinsale (Dunderow) Co.Cork	0.142	0.194	0.152	0.346
B14	Ringaskiddy area. Co.Cork	0.226	0.273	0.246	0.519
B15	Crossakiel (nr Kells). Co.Meath	0.154	0.199	0.184	0.383
B17	Carranstown Co.Meath	0.224	0.255	0.224	0.479

Samples corresponding to B10, B11 and B12 in the 1995 survey were not taken in 2000 or 2004.

Sample corresponding to B16 in the 2000 survey was not taken in 1995 or 2004

All “B” samples were taken from road tankers

Table 5
Summary of Milk Fat Data in pg TEQ/g fat

	"A" Samples				*"B" Samples*				*"A and "B" Samples combined*			
Parameter	**Dioxins**		**PCBs**	**Dioxins & PCBs**	**Dioxins**		**PCBs**	**Dioxins & PCBs**	**Dioxins**		**PCBs**	**Dioxins & PCBs**
	I-TEQ	*WHO-TEQ*	*WHO-TEQ*	*WHO-TEQ*	*I-TEQ*	*WHO-TEQ*	*WHO-TEQ*	*WHO-TEQ*	*I-TEQ*	*WHO-TEQ*	*WHO-TEQ*	*WHO-TEQ*
Minimum	0.051	0.056	0.045	0.157	0.097	0.111	0.113	0.224	0.051	0.056	0.045	0.157
Maximum	0.334	0.387	0.389	0.657	0.373	0.452	0.608	1.060	0.373	0.452	0.608	1.060
Mean	0.159	0.189	0.176	0.365	0.170	0.205	0.206	0.411	0.163	0.195	0.187	0.381
Median	0.153	0.174	0.153	0.326	0.151	0.181	0.166	0.346	0.151	0.178	0.165	0.334
Samples	24	24	24	24	13	13	13	13	37	37	37	37

Discussion

Considering the entire set of samples (Tables 1 and 3), the reported I-TEQ ranges for dioxins in whole milk are 1.7 to 13.4 pg I-TEQ/kg and 1.9 to 16.2 pg WHO-TEQ/kg. When PCBs are included the ranges are 5.3 to 38.0 pg WHO-TEQ/kg for dioxins and PCBs.

For milk fat (Tables 2 and 4), the respective ranges are 0.05 to 0.37 pg I-TEQ/g and 0.06 to 0.45 pg WHO-TEQ/g. Including PCBs, the ranges are 0.16 to 1.06 WHO-TEQ.

For comparison purposes it is probably more valid to use the milk fat rather than whole milk data due to the varying composition of fat in milk. Using the fat data also facilitates comparisons with other dairy products such as butter and cheese and also with human milk. A summary of the milk fat data showing a breakdown of the background (type A), and the potential impact (type B) along with the combined data set is presented in Table 5. Comparing the two groups of samples, the overall mean values for WHO-TEQ "A" and "B" were 0.189 pg WHO-TEQ/g and 0.205 pg WHO-TEQ/g respectively. However application of statistical tests for means showed that this slight difference was not statistically significant and therefore the two groups should not be considered as distinct.

Sample B8 gave the highest levels although well within EU limits. It was taken from a single farm near Dublin and when grouped with the more urban East coast values alone it is a borderline 95% outlier (dioxin + PCB) according to the standard Grubbs statistical test. However, subjecting dioxins alone to the Grubbs test, B8 is no longer an outlier among the East coast samples (A3, A4, A20, A21, A23, B8, B15, B17) and based on statistical considerations it should not merit particular attention. An obvious conclusion is that the PCB contribution is relatively high due to its ubiquitous presence in the urban environment. A similar conclusion was drawn in the 2000 report.

Figure 1 Comparison of 1995, 2000 & 2004 surveys
A Samples

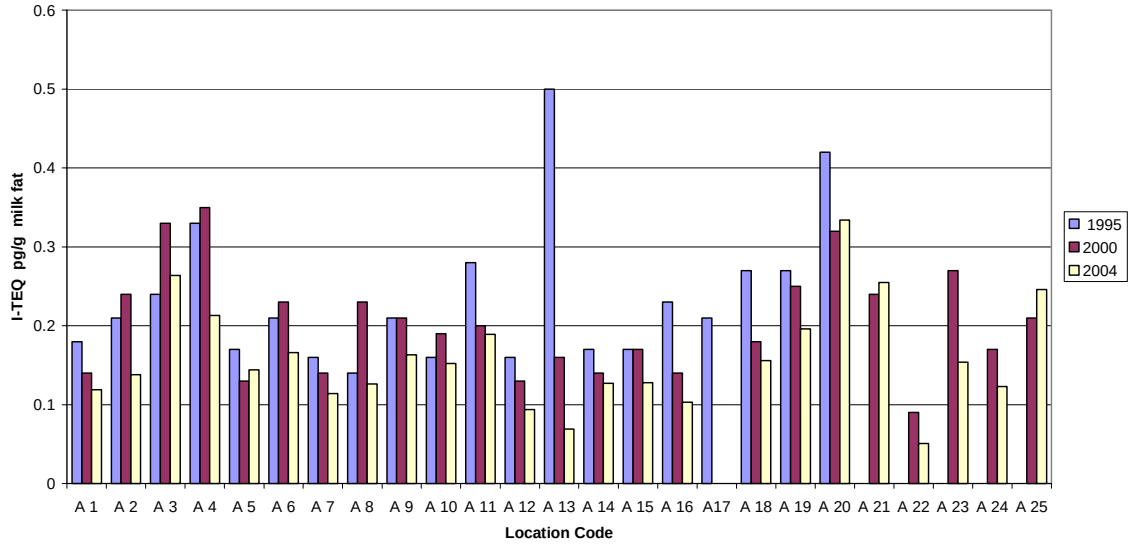
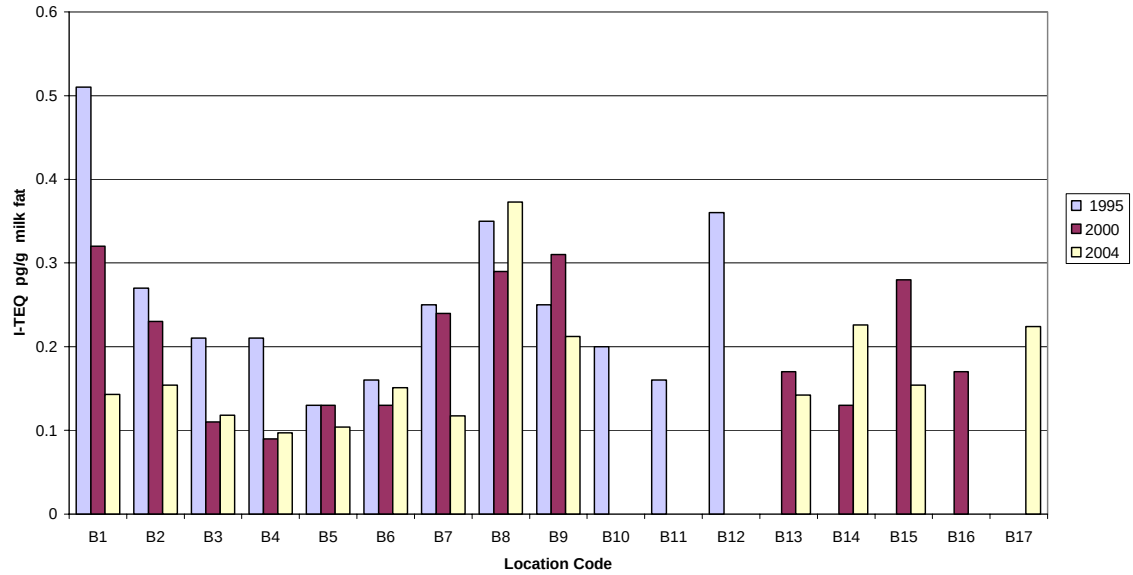


Figure 2 Comparison of 1995, 2000 & 2004 surveys
B Samples



3. COMPARISON WITH 1995 and 2000 SURVEYS

Figures 1 and 2 show a comparison of the I-TEQ milk fat data with the previous two surveys. Comparisons incorporating PCBs are not included, as they were not analysed in the first survey. As previously mentioned comparisons should be made with certain amount of caution.

