PCDD/F and PCB content in feed in Denmark, 2004

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Introduction

Since the Belgian dioxin crisis in 1999, the Danish Plant Directorate has surveyed the PCDD/F and PCB level in feed in Denmark. In the period, approximately 600 samples were analysed. The EU directive[1] prescribing maximum content limits for dioxins in feed is implemented into Danish law[2]. In 2004, 74 samples of different kind of feedingstuff were analysed, and only one sample of fish meal had content above the permitted limit.

In 2004, the analysis of the feed was performed at the new Danish dioxin laboratory in Region Ringsted, which is a part of the Danish Veterinary and Food Administration. The laboratory has a capacity of about 500 samples pr year. Rebuilding of the laboratory into dioxin analyses began in 2002 and by the end of 2002 all instruments were running. In 2004, accreditation for the analysis in food and feed of the seventeen 2,3,7,8-chlorine-containing dibenzo-p-dioxins and dibenzofurans (PCDD/F) and nineteen PCB's (4 non-ortho PCBs, 8 mono-ortho PCBs and 7 marker PCBs) was achieved.

Materials and Methods

Sampling

Feed samples were taken as random samples by the regional Danish Plant Directorate authorities throughout Denmark. The samples were grinded and the moisture content determined by the central Danish Plant Directorate, followed by analysis for dioxin and PCB at Region Ringsted.

Analysis

The requirements for the analysis of dioxins and PCBs laid down in the Commission Directive 2002/70/EF[3] were followed.

Typical sample size of pure fat samples were 1-3g and of other matrices 15-20g.

Fat extraction was performed with accelerated solvent extraction on ASE300 (Dionex) using acetone/pentane (88/12), 2 cycles, a temperature of 80^{o}C and static time 10 min. 100ml extraction cells filled with sample, sea sand and Hydromatrix were used.

Cleanup and fractionation was done by Power Prep (FMS, USA) using multilayer silica (part no CLDS-ABN-STD), alumina (part no CLDA-BAS-011) and carbon columns (Part no CLDC-CCE-034). In addition, for sample sizes above 1g a Jumbo silica column (Part no HCDS-ACD-STD) was used. The Power Prep program was based on the method used at the University of Liege[4].

Detection and quantitation was done using a gas chromatograph – high resolution mass spectrometer (GC-HRMS, Trace GC ultra and Finnigan MAT95). The GC was equipped with split/splitless injector and DB5MS-DG column (10m pre-column, 60m, 0.25mm I.D, film thickness 0.25 µm). For the dioxin fraction from Power Prep containing the 17 PCDD/F and 4 non-ortho-PCBs the following GC-program was used: 140^{o}C hold 2min, 15^{o}C/min up to 240^{o}C, 1^{o}C/min up to 255^{o}C hold 10min, 10^{o}C/min up to 325^{o}C hold 11min. For the fraction containing the 15 other PCBs the following GC-program was used: 90^{o}C hold 2min, 20^{o}C/min up to 180^{o}C, 2^{o}C/min up to 260^{o}C, 5^{o}C/min up to 310^{o}C, hold 8min. FC43 was used as calibration substance for the mass spectrometric detection.

Quantification was done using the QuanDesk software (ThermoFinnigan, Germany).

Standards were purchased from Cambridge Isotope Laboratories, INC. (USA) and Dr. Ehrenstorfer (Germany) and further diluted in toluene.

Quality assurance

Each analytical series consists of 6-12 samples, one double determination of a sample, one reagent blank, one spiked sample and/or a natural contaminated control sample. Each sample was spiked with 13C-labelled standards at the beginning of the analysis.

In 2004, we participated with satisfactory results in the Norwegian Food 2004 Round Robin test, which included one trout, one chicken and one palm oil sample.

Results and Discussion

In the table, an overview of our results is presented. The 74 analysed samples are listed according to the respective group in the EU directive containing the maximum content limits[1,2]. The average WHO-PCDD/F-TEQ content and WHO-PCB-TEQ content are given as well as the maximum content measured. All values are recalculated to a moisture content of 12% as prescribed in the directive.

Table 1. Maximum content limit for PCDD/F[1,2] measured average content and measured maximum content for PCDD/F and PCB. All values are upper bound and recalculated to a moisture content of 12%. For each category the number of samples is given. All samples are from 2004.

