

# FORMATION AND SOURCES: FIELD CASES

## LEVELS OF PCDD/PCDFs AND DIOXIN-LIKE PCBs IN DIFFERENT FEED MATERIALS OF PLANT ORIGIN FROM GERMANY

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### Introduction

After the recent crisis occurred with feed materials, great efforts have been done to determine them in several feedingstuffs (1). Limit levels for dioxins in feedingstuffs enter into force in the EU Member States as of 1 July 2002. The European Community is also planning to include dioxin-like PCBs in the limit levels for feeds and foods after their first review by 31 December 2004, including new data on the presence of both compound classes (2).

To assess the presence of Polychlorinated Dibenz(o,p)dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and dioxin-like PCBs in several feedingstuffs of plant origin one of the main cereal distributor of Germany, the Deutscher Raiffeisenverband, conducted in 2002 a study on the levels of these dioxin-like persistent organic pollutants (POPs).

The study consisted in the analyses of 12 different feedingmaterials with a total sum of 22 samples.

It was found that WHO-TEQ levels in all samples have been below the new regulated level of 0.75 ng WHO-PCDD/F-TEQ/kg relative to feedingstuffs with a moisture content of 12 %, calculated by including the upper-bound concentration. By including the WHO-PCB-TEQ to the sum of WHO-TEQ the values would increase with a mean value of around 30 %.

### Materials and Methods

A series of 22 feed materials of plant origin were collected by several offices of the Deutscher Raiffeisenverband from their production facilities all over Germany. The samples were taken between February and June 2002 from storage silos or tankers at representative regional storage places.

The feed materials were analysed for PCDD/Fs and dioxin-like PCBs by means of sample extraction, gravimetrical determination of the moisture, destroying of non persistent compounds by sulphuric acid, clean-up of the remaining fraction on different adsorbents, analysis of the purified extracts by means of capillary gas chromatography/high resolution mass spectrometry (HRGC/HRMS) and quantification via internal  $^{13}\text{C}_{12}$ -labelled standards (isotope dilution). The PCB analyses covered the 12 dioxin-like PCBs for which toxic equivalency factors (TEFs) recently recommended by the new EU guidelines.

The detection limit showed an mean value of 0.06 ng WHO-PCDD/F-TEQ/kg and 0.02 ng WHO-PCB-TEQ/kg relative to feedingstuffs with a moisture content of 12 %, calculated by including the upper-bound concentration. In contrast to the dioxin measurements, dioxin-like PCBs showed significant background levels, which have been in this study deducted from the samples. Therefore, the PCB levels here measured could be possibly higher compared to other studies. Significant background levels occurred especially with PCB-118 and PCB-180, while in case of the most toxic PCB congener 126 and 169 no blank values were obtained.

PCDD/Fs  $^{13}\text{C}_{12}$ -labelled standards were obtained from Cambridge Isotope Laboratories and Co-PCBs  $^{13}\text{C}_{12}$ -labelled standards were obtained from Wellington Laboratories.

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## Results and Discussion

All TEQs are reported in moisture contents of 12%. TEQs were calculated using WHO-TEF for PCDD/Fs and PCBs for humans. Non-detects were included by adding the upper-bound concentration regulated by the new EU guidelines. TEQ values determined for 22 feedmaterials on plant origin from the year 2002 are presented in Table 1.

Our analyses was done according to harmonised quality guidelines published earlier by several experts (3); e.g. the determination limit of the method was in all cases below 1/5 of the regulated level (0.15 ng WHO-PCDD/F-TEQ/kg).

The values for the moisture content presented in Table 1 shows that all values have been around 12% moisture, with a mean value of 11.2 % (range from 5.1-14.8 %).

None of the feed materials here tested were higher than the action level (0.50 ng WHO-PCDD/F-TEQ/kg) or the maximum content regulated by the new EU-guidelines (0.75 ng WHO-PCDD/F-TEQ/kg) (4).

In the present study the mean value of the PCDD/F-TEQ was 0,15 ng WHO-PCDD/F-TEQ/kg (range: 0,05-0,36 ng WHO-PCDD/F-TEQ/kg). In comparison to already published data our study demonstrates that most of the here analysed samples are below the typical background level between 0.1-0,4 ng WHO-PCDD/F-TEQ/kg (1, 5, 6).

The earlier published SCAN review of the EU (1) reported about to be expected concentrations for cereals and seeds between 0.01 (low) – 0.1 (mean) - 0.4 (high) ng WHO-TEQ/kg dry matter and for by-products of plant origin between 0.02 (low) – 0.1 (mean) - 0.7 (high) ng WHO-TEQ/kg dry matter.

The highest concentrations obtained in our study came from soya and rape shot, citrus pellets and pea, but have been still in the background level. In these cases the values are still significantly lower than the from the EU proposed action levels (0.5 ng WHO-TEQ/kg dry matter) or the maximum amounts (0.75 ng WHO-TEQ/kg dry matter).

Until today only a few data are published for coplanar PCBs in feedingstuffs of plant origin. The additional input of dioxin-like PCBs in the sum of WHO-TEQ in our study would varying between 8-80%, with a mean value of 31% (see Table 1).

These values are comparable to the values for cereals published earlier (in case of England between 13-50%) (7).

The values of the presented study fit well into the frame of literature, showing that without any potential source these feed materials based on plant original usually are below the new EU-guidelines.

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**Table 1.** WHO-TEQ values of PCDD/Fs and dioxin-like PCBs of 22 feed materials based on plant original <sup>a, b)</sup>

Feed material	WHO-TEQ [ng/kg]				
	Moisture content [%]	PCBs	PCDD/Fs	Sum	% PCB on Sum WHO-TEQ
Sunflower seeds	8.6	0.05	0.16	0.21	25
Soybean	9.8	0.08	0.08	0.15	50
Soya husk	9.8	0.21	0.05	0.26	80
Palm oil pellets	6.2	0.05	0.08	0.12	38
Malt sprout	5.1	0.11	0.10	0.20	53
Luzerne green flower	10.4	0.13	0.20	0.33	39
Weizarin	9.6	0.04	0.05	0.09	43
Palm oil pellets	12.5	0.03	0.08	0.11	27
Dried seeds	9.3	0.09	0.14	0.22	39
Soya shot	12.3	0.03	0.36	0.39	8
Rape shot	12	0.04	0.34	0.38	11
Sunflower shot	12.2	0.04	0.11	0.14	25
Flax shot	10.5	0.03	0.04	0.06	44
Citrus pellets	9.2	0.03	0.09	0.11	22
Soya shot	13.2	0.04	0.06	0.10	39
Corn gluten	11.1	0.02	0.18	0.20	10
Green flower	10.1	0.06	0.23	0.30	21
Citrus pellets	8.0	0.10	0.30	0.40	25
Soya shot	11	0.02	0.13	0.15	14
Soya husk	12	0.06	0.16	0.23	28
Pea	14.2	0.05	0.23	0.29	19
Sunflower shot	11.8	0.02	0.11	0.13	15
Mean value	10.4	0.06	0.15	0.21	31

<sup>a)</sup> WHO-TEQ; based on 12% moisture

<sup>b)</sup> Upper-bound concentrations calculated assuming that all values of the different congeners less than the limit of determination are equal to the limit of determination