A few cautionary points should be noted in comparing data, especially low-level data, between 2000 and 2004. As mentioned above limits of quantification (LOQs) are reported instead of limits of detection (LODs) but, on the other hand, the dioxin analytical method has improved compared to 2000 so that the laboratory was able to detect lower levels than before. This resulted in similar or even lower LOQs in 2004 compared to the LODs in 2000. Consequently, the change from LODs to LOQs should not have a significant impact in terms of giving higher TEQs for PCDD/Fs and PCBs. For the second factor, taking full instead of 1/2 LOQ, there is a tendency towards slightly higher values for the dioxins as can be seen from the tables of results.

For PCBs, this did not apply since in nearly all cases all TEQ-relevant PCB congeners were detected.

The mean value for milk fat in the 2004 survey was 0.16 pg I-TEQ/g compared to mean values of 0.20 pg I-TEQ/g in 2000 and 0.24 pg I-TEQ/g for the 1995 survey, corresponding to a reduction of around 33% per cent over the 5 year period. It will be readily seen that only sample B8 which was referred to above, showed a slightly higher result than for the 2000 and 1995 surveys. This sample was taken from the Abbotstown farm in the Castleknock area of the north Dublin suburbs. In all other cases where there was a significant difference in levels, the higher value was recorded in the earlier survey. It is also noteworthy that, as in the 2000 survey, the three highest A values were taken from areas along the East Coast (A3, A20 and A21) and that samples taken in the South West and West were all lower than the national average. Other similarly low results were found in other rural areas in the country which tends to confirm the expectation of particularly low values in such areas.

Notwithstanding the usual difficulties in comparing historical data and bearing in mind that there were only three complete surveys, there is little doubt that the temporal reduction in levels represents a real decrease. This reflects the pattern shown in similar surveys across Europe which have been attributed to a number of regulatory measures and various technological advances. Examples of measures that were taken in Ireland and which may have had an impact on dioxin levels were the virtual abolition of leaded petrol and the shutting down of all hospital incinerators as they were found to be inadequate and could not meet the high standards required under IPC licensing. The shutting down of the iron smelting facility in Cork may also have had an effect (sample B1 Carrigtwohill/ Cobh/Great Island in Figure 2).

4. OTHER STUDIES IN MILK AND DAIRY PRODUCTS

Milk Studies In Other Countries

A series of measurements were carried out in Switzerland in 1984, 1990/1991 and 2001 indicated a similar downward trend to the EPA survey. Samples taken from rural and Alpine locations showed a reduction from mean values of 1.1 pg I-TEQ/g fat in 1990/91 to 0. 36 pg I-TEQ/g fat in 2001. Mean values of samples taken near point sources showed an even greater pro rata reduction from 3.0 pg I-TEQ/g fat in 1990 to 0.63 pg I-TEQ/g milk fat in 2001. An Austrian study of dairy samples from 2003 (Thanner and Moche, 2004) showed a similar pattern to the Swiss 2001 study with mean levels of 0.14 pg I-TEQ/g fat with a range from non-detect to 0.33 pg I-TEQ/g fat. Samples from Alpine areas showed a range from non-detect to 0.29 pg I-TEQ/g fat, with no mean value reported.

Data submitted to the EU Commission on 152 dairy samples (milk and milk products) between 1997 and 2003 from the then 15 member states plus Iceland and Norway as part of an EU-wide survey showed an overall mean of 0.77 pg WHO-TEQ/g fat (Gallani et al, 2004). No upper or lower limits are shown in the study.

A US EPA study of samples taken from eight different regions in the US in July 2000 and January 2001 showed an overall composite mean of 0.71 pg WHO-TEQ/g fat. Again no upper or lower limits are shown in the study. (Schuda et al 2004)

Dioxin Limits in Milk

The EU limit for milk and milk products is currently 3.0 pg WHO-TEQ/g fat (EC 2001). The action level is set at 2.0 pg WHO-TEQ/g fat. The question of incorporating dioxin like PCBs in the limit is currently under review.

It is clear that the overall mean levels found in all of the Irish surveys are over an order of magnitude below the above limit.

5. CONCLUSIONS

1. All levels recorded in this survey compare favourably with those taken from a random selection of similar studies in other EU countries. While assessment of consumer exposure to dioxins through the consumption of milk was not the object of this survey, the highest levels were close to an order of magnitude below legislative limits.

2. The reduction of c 33 per cent in I-TEQ values compared with the 1995 study is in line with similar reductions in environmental levels across Europe.

3. In keeping with the outcome of the 2000 survey there is some evidence of slightly higher values from samples taken along the East coast with correspondingly lower values from rural samples in other areas. This is hardly surprising in view of the population distribution. However, undue significance should not be attached to this as levels are still very low by international standards.

4. There was no basis for considering the set of results from the Type A potential impact stations or the Type B background stations as being distinct from each other.

5. On a practical note, for the organisation of future surveys, it is clear that if the trend towards suburbanisation of the countryside continues, very few suitable dairy farms will remain in existence near urban areas. For example, the farm which was used for the south Dublin component of sample A3 will not be available for future surveys. This should be borne in mind when including milk dioxin analysis in license conditions with respect to facilities in urban areas.

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Glossary

"A" samples	background samples covering the entire country
"B" samples	potential impact samples from areas of perceived potential risk
2,4,5-T	2,4,5-trichlorophenoxyacetic acid
2,4-D	2,4-dichlorophenoxyacetic acid
EPA	Environmental Protection Agency (Ireland)
g	gramme
GfA	Gesellschaft für Arbeitsplatz und Umweltanalytik laboratory, Münster, Germany
IPC	Integrated Pollution Control
I-TEQ	Toxic Equivalent (weighted toxicity of a mixture of dioxin congeners expressed as PCDD) using NATO convention
LOD	limit of detection
LOQ	limit of quantification
NATO	North Atlantic Treaty Organisation
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-para-dioxin
PCDF	polychlorinated dibenzofuran
pg	picogram, 10^{-12} of a gramme.
TEF	Toxic Equivalent Factor (toxicity weighting factor for individual congeners)
USEPA	Environmental Protection Agency (United States)
WHO	World Health Organisation
WHO TEQ	Toxic Equivalent (weighted toxicity of a mixture of dioxin congeners expressed as PCDD) using WHO convention

APPENDIX

Extract from GfA report[a]

[a]The GfA report is not reproduced in full since a number of sections largely overlap with the EPA report. The entire report including the detailed congener analyses referred to the GfA report is available on the EPA website, epa.ie.

Analyses of Irish Cow's Milk samples within the 3rd National Survey of Dioxin Levels in the Irish Environment

Report

61243-003 B01

submitted
by

Eurofins / GfA mbH
Gesellschaft für Arbeitsplatz- und Umweltanalytik mbH
Otto-Hahn-Straße 22
48161 Münster
Germany

Client: **EPA, Environmental Protection Agency**
Richview
Clonskeagh Rd.
Dublin 14
Ireland

June 03, 2005 **103 Pages**

Content

1 Subject of Investigations

On behalf of the Environmental Protection Agency of Ireland (EPA), 37 Irish cow's milk samples, collected in 2004, were analysed for Polychlorinated Dibenzo(p)dioxins (PCDDs), Dibenzofurans (PCDFs) and Polychlorinated Biphenyls (PCBs) by the GfA. All milk samples were provided by the Irish Environmental Protection Agency. As specified by EPA, one part of the samples was collected at so-called background stations (24 A-samples) and a second part at potential impact stations (13 B-samples).