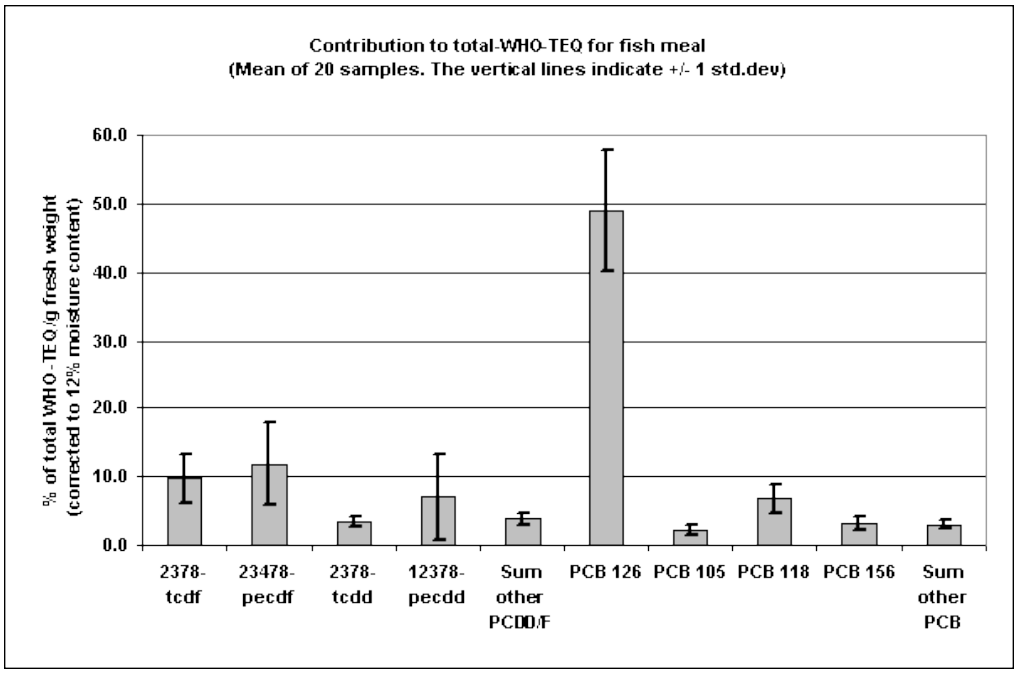
	PCDD/F	PCDD/F		PCB		
Feedingstuffs	Max content limit (moisture content 12%) [1,2].	Average content	Maximum content	Average content	Maximum content	No. of samples
	ng WHO-PCDD/F TEQ/kg	ng WHO-PCDD/F TEQ/kg	ng WHO-PCDD/F TEQ/kg	ng WHO-TEQ PCB/kg	ng WHO-TEQ PCB/kg	
1. All feed materials of plant origin including vegetable oils and by-products	0.75	0.208	0.738	0.054	0.158	14
2. Minerals	1.0	0.041	0.104	0.007	0.0092	6
3. Animal fat, including milk fat and egg fat	2.0	0.398	0.826	0.112	0.275	8
4. Other land animal products including milk and milk products and eggs and egg products	0.75	-	-	-	-	0
5. Fish oil	6	1.869	5.34	5.523	9.53	7
6. Fish, other aquatic animals, their products and by-products with the exception of fish oil	1.25	0.467	1.61	0.832	2.53	21*
7. Compound feedingstuffs, with the exception of feedingstuffs for fur animals, pet foods and feedingstuffs for fish	0.75	0.115	0.634	0.886	6.14	7
8. Feedingstuffs for fish and pet foods	2.25	0.778	1.70	1.119	2.046	8
9. Additives	0.75	0.020	0.029	0.007	0.0102	3

*One of the samples of fish meal had content above the limit (1.6ng WHO-PCDD/F TEQ/kg)

Only 1 sample of fish meal with a dioxin content of 1.6ng WHO-PCDD/F TEQ/kg was above the maximum content

limit of 1.25 WHO-PCDD/F TEQ/kg.

For all of the fish oil samples (group 5), all of the feedingstuffs for fish and fur animals (group 8) and most of the fish products (group 6) the PCBs contributed more to the total WHO-TEQ than the PCDD/F. For the 20 samples of fish meal (part of group 6 in the table), the percentage contribution of each congener to the total WHO-TEQ is shown in the figure. In generally, the most important dioxin is the 2,3,4,6,7-pentachloro-dibenzofuran (23478-pecdf) and by far the most important PCB is the non-ortho PCB126.



The dominating dioxin congener for six out of eight samples of vegetable fat and fat of unknown composition was OCDD, the highest content being 400ng/kg. The TEF for OCDD is 0.0001 and the content therefore generally contributes very little to the TEQ.

For a few of the samples it was not possible to get a stable signal from the reference substance used for locking and calibration of the masses during mass spectrometric analysis. This indicated that the extracts from the Power Prep were not clean enough. For these problematic samples, the amount of sample was reduced. When reducing the amount of sample it is not always possible to fulfil the recommendation[3] that the detection limit should be one fifth of the maximum content limit. This was the case for seven of the 74 samples. Samples of pure fat are normally added to the first column of the Power Prep system without prior extraction on ASE. In order to analyse one of the samples of animal fat it was necessary to extract/clean the sample on ASE, in addition to reducing the amount of sample.

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References

1. Commission Directive 2001/102/EF of 27 November 2001 amending Directive 1999/29/EC on the undesirable substances and products in animal nutrition.

2. Danish legal provision concerning feed (Bekendtgørelse no 998 12/10/2004).

3. Commission Directive 2002/70/EF of 26 July 2002 establishing requirements for the determination of levels of dioxins and dioxin-like PCBs in feedingstuffs.

4. Focant J-F., Eppe G., Pirard C. and De Pauw E. (2001) *J.Chrom.A*. 925: 207-221.