The milk analyses included the determination of the seventeen PCDF/D and the twelve dioxin-like PCB congeners[8] for which toxicity equivalent factors (TEFs) relative to 2,3,7,8-Tetrachlorodibenzo(p)dioxin were specified by the World Health Organisation (WHO)[9]. For quality control, four blank samples were analysed parallel to the milk sample analyses. Triplicate analysis of a milk powder reference material was also included in the QC program.

On the basis of the PCDF/D and PCB concentrations determined analytically, Toxic Equivalents (TEQs) were calculated for both classes of compounds by using the WHO-TEFs[1] and the so-called I-TEFs[10] (for dioxins only). In case of the WHO-TEFs total PCDF/D- and PCB-TEQs could be reported. The analytical results and the TEQs were related to the whole milk and to the fat content of each cow's milk sample. Finally, the TEQ values determined for the Irish cow's milk samples were summarised and compared to previous Irish and recent European data and regulations.

2 Materials and methods

2.1 Sample Materials

After sampling in Ireland, portions of 400 ml of each milk sample were frozen in 500 ml bottles and shipped to GfA in cooling boxes. On arrival at GfA on 7th of July 2004, the samples were still frozen and immediately transferred into a deep freezer (-20°C), where they were stored until start of the analyses. The designation of the cow's milk samples can be seen from Table 01.

2.2 Analytical methods

2.2.1 Sample preparation and fat extraction

PCDF/Ds and PCBs are extracted from milk by means of fat extraction. The contaminants subsequently are separated from the fat and other interfering components and finally analysed by gas chromatography/mass spectrometry (GC/MS).

The Irish milk samples were first defrosted and homogenised and 200 ml subjected to freeze drying (Christ, Beta 1-8 Freeze-dryer). Approximately 15 g of the dry matter were used for fat extraction resulting in a final fat fraction of about 3 to 4 g.

The fat extraction was performed by means of **A**ccelerated **S**olvent **E**xtraction (ASE) using an ASE 300 instrument of Dionex Corp., Sunnyvale, CA, USA.

For fat extraction, 15 g of the freeze-dried sample material were 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 $^{13}C_{12}$-labelled 1,2,3,4-TetraCDD) was added to the top of the sample for controlling of the extraction efficiency. The operation parameters for the subsequent ASE extraction are shown in Table 02.

After ASE extraction the solvent was removed from the fat extract by means of a Syncore PolyVap (Büchi Switzerland) which was operated under defined conditions. The fat fraction finally was determined gravimetrically.

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[8] congeners = single PCDF/D or PCB isomers

[9] TEFs proposed by the WHO European Centre for Environment and Health (WHO-ECEH) in colaboration with the International Program on Chemical Safety (IPCS) in 1998

[10] So-called international TEFs according to the NATO/CCMS model established in 1989

2.2.2 Analysis of cow's milk samples for PCDF/Ds

The PCDF/D analysis was performed according to the DIN EN ISO 17025:2000 accredited methods QMA504-191/203/205. Each analysis included the determination of the seventeen PCDF/D congeners with 2,3,7,8-chlorosubstitution.

For PCDF/D analysis, sixteen $^{13}C_{12}$-labeled PCDF/D congeners[1] were added to the fat extract of each milk sample as internal standards. As can be seen from Table 02, for 16 of the 17 native PCDF/D congeners to be determined, the corresponding $^{13}C_{12}$-labeled PCDF/D standard was added (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 introduced 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 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 (see Table 03) were added to the PCDF/D fraction to determine the recovery of the $^{13}C_{12}$-labeled internal PCDF/D standards through the clean-up and of the surrogate standard.

For the PCDF/D 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 performed 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 PCDF/D standards. A mixture of the seventeen $^{13}C_{12}$-labelled standards mentioned above (see Table 03) and of the corresponding seventeen native standards was always injected to determine the relative retention times[11] and the relative response factors[12] for identification and quantification. During sample analysis, the stability of the mass focus was assured by means of perfluorokerosene lock masses.

2.2.3 Analysis of cow's milk samples for PCBs

The PCB analyses were performed by a combination of the DIN EN ISO/IEC 17025:2000 accredited methods QMA504-191/203. The analyses covered the determination of the twelve dioxin-like PCB congeners for which TEFs were established by the WHO in 1998 (see Table 05).

Similar to the dioxin analysis, for each native PCB congener to be determined the corresponding $^{13}C_{12}$-labelled PCB was added as internal standard to the fat extract (isotope dilution). After fat and matrix separation by means of the silica and alumina columns 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 PTV injector and connected to a high resolution mass spectrometer (HRMS, VG-AutoSpec) was used also. The operation parameters of the instruments used for PCB analyses are listed in Table 06. The procedures for the instrument tuning, the determination of relative retention times and response factors, and the lock mass check were basically the same as described for the PCDF/Ds, however, adjusted to the PCB determinations. The twelve $^{13}C_{12}$-labelled internal PCB standards used for the identification and quantitative determination of native PCB congeners are listed in Table 05.

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11 Retention time relative to the corresponding $^{13}C_{12}$-labelled internal standard

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

2.2.4 Calculation of toxic equivalents (TEQs)

Dioxin-like compounds are often found in complex mixtures. For risk assessment purposes, a toxicity equivalent procedure was developed to describe the cumulative toxicity of such mixtures. This involves assigning individual toxic equivalency factors (TEFs) to single compounds. TEFs are estimates of the toxicity of a compound relative to the toxicity of a reference compound. Such a scheme was first established for PCDF/Ds with 2,3,7,8 Tetrachlorodibenzo(p)dioxin (2,3,7,8-TCDD) as reference compound. TCDD is the most toxic member of this class of compounds. A TEF of 1 is assigned to TCDD, while the other congeners with 2,3,7,8-chlorosubstitution as a rule have lower TEFs. Calculating the toxic equivalency (TEQ) of a PCDF/D mixture involves multiplying the concentration of individual congeners by their respective TEF. The sum of the TEQ concentrations for the individual congeners is the TEQ concentration of the mixture. Meanwhile not only PCDF/D but also twelve dioxin-like PCB congeners are included in the TCDD TEQ system.
Until recently, the so-called international TEF scheme (I-TEF scheme), developed by NATO/CCMS in 1988[2,13] was mainly used for PCDF/D risk assessment. The I-TEF scheme covered the 7 PCDDs and 10 PCDFs with 2,3,7,8-chlorosubstitution only. In 1997 a working group of the WHO re-evaluated the previously established TEFs and further proposed a new set of TCDD TEFs for dioxin-like PCBs. The newer WHO-TE-factors for PCBs can be seen from Table 05. With respect to the TEFs for PCDF/Ds two changes were made:

- for 1,2,3,7,8-PentaCDD, the WHO-TEF is 1 instead of 0,5 within the I-TEF scheme.
- for OctaCDF and OctaCDD, the WHO-TEF is 0.0001 instead of 0.001.

A comparison of the I-TEFs and the WHO TEFs for human risk assessment and mammals can be seen from Table 03. The TEFs for the dioxin-like PCBs are shown in Table 05.
For the milk samples analysed here, both, the I-TEQs and the newer WHO-TEQs were calculated. By addition of the WHO-TEQs for the seventeen PCDF/Ds and the twelve WHO-PCBs, total WHO-TEQs were determined.

2.2.5 Quality control

The recoveries of the sixteen $^{13}C_{12}$-labelled internal PCDF/D and twelve PCB standards through the fat separation and extract clean-up are listed for each analysis in the tables of results in the annex.
The recovery of the $^{13}C_{12}$-labelled TetraCDD surrogate standard was above 90 % for all analyses.
As can be seen from the Tables 01 to 37 of the annex, internal standard recoveries most of all above 70 % were achieved in the PCDD/F analyses. Only in a few cases lower recoveries for individual congenrs were observed. However, those recoveries were still above 50 % in nearly all cases.
For the internal $^{13}C_{12}$-labelled PCB standards the recoveries were above 60 % (see Tables 38 to 74 of the annex). Lower recoveries were found only in a few exceptional cases.
According to the Commission Directive 2002/69/EC laying down the methods of analaysis for the official control of dioxins and the determination of dioxin-like PCBs in foodstuffs, recoveries of the individual internal standard should be in the range of 60 % to 120 %, while lower or higher recoveries for individual congerns are acceptable on the condition, that their contribution to the TEQ does not exceed 10 % of the total PCDD/F-TEQ value. With respect to those requirements the recoveries observed in the PCDD/F and PCB analyses are in a reasonable and acceptable range.

Within the PCDF/D and PCB analyses of the milk samples, four method blanks were determined for each parameter. The blanks were analysed within the series of milk sample

[13] North Atlantik Treaty Organization, Committe on the challenges of Modern Society, Report No. 176, NATO, Brussels, 1988

analyses. Each method blank covered all steps of the analyses, starting with the solvents used for fat extraction and running through all steps of the clean-up. The results of the blank analyses are presented in the Tables 75 and 76 of the annex. To make the results of the method blanks directly comparable to the sample results, the blanks were referred to a hypothetical sample amount of 125 ml milk and to a mean fat content of 3,7 %. Only fat related Data was reported to keep the survey simple.

As can be seen from the Table 75 of the annex, only OctaCDD and in one case OctaCDF were detected at levels slightly above the limits of quantification. Expressed in TEQ-values, blanks below 0,0004 pg WHO-TEQ/g fat were found. Compared to the PCDF/D TEQ-values determined for the cow's milk samples (> 0,05 pg TEQ/g fat) the blank values are negligible.

In case of the PCB analyses, the method blanks were higher, showing WHO-TEQs between 0,012 and 0,023 pg WHO-TEQ/g fat. For the samples with the lowest PCB values (e.g. A12, A22 and B4) such a blank level could contribute to more than 20 % to the PCB-TEQ determined. For all the other samples the blank contribution should be below 20 %.

Accuracy of PCDD/F and PCB analysis was verified by analysing a milk powder reference material (BCR RM 533 No. 197). This milk powder was certified for most of the 17 PCDD/F congeners but not for the dioxin-like PCBs, although present. For this reason the sample material had been repeatedly analysed for PCBs in former times and was used now as in-house reference material for this class of compounds. Commercially available reference materials for PCBs are mostly certified for other congeners (e.g. indicator PCBs) at higher concentration levels. The reference milk powder was analysed quadruplicate for dioxin/furans and PCBs.

The results of the multiple PCDD/F analysis of the milk powder are shown in Table 77. For individual PCDD/F congeners original sample material related data is reported since only this kind of data is certified. For the TEQ value only a fat related I-TEQ is certified and is therefore also reported for the analyses carried out here. The mean values of the fourfold analysis of the reference milk powder are compared to the certified values (see last column of Table 77). As can be seen from Table 77 the deviation of individual congeners from the certified value range from -4,3 % to -31 %. However, the I-TEQ shows a deviation of only -6 % from the certified value which is fully acceptable.

The PCB data of the replicate analysis of the milk powder are presented in Table 78. All data is related to the origianl sample material (milk powder). Since no certification for the dioxin-like PCBs is available for this material, the data is compared to the means of former analyses. The deviations of the means are in the range of -4 % to 20 % for individual PCB congeners while for

the WHO-PCB-TEQ a difference of only 2,2 % was observed. Again, this is a very reasonable value.

For external quality assurance, participation on proficiency tests for PCDD/Fs and PCBs in food or feed is mandatory. The following table summarizes the results of the international tests for dioxins and dioxin-like PCBs in food in which the GfA laboratory took part in the last four years:

Year	Testing scheme	Food matrices tested	Eurofins / GfA data	
			PCDD/F z-score for WHO-TEQs	Dioxin-like PCB congeners [a]
2004	Folkehelsa, N	Chicken meat	-0,63 [d]	< 2 x median [c]
		Trout	-0,43 [d]	< 2 x median [c]
		Palm-oil	-0,78	< 2 x median [c]
2003	Folkehelsa, N	Turkey meat	0,17 / -0,12 [b]	< 2 x median [c]
		Cheese	0,43 / 0,23 [b]	< 2 x median [c]
		Salmon	-0,51 / -0,76 [b]	< 2 x median [c]
	FAPAS, U.K.	Cod liver oil	0,5	no z-scores calculated
2002	Folkehelsa, N	Tuna filet	-1,55 / -1,52 [b]	< 2 x median [c]
		Pork meat	-1,29 / -1,96 [b]	< 2 x median [c]
		Egg yolk	-0,08 / -0,16 [b]	< 2 x median [c]
	FAPAS, U.K.	Cod liver oil	1,1	z-scores PCB 77: 0,6 PCB 81: n.det. PCB 126: -0,2 PCB 169: 0,8
	UMEA University, S	Fish	no z-scores calculated	no z-scores calculated
2001	Folkehelsa, N	Beef meat	not applicable	not applicable
		Breast milk	-0,5 / -0,3 [b]	< ± 2 SD [c]
		Cod liver	0,1 / -0,5 [b]	< ± 2 SD [c]

[a] : For PCBs different evaluation of the data has been reported
[b] : Fresh weight based data first value / lipid based data second value
[c] : No z-scores calculated, individual data as a rule below 2 x median or within the ± 2 SD quality criteria
[d] : Lipid based data

For PCDD/Fs the z-scores with respect to the WHO-PCDD/F-TEQ are shown in the Table. Data in a z-score range of -2 to +2 are considered to be satisfactory. As can be seen from the above Table, all z-scores of the PCDD/F-TEQs determined by GfA Münster fulfil these quality criteria.
For dioxin-like PCBs, z-scores on a PCB-TEQ basis have not yet been calculated in most cases. The data evaluation was performed on the basis of the concentrations of individual PCB congeners. Sometimes z-scores, values below 2 x median or concentration values within the range of ± 2 x standard deviation around the consensus mean were applied as quality criteria. As a rule, GfA Münster also met the quality criteria of the international proficiency tests for the analysis of dioxin-like PCBs in food.

3 Results and Comments

The results of the PCDF/D analyses of the Irish cow's milk samples from the year 2004 are presented in the Tables 01 to 37 of the annex; the PCB results are shown in the Tables 38 to 74. The PCDF/D and PCB data are related to the milk fat and to the whole milk for each sample. The dimension is pg/g (ppt) in both cases.
On the basis of the concentrations determined for the 17 PCDF/D congeners with 2,3,7,8-chlorosubstitution and the 12 dioxin-like PCBs, TEQ-values were calculated according to the I-TEQ (PCDF/Ds only) and WHO-TEQ scheme (PCDF/Ds and PCBs). For both schemes the TEQs were calculated firstly by considering the detected PCDF/D or PCB congeners only (lower bound values) and further by including the not detected congeners by taking half of the value and the full value of their detection limit (upper bound values). All three types of TEQ reporting are met in the literature. However, with respect to the EC limit values, upper bound values have to be considered.
The TEQ-values of the cow's milk samples determined within this study are summarised in the Tables 07 to 10. The data of the background samples A1 - A25 are presented separately from the data of the potential impact samples B1 - B17 (Tables 09 and 10). To avoid confusion, the lipid based and the whole milk based TEQ data are reported on separate tables for both sample groups.
Some statistical data with respect to the TEQ-values of the milk samples are presented in the Tables 11 to 14. The Minimum and Maximum TEQ values as well as the Mean and Median values are reported for both sets of samples. For statistical calculations the TEQ values including the full value of the detection limit for the not detected congeners were taken (upper bound values).
For the background samples A1 - A25, the milk fat related TEQs resulting for the dioxins/furans are between 0,06 and 0,39 pg WHO TEQ/g fat (with a mean of 0,19 pg WHO-TEQ/g fat). The TEQs resulting from the PCB congeners lay in a similar range between 0,05 and 0,39 pg WHO-TEQ/g fat with a mean of 0,18 pg TEQ/g fat. This corresponds to a mean contribution of the PCBs to the total TEQ values of 48 %. Actually, the range of PCB contribution to the total TEQ is 27 to 68 %. Accordingly, the total PCDF/D and PCB WHO-TEQ values show a range between 0,16 and 0,66 pg TEQ/g fat for the background milk samples.
The data set of the potential impact samples show only minor differences to those of the background samples (see Tables 13 and 14). For the PCDF/D TEQs values between 0,11 and 0,45 pg WHO-TEQ/g fat and for the PCB assigned TEQs values between 0,11 and 0,61 pg TEQ/g milk fat were observed. The mean value was 0,21 pg/g fat for the PCDD/F-TEQ and the PCB- TEQ respectively.

On the basis of the data, total WHO-TEQs between 0,22 and 1,06 pg TEQ/g fat with a mean of 0,41 pg TEQ/g fat result for the potential impact samples. The mean PCB contribution is also around 50 % ranging from 44 to 58 %.
In 1995 and 2000 the EPA Ireland already conducted national studies on the dioxin levels in cow's milk. By taking the PCDF/D data of the background samples from the current study (year 2004 samples), a comparison can be made with those of the 1995 and 2000 studies. Table 15 compares the PCDF/D data from the background milk samples of the previous programmes with those of the year 2004 study. The comparison is made on the basis of the I-TEQ values since the 1995 data is only available in theses units. The I-TEQ scheme was used in the past before the WHO-TEF scheme was established.
Both, the mean dioxin I-TEQ and the range of dioxin I-TEQs of the background samples show slightly lower values in 2004 than in the previous studies. Although starting already at a low level the data indicates a decline of the dioxin background level in Irish cow's milk over the past decade. This is in line with the overall tendency of dioxin background contamination in food from other West European contries[14].
Table 16 compares the dioxin and dioxin-like PCB data of the Irish cow's milk samples to data from milk/milk product samples collected in European monitoring programmes from 1997 to 2003. It is quite obvious that both, the mean dioxin and dioxin-like PCB levels in the Irish cow's milk are consistently lower than the mean levels found in the European monitoring programmes. Although it can be assumed that current European dioxin and PCB levels in milk and milk products are lower than those reported for the period 1997 to 2003 the mean levels of Irish cow's milk for 2004 should still be considerably lower than the current mean European levels.
With the council regulation No. 2375/2001 the European Commission set maximum levels for dioxins and furans in various foodstuffs. Inclusion of dioxin-like PCBs shall occur until mid of this year (2005). The maximum EC level for dioxins in milk is 3 pg WHO-TEQ/g fat. A limit value of 6 pg WHO-TEQ/g fat is discussed for the total of dioxins and dioxin-like PCBs in milk and milk products. Furthermore, the European Commission introduced so-called action levels for dioxins in food and feed in 2002 (Commission Recommendation 2002/201/EC). The action levels shall be a tool for authorities and companies to identify sources of contamination and to take measures for its reduction or elimination. For milk, a dioxin action level of 2 pg WHO-TEQ/g fat was recommended.
Referring to the Dioxin- and PCB-TEQs determined in the Irish cow's milk survey of 2004 it can be stated that all milk samples show TEQ values significantly below the European maximum PCDD/F level (factor of 7 to 54 lower) and the PCDD/F action level for milk (factor of 4 to 36 lower). The same applies to the total of dioxins and dioxin-like PCBs with respect to the proposed maximum level (factor of 6 to 38 lower).

Münster, June 03, 2005

Dr. Stephan Hamm
Analytical Chemist
(Head of Special Investigations Department)

[14] Fürst, P., Dioxine in Lebensmitteln, eine Bilanzierung, ERNO 1 (1) 29-35 (2000)

T a b l e s

Tab. 01: Designation of Irish cow's milk samples from 2004 analysed for PCDF/Ds and PCBs

Background samples[a]		**Potential impact samples**[a]	
EPA sample number[a]	GfA sample number	EPA sample number[a]	GfA sample number
A1	4N287001	B1	4N287026
A2	4N287002	B2	4N287027
A3	**4N287003**	B3	4N287028
A4	4N287004	B4	4N287029
A5	4N287005	B5	4N287030
A6	4N287006	B6	4N287031
A7	4N287007	B7	4N287032
A8	4N287008	B8	4N287033
A9	4N287009	B9	4N287034
A10	4N287010	B13	4N287035
A11	4N287011	B14	4N287036
A12	4N287012	B15	4N287037
A13	4N287013	B17	4N287038
A14	4N287014		
A15	4N287015		
A16	4N287016		
A18	4N287018		
A19	4N287019		
A20	4N287020		
A21	4N287021		
A22	4N287022		
A23	4N287023		
A24	4N287024		
A25	4N287025		

[a] : Information provided by EPA Ireland

Tab. 02: ASE operation parameters for the extraction of freeze dried milk samples

Accelerated Solvent Extraction (ASE): ASE 300, Dionex, Sunnyvale, USA	
Pressure:	103,4 bar
Temperature:	100 °C
Heat Time:	5 minutes
Static Time:	5 minutes
Flush Volume:	125 %
Purge Time:	90 seconds
Static Cycles:	3
Solvent:	Dichloromethane: 15 %, Hexane 60 %, Methanol 25 %

Tab. 03: $^{13}C_{12}$-labelled standards used for the PCDD/F analysis of the cow's milk samples and Toxicity Equivalent Factors (TEFs) used for calculation of I-TEQs and WHO-TEQs

PCDD/F parameter to be determined	$^{13}C_{12}$-labelled standard [b]	I-TEF	WHO-TEF (1998)
Surrogate standard [a]	$^{13}C_{12}$-1,2,3,4-TetraCDD	---	---
PCDFs			
2,3,7,8-TetraCDF	$^{13}C_{12}$-2,3,7,8-Tetrachlorodibenzofuran	0,1	0,1
1,2,3,7,8-PentaCDF	$^{13}C_{12}$-1,2,3,7,8-Pentachlorodibenzofuran	0,05	0,05
2,3,4,7,8-PentaCDF	$^{13}C_{12}$-2,3,4,7,8-Pentachlorodibenzofuran	0,5	0,5
1,2,3,4,7,8-HexaCDF	$^{13}C_{12}$-1,2,3,4,7,8-Hexachlorodibenzofuran	0,1	0,1
1,2,3,6,7,8-HexaCDF	$^{13}C_{12}$-1,2,3,6,7,8-Hexachlorodibenzofuran	0,1	0,1
2,3,4,6,7,8-HexaCDF	$^{13}C_{12}$-2,3,4,6,7,8-Hexachlorodibenzofuran	0,1	0,1
1,2,3,7,8,9-HexaCDF	$^{13}C_{12}$-1,2,3,7,8,9-Hexachlorodibenzofuran	0,1	0,1
1,2,3,4,6,7,8-HeptaCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-Heptachlorodibenzofuran	0,01	0,01
1,2,3,4,7,8,9-HeptaCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-Heptachlorodibenzofuran	0,01	0,01
OctaCDF	$^{13}C_{12}$-1,2,3,4,6,7,8,9-Octachlorodibenzofuran	0,001	0,0001
PCDDs			
2,3,7,8-TetraCDD	$^{13}C_{12}$-2,3,7,8-Tetrachlorodibenzo-p-dioxin	1,0	1,0
1,2,3,7,8-PentaCDD	$^{13}C_{12}$-1,2,3,7,8-Pentachlorodibenzo-p-dioxin	0,5	1,0
1,2,3,4,7,8-HexaCDD	$^{13}C_{12}$-1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	0,1	0,1
1,2,3,6,7,8-HexaCDD	$^{13}C_{12}$-1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	0,1	0,1
1,2,3,7,8,9-HexaCDD	$^{13}C_{12}$-1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	0,1	0,1
1,2,3,4,6,7,8-HeptaCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	0,01	0,01
OctaCDD	$^{13}C_{12}$-1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	0,001	0,0001
Recovery standards [c]	$^{13}C_{6}$-1,2,3,4-TetraCDD	---	---
	$^{13}C_{12}$-1,2,3,7,8,9-HexaCDD	---	---

[a] : Standard used for the control of the extraction efficiency
[b] : Standards used for the quantification of the native PCDD/Fs in the sample
[c] : Standards used for the determination of the recovery of the internal standards

Tab. 04: HRGC/HRMS operation parameters for the PCDF/D analysis of cow's milk samples

Capillary gas chromatograph, Hewlett Packard 5890	
Injection:	PTV injection, 4 µl injection volume, solvent: toluene
GC-Column:	DB-5, 60 m x 0,25 mm ID, film thickness: 0,25 µm
Carrier gas:	Helium
High resolution mass spectrometer, VG-AutoSpec	
Transfer line:	320 °C
Source temperature:	300 °C
Ionization:	EI positive, electron energy: 34 eV
Mass reference:	PFK (Perfluorokerosene)
Mass resolution:	≥ 8000
Mode:	SIM, monitoring of several masses of the molecular ion duster, setting of time windows

Tab. 05: $^{13}C_{12}$-labelled internal standards used for quantification of the WHO-PCBs and Toxicity Equivalent Factors (TEFs) used for calculation of TE-values (TEQ)

PCB congeners		**Internal $^{13}C_{12}$-labelled standard used for quantification**	**WHO-TEF (1998)**
Chlorosubstitution Pattern	IUPAC Number		
3,4,4‘,5-Tetrachlorobiphenyl	PCB 81	$^{13}C_{12}$-3,4,4‘,5-Tetrachlorobiphenyl ($^{13}C_{12}$-PCB 81)	0,0001
3,3‘,4,4‘-Tetrachlorobiphenyl	PCB 77	$^{13}C_{12}$-3,3‘,4,4‘-Tetrachlorobiphenyl ($^{13}C_{12}$-PCB 77)	0,0001
2‘,3,4,4‘,5-Pentachlorobiphenyl	PCB 123 [a]	$^{13}C_{12}$-2‘,3,4,4‘,5-Pentachlorobiphenyl ($^{13}C_{12}$-PCB 123)	0,0001
2,3‘,4,4‘,5-Pentachlorobiphenyl	PCB 118	$^{13}C_{12}$-2,3‘,4,4‘,5-Pentachlorobiphenyl ($^{13}C_{12}$-PCB 118)	0,0001
2,3,4,4‘,5-Pentachlorobiphenyl	PCB 114	$^{13}C_{12}$-2,3,4,4‘,5-Pentachlorobiphenyl ($^{13}C_{12}$-PCB 114)	0,0005
2,3,3‘,4,4‘-Pentachlorobiphenyl	PCB 105	$^{13}C_{12}$-2,3,3‘,4,4‘-Pentachlorobiphenyl ($^{13}C_{12}$-PCB 105)	0,0001
3,3‘,4,4‘,5,-Pentachlorobiphenyl	PCB 126	$^{13}C_{12}$-3,3‘,4,4‘,5,-Pentachlorobiphenyl ($^{13}C_{12}$-PCB 126)	0,1
2,3‘,4,4‘,5,5‘-Hexachlorobiphenyl	PCB 167	$^{13}C_{12}$-2,3‘,4,4‘,5,5‘-Hexachlorobiphenyl ($^{13}C_{12}$-PCB 167)	0,00001
2,3,3‘,4,4‘,5-Hexachlorobiphenyl	PCB 156	$^{13}C_{12}$-2,3,3‘,4,4‘,5-Hexachlorobiphenyl ($^{13}C_{12}$-PCB 156)	0,0005
2,3,3‘,4,4‘,5‘-Hexachlorobiphenyl	PCB 157	$^{13}C_{12}$-2,3,3‘,4,4‘,5‘-Hexachlorobiphenyl ($^{13}C_{12}$-PCB 157)	0,0005
3,3‘,4,4‘,5,5‘-Hexachlorobiphenyl	PCB 169	$^{13}C_{12}$-3,3‘,4,4‘,5,5‘-Hexachlorobiphenyl ($^{13}C_{12}$-PCB 169)	0,01
2,3,3‘,4,4‘,5,5‘-Heptachlorobiphenyl	PCB 189	$^{13}C_{12}$-2,3,3‘,4,4‘,5,5‘-Heptachlorobiphenyl ($^{13}C_{12}$-PCB 189)	0,0001

[a] : Coelutes with PCB 106

Tab. 06: HRGC/HRMS operation parameters for the PCB analysis of cow's milk samples

Capillary gas chromatograph, Hewlett Packard 5890	
Injection:	PTV injection, 2 µl injection volume, solvent: methyl acetate / hexane
GC-Column:	HT-5, 25 m x 0,22 mm ID, film thickness: 0,10 µm
Carrier gas:	Helium
High resolution mass spectrometer, VG-AutoSpec	
Transfer line:	320 °C
Source temperature:	300 °C
Ionization:	EI positive, electron energy: 34 eV
Mass reference:	PFK (Perfluorokerosene)
Mass resolution:	≥ 8000
Mode:	SIM, monitoring of several masses of the molecular ion duster, setting of time windows

Tab. 07: Survey on the whole milk related PCDD/F and PCB-TEQ values determined in the background samples A 1 - A 25 of 2004 (upper bound values)

Sample	Dioxins		PCBs	Dioxins and PCBs
	I-TEQ incl. LOQ [a]	WHO-TEQ incl. LOQ [a]	WHO-TEQ incl. LOQ [a]	Total WHO-TEQ incl. LOQ [a]
Unit	pg/kg whole milk	pg/kg whole milk	pg/kg whole milk	pg/kg whole milk
A 1	4,9	6,0	5,1	11,1
A 2	4,9	5,8	5,2	11,0
A 3	9,1	10,7	10,5	21,2
A 4	7,7	8,9	14,1	23,0
A 5	4,2	5,1	5,1	10,2
A 6	6,3	7,4	5,8	13,2
A 7	5,3	6,2	5,6	11,8
A 8	5,1	6,1	5,3	11,4
A 9	6,6	7,3	7,1	14,4
A 10	5,5	6,4	6,0	12,4
A 11	7,0	8,6	7,0	15,6
A 12	3,3	4,2	1,6	5,8
A 13	2,3	2,7	5,6	8,3
A 14	4,2	5,1	5,0	10,1
A 15	5,3	6,4	4,9	11,3
A 16	4,4	5,3	5,3	10,6
A 18	6,1	7,5	5,6	13,1
A 19	6,7	7,8	7,7	15,5
A 20	13,3	15,4	10,8	26,2
A 21	9,4	11,1	11,4	22,5
A 22	1,7	1,9	3,4	15,3
A 23	5,8	6,9	6,6	13,5
A 24	4,2	5,2	4,3	9,5
A 25	9,4	11,5	7,6	19,1

[a] : TEQ value calculated by including the not detected congeners also by taking the full value of their limits of quantification (LOQ)

Tab. 08: Survey on the milk fat related PCDD/F and PCB-TEQ values determined in the background samples A 1 - A 25 of 2004 (upper bound values)

Sample	Dioxins		PCBs	Dioxins and PCBs
	I-TEQ incl. LOQ [a]	WHO-TEQ incl. LOQ [a]	WHO-TEQ incl. LOQ [a]	Total WHO-TEQ incl. LOQ [a]
Unit	pg/g milk fat	pg/g milk fat	pg/g milk fat	pg/g milk fat
A1	0,119	0,146	0,122	0,268
A2	0,138	0,163	0,147	0,310
A3	0,264	0,312	0,306	0,618
A4	0,213	0,245	0,389	0,634
A5	0,144	0,139	0,138	0,277
A6	0,166	0,197	0,154	0,351
A7	0,114	0,169	0,152	0,321
A8	0,126	0,151	0,133	0,284
A9	0,163	0,181	0,176	0,357
A10	0,152	0,178	0,167	0,345
A11	0,189	0,232	0,188	0,420
A12	0,094	0,118	0,045	0,163
A13	0,069	0,079	0,165	0,244
A14	0,127	0,154	0,150	0,304
A15	0,128	0,157	0,119	0,276
A16	0,103	0,126	0,124	0,250
A18	0,156	0,190	0,141	0,331
A19	0,196	0,231	0,225	0,456
A20	0,334	0,387	0,270	0,654
A21	0,255	0,303	0,311	0,614
A22	0,051	0,056	0,101	0,157
A23	0,154	0,183	0,175	0,358
A24	0,123	0,152	0,124	0,276
A25	0,246	0,301	0,198	0,499

[a] : TEQ value calculated by including the not detected congeners also by taking the full value of their limits of quantification (LOQ)

Tab. 09: Survey on the whole milk related PCDD/F and PCB-TEQ values determined in the potential impact samples B 1 - B 17 of 2004 (upper bound value)

Sample	Dioxins		PCBs	Dioxins and PCBs
	I-TEQ incl. LOQ [a]	WHO-TEQ incl. LOQ [a]	WHO-TEQ incl. LOQ [a]	Total WHO-TEQ incl. LOQ [a]
Unit	pg/kg whole milk	pg/kg whole milk	pg/kg whole milk	pg/kg whole milk
B1	5,5	6,5	6,4	12,9
B2	5,9	6,5	6,4	12,9
B3	5,7	6,9	7,2	14,1
B4	3,7	4,2	4,3	8,5
B5	3,7	4,5	4,9	9,4
B6	5,7	6,9	6,4	13,3
B7	4,4	5,0	6,0	11,0
B8	13,4	16,2	21,8	38,0
B9	8,4	10,3	8,6	18,9
B13	6,0	8,2	6,5	14,7
B14	7,8	9,4	8,4	17,8
B15	5,6	4,7	6,7	11,4
B17	7,1	8,1	7,1	15,2

[a] : TEQ value calculated by including the not detected congeners also by taking the full value of their limits of quantification (LOQ)

Tab. 10: Survey on the milk fat related PCDD/F and PCB-TEQ values determined in the potential impact samples B 1 - B 17 of 2004 (upper bound values)

Sample	Dioxins		PCBs	Dioxins and PCBs
	I-TEQ incl. LOD [a]	WHO-TEQ incl. LOD [a]	WHO-TEQ incl. LOD [a]	Total WHO-TEQ incl. LOD [a]
Unit	pg/g milk fat	pg/g milk fat	pg/g milk fat	pg/g milk fat
B1	0,143	0,168	0,166	0,334
B2	0,154	0,168	0,167	0,335
B3	0,118	0,143	0,149	0,292
B4	0,097	0,111	0,113	0,224
B5	0,104	0,127	0,137	0,264
B6	0,151	0,181	0,168	0,349
B7	0,117	0,134	0,160	0,294
B8	0,373	0,452	0,608	1,06
B9	0,212	0,259	0,218	0,477
B13	0,142	0,194	0,152	0,346
B14	0,226	0,273	0,246	0,519
B15	0,154	0,199	0,184	0,383
B17	0,224	0,255	0,224	0,479

[a] : TEQ value calculated by including the not detected congeners also by taking the full value of their limits of quantification (LOQ)

Tab. 11: Statistical data on the whole milk related PCDD/F and PCB-TEQ values determined in the background samples A 1 - A 25 of 2004 (n = 24, upper bound values)

Statistical *Parameter*	**Dioxins**		**PCBs**	**Dioxins and PCBs**
	I-TEQ incl. LOQ	**WHO-TEQ incl. LOQ**	**WHO-TEQ incl. LOQ**	**Total WHO-TEQ incl. LOQ**
	pg/kg whole milk	pg/kg whole milk	pg/kg whole milk	pg/kg whole milk
Minimum	1,7	1,9	1,6	5,8
Maximum	13,3	15,4	14,1	26,2
Mean	5,9	7,1	6,5	14,0
Median	5,4	6,4	5,6	12,8

n = number of samples

Tab. 12: Statistical data on the milk fat related PCDD/F and PCB-TEQ values determined in the background samples A 1 - A 25 of 2004 (n = 24, upper bound values)

Sample	**Dioxins**		**PCBs**	**Dioxins and PCBs**	**Percentage**
	I-TEQ incl. LOQ	**WHO-TEQ incl. LOQ**	**WHO-TEQ incl. LOQ**	**Total WHO-TEQ incl. LOQ**	**PCB-WHO-TEQ**
Unit	pg/g milk fat	pg/g milk fat	pg/g milk fat	pg/g milk fat	%
Minimum	0,051	0,056	0,045	0,157	27,6
Maximum	0,334	0,387	0,389	0,657	67,6
Mean	0,162	0,189	0,176	0,365	48,2
Median	0,153	0,174	0,153	0,326	47,9

n = number of samples

Tab. 13: Statistical data on the whole milk related PCDD/F and PCB-TEQ values determined in the potential impact samples B 1 - B 17 of 2004 (n = 13, upper bound value)

Sample	Dioxins		PCBs	Dioxins and PCBs
	I-TEQ incl. LOQ	WHO-TEQ incl. LOQ	WHO-TEQ incl. LOQ	Total WHO-TEQ incl. LOQ
Unit	pg/kg whole milk	pg/kg whole milk	pg/kg whole milk	pg/kg whole milk
Minimum	3,7	4,2	4,3	8,5
Maximum	14,3	16,2	21,8	38,6
Mean	6,4	7,5	7,7	15,5
Median	25,7	6,9	6,5	14,0

n = number of samples

Tab. 14: Statistical data on the milk fat related PCDD/F and PCB-TEQ values determined in the potential impact samples B 1 - B 17 of 2004 (n = 13, upper bound values)

Sample	Dioxins		PCBs	Dioxins and PCBs	Percentage
	I-TEQ incl. LOQ	WHO-TEQ incl. LOQ	WHO-TEQ incl. LOQ	Total WHO-TEQ incl. LOQ	PCB-WHO-TEQ
Unit	pg/g milk fat	pg/g milk fat	pg/g milk fat	pg/g milk fat	%
Minimum	0,097	0,111	0,113	0,224	43,9
Maximum	0,373	0,452	0,608	1,060	57,4
Mean	0,170	0,205	0,206	0,411	49,6
Median	0,151	0,181	0,166	0,346	49,7

n = number of samples

Tab. 15: Comparison of the PCDD/F I-TEQ values from the 2004 Irish cow's milk samples with data from the preceeding studies

Country	Period of sampling	Number of samples	Mean value (pg I-TEQ/ g fat)	Range (pg I-TEQ/ g fat)	Remarks	Literature
Ireland	1995	20	0,23	0,13 - 0,36	**background samples**	*a*
Ireland	2000	24	0,20	0,09 - 0,35	**background samples**	*b*
Ireland	2004	24	0,16	0,05 - 0,33	**background samples**	*c*

[a] : Dioxins in the Irish Environment, An assessment based on levels in cow's milk sampled in June 1995, EPA Ireland, Ardcavon, Wexford, 1996
[b] : Dioxin levels in the Irish Environment; Second Assesment (Summer 2000) based on levels in cow's milk, EPA Ireland, Wexford, 2001
[c] : Current study

Tab. 16: Comparison of dioxin and PCB WHO-TEQ values from Irish cow's milk samples with data from European monitoring programs

Country	Period of sampling	Number and specification of samples	Dioxins/Furans Mean values pg WHO-TEQ/g fat	PCBs Mean values pg WHO-TEQ/g fat	Dioxin/Furans plus Mean values pg WHO-TEQ/g fat
Ireland [a]	2000	24 A-samples	0,24	0,25	0,49
		13 B-samples	0,24	0,24	0,48
Ireland [b]	2004	24 A-samples	0,19	0,18	0,37
		13 B-samples	0,21	0,21	0,41
European Union [c,d]	1997 - 2003	152 Milk and milk products from EC monitoring programmes	0,77	1,65	2,42

[a] : Dioxins in the Irish Environment, An assessment based on levels in cow's milk sampled in June 1995, EPA Ireland, Ardcavon, Wexford, 1996
[b] : Dioxin levels in the Irish Environment; Second Assesment (Summer 2000) based on levels in cow's milk
[c] : Gallani, B., Verstraeter, F., Boix, A., von Holst, C., Anklam, E., Levels of dioxins and dioxin-like PCBs in food and feed in Europe, Organohalogen Compounds, 66, 1893-1900, 2004
[d] : Joint report DG Sanco, DG IRC-IRMM, EC, Brussels, 2004

An Ghníomhaireacht um Chaomhnú Comhshaoil

STÁDAS NA GNÍOMHAIREACHTA

Is comhlacht poiblí neamhspleách í an Ghníomhaireacht um Chaomhnú Comhshaoil (EPA) a bunaíodh i mí Iúil 1993 faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil, 1992. Ó thaobh an Rialtais, is í an Roinn Comhshaoil agus Rialtais Áitiúil a dhéanann urraíocht uirthi.

Déanann Bord Feidhmeach lánaimseartha comhdhéanta d'Ard-Stiúrthóir agus ceathrar Stiúrthóirí bainistíocht ar an EPA. Cinntítear neamhspleáchas trí nósanna imeachta roghnaithe i gcás an Ard-Stiúrthóra agus na Stiúrthóirí agus an tsaoirse, de réir mar a sholáthraítear sa reachtaíocht, gníomhú as a stuaim féin. Tá an sannadh, faoin reachtaíocht, maidir le freagracht dhíreach as réimse leathan feidhmeanna mar bhonn taca ag an neamhspleáchas sin. Faoin reachtaíocht, is cion sainiúil é iarracht a dhéanamh tionchar a imirt ar an Ghníomhaireacht, nó ar aon duine a bhíonn ag gníomhú thar ceann na Gníomhaireachta, ar bhealach míchuí.

Cuidíonn Coiste Comhairleach ar a bhfuil dhá chomhalta déag arna gceapadh ag an Aire Comhshaoil, Oidhreachta agus Rialtais Áitiúil leis an nGníomhaireacht.

FREAGRACHTAÍ

Tá réimse leathan dualgas agus cumhachtaí reachtúla ag an EPA faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil. Chomh maith leis sin, tá curtha le hacmhainn an EPA maidir le forfheidhmiú le cumhachtaí san Acht um Chaomhnú an Chomhshaoil 2003. Áirítear orthu seo a leanas príomhfhreagrachtaí an EPA:

- ceadúnú a dhéanamh ar phróisis thionsclaíocha mhóra/choimpléascacha a bhféadfadh cumas truaillithe suntasach a bheith ag baint leo;
- monatóireacht ar chaighdeán comhshaoil, lena n-áirítear bunachair shonraí a bhunú ar a mbeidh rochtain ag an bpobal;
- tuarascálacha tréimhsiúla maidir le staid an chomhshaoil a fhoilsiú;
- sárchleachtais comhshaoil a chur chun cinn;
- taighde comhshaoil a chur chun cinn agus a chomhordú;
- gníomhaíochtaí diúscartha dramhaíola agus aisghabhála suntasacha, lena n-áirítear láithreacha líonta talún a cheadúnú agus plean bainistíochta guaisdramhaíola náisiúnta a ullmhú;
- córas a chur i bhfeidhm a cheadaíonn rialú astaithe VOC a bhíonn mar thoradh ar scaoileadh GMOanna isteach sa chomhshaol in aon turas;
- rialacháin GMO a chur i bhfeidhm agus a fhorfheidhmiú ó thaobh GMOanna a choinneáil agus a scaoileadh amach sa chomhshaol in aon turas;
- clár hidriméadrach náisiúnta a ullmhú agus a chur i bhfeidhm;
- dréacht a chur le chéile de Phlean Leithroinnte Náisiúnta do thrádáil liúntas astaithe gáis ceaptha teasa; Údarás Inniúla Náisiúnta a bhunú le ceadanna trádála agus liúntais a eisiúint orthu siúd atá clúdaithe ag an scéim; monatóireacht, léargas, agus fíorú maidir le hastuithe ó chuideachtaí rannpháirteacha; agus Clár Trádála Astuithe Náisiúnta a bhunú;

agus, faoin Oifig Forfheidhmiúcháin Comhshaoil, a bunaíodh i 2003 agus atá tiomanta as reachtaíocht comhshaoil a chur i bhfeidhm agus a fhorfheidhmiú in Éirinn;

- feabhas a chur ar chomhlíonadh reachtaíocht cosanta comhshaoil in Éirinn;
- feasacht a ardú maidir leis an tábhacht a bhaineann le forfheidhmiú i gcás reachtaíochta cosanta comhshaoil in Éirinn;
- ceadúnais IPPC agus ceadúnais Dramhaíola a eisíonn an EPA a fhorfheidhmiú;
- iniúchadh agus tuairisciú ar fheidhmíocht údarás áitiúil maidir lena bhfeidhmeanna cosanta comhshaoil a chur ar bun, lena n-áirítear:
  - forfheidhmiú maidir le ceadúnais dramhaíola a sháraítear;
  - gníomh maidir le dumpáil mhídhleathach;
  - ceadanna bailithe dramhaíola a chur i bhfeidhm, agus
  - tionscnaimh a bheidh mar fhreagracht ar an táirgeoir a fhorfheidhmiú (mar shampla, sa réimse a bhaineann le dramhaíl pacáiste);
- gníomh in aghaidh údarás áitiúil nach bhfuil ag comhlíonadh a gcuid feidhmeanna cosanta comhshaoil ar bhealach cuí;
- an dlí a chur nó cuidiú le húdaráis áitiúla an dlí a chur ó thaobh sháraithe suntasacha reachtaíochta cosanta comhshaoil ar bhealach caoithiúil; agus
- cuidiú le húdaráis áitiúla a gcuid feidhmíocht cosanta comhshaoil a fheabhsú ar bhonn cás ar chás, trí ghréasán forfheidhmithe a bhunú le malartú eolais a chur chun cinn chomh maith le sárchleachtas, agus trí threoir chuí a sholáthar.

Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

Headquarters
PO Box 3000, Johnstown Castle Estate
County Wexford, Ireland

Bosca Poist 3000, Eastát Chaisleán Bhaile Sheáin
Contae Loch Garman, Éire

T: +353 53 60600
F: +353 53 60699

Regional Inspectorate
McCumiskey House, Richview
Clonskeagh Road, Dublin 14, Ireland

Cigireacht Réigiúnach, Teach Mhic Chumascaigh
Dea-Radharc, Bóthar Cluain Sceach
Baile Átha Cliath 14, Éire

T: +353 1 268 0100
F: +353 1 268 0199

Regional Inspectorate
Inniscarra, County Cork, Ireland

Cigireacht Réigiúnach, Inis Cara
Contae Chorcaí, Éire

T: +353 21 487 5540
F: +353 21 487 5545

Regional Inspectorate
John Moore Road, Castlebar
County Mayo, Ireland

Cigireacht Réigiúnach, Bóthar Sheán de Mórdha
Caisleán an Bharraigh, Contae Mhaigh Eo, Éire

T: +353 94 904 8400
F: +353 94 902 1934

Regional Inspectorate
Butts Green, Kilkenny, Ireland

Cigireacht Réigiúnach, Faiche an Bhúit
Cill Chainnigh, Éire

T: +353 56 772 2329
F: +353 56 776 5085

Regional Inspectorate
The Glen, Monaghan, Ireland

Cigireacht Réigiúnach, An Gleann
Muineachán, Éire

T: +353 47 77600
F: +353 47 84987

E: info@epa.ie
W:www.epa.ie
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