THE CONTENT OF POLYCHLORINATED-P-DIOXINS AND -FURANS IN BATCHES OF RAW MATERIAL FOR FEEDINGSTUFFS ANALYSED DURING A ONE YEAR PERIOD AT VTT PROCESSES

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[1]VTT PROCESSES

Introduction

The aim of this study was to monitor the levels of polychlorinated-p-dioxins (PCDD) and –furans (PCDF) in raw materials for animal feed production. The samples presented in this study are base raw materials for animal feed production. The samples from A to Q where sampled during 17.4.2003-5.2.2004. All results are given as "upper bound limits". The levels of PCDD&PCDF are normally very low. The results are at least 0,34 pg WHO-TEQ /g fresh weight due to the achieved detection limit of the method[1], which in this case was 0,1 pg /g fresh weight.

Methods and Materials

Sample preparation included grinding the samples. The samples were each mixed with twice amount of hydromatrix and then split into 2 equal specimens for ASE-extraction with hexane[2]. The internal standards were added to the extraction cells (10 µl ^{13}C-labelled PCDD/PCDF standard solution (16 out of 17 possible congeners) to each cell, total of 20 µl. The two extracts were combined, dried with sodium sulphate and evaporated. The certified standards (CRM-614) used were: Solutions S 0-S 5 for calculation of response factors and testing the mass spectrometer linearity, internal standard solutions S 6, S 7 for quantitation and solution S 8 for recovery calculations of added ^{13}C-labeled standards.
The clean up consisted of basic silica/silica (so called fish column), AX-21 activated carbon on glass fibre[3] followed by basic alumina (ICN, Super grade I).

Gas chromatographic-high resolution mass spectrometry-selected ion monitoring (GC-HRMS-SIM) analyses were performed on a JEOL SX-102 double focusing mass spectrometer equipped with a HP-5890 GC Series II. The ionization current was 600 µA, ionization voltage 40 eV. The resolution used was 9000-10000. The capillary columns used were a Supelco EQUITY 5 (60 m, 0.25 mm id, 0.25 µm phase thickness) and a DB-5ms (60 m, 0.25 mm id, 0.25 µm phase thickness). The gas chromatographic conditions used were, injection temperature 290 ° C, splitless injection 1.0 minute, transfer line temperature 290 ° C and source temperature 250 ° C. Helium (purity grade ≥ 4.6) and an injection pressure about 30 psi (at 180 °C oven temperature) was used. The oven temperature program used was, 180 °C for 2 min-4 ° C/min-220 °C for 12 min-5 °C/min-235 ° C for 7 min- 5 ° C/min-330 ° C for 2 min. Total runtime was 55.0 minutes.

Results and Discussion

The samples presented in the table 1 are giving an overview of the dioxin and furan content in the raw material for feed samples in different batches during a 1 year period. The fat oil originating from fish species have a greater contribution to the final WHO-TEQ value of the final product than those raw materials from plant origin. All samples were within the regulations stated by the Commission Directive 2002/70/EU[4].

The dioxin and furan content in the fish oil is rather close to the limit value of 6 ng WHO-TEQ/kg stipulated in Regulation No. 80/03 given by the Finnish Ministry of Agriculture and Forestry 15.1.2004 (Commission Directives 2002/32/EU, 2003/57/EU and 2003/100/EU). The results are presented in the Table 1, samples B and L.

The dioxin and furan content in the samples of plant origin are mostly correlating to the upper bound limit values given by the detection limit values.

All analysed raw material batches were below the values stipulated in the EU Commission Directives in force during the time period.

There is a clear need to monitor the dioxin and furan content in especially fish oil. The new regulation will be first checked in relation to dioxins and furans 31.12.2004 and later the dioxin like PCBs will be checked again 31.12.2006.

Table 1. The content of PCDD&PCDF given as WHO-TEQ equivalents, from raw materials in animal feed production.

"Upper bound limit"

Dioxins and furans	Sample A bl. sub. pg/g fw	Sample B bl. sub. pg/g fat	Sample C bl. sub. pg/g fw	Sample D bl. sub. pg/g fw	Sample E bl. sub. pg/g fw	Sample F bl. sub. pg/g fw
2,3,7,8-TCDD	0.1	0.1	0.1	0.1	0.1	0.1
1,2,3,7,8-PeCDD	0.1	0.95	0.1	0.1	0.1	0.1
1,2,3,4,7,8-HxCDD	0.01	0.01	0.01	0.01	0.01	0.01
1,2,3,6,7,8-HxCDD	0.01	0.052	0.01	0.01	0.01	0.036
1,2,3,7,8,9-HxCDD	0.01	0.030	0.01	0.01	0.01	0.01
1,2,3,4,6,7,8-HpCDD	0.0016	0.00	0.001	0.001	0.001	0.0043
1,2,3,4,6,7,8,9-OCDD	0.000074	0.00001	0.00001	0.00001	0.00002	0.000042
2,3,7,8-TCDF	0.11	0.97	0.01	0.14	0.14	0.26
1,2,3,7,8-PeCDF	0.0090	0.082	0.005	0.013	0.0078	0.026
2,3,4,7,8-PeCDF	0.13	2.7	0.05	0.22	0.096	0.072
1,2,3,4,7,8-HxCDF	0.01	0.050	0.01	0.01	0.01	0.020
1,2,3,6,7,8-HxCDF	0.01	0.058	0.01	0.011	0.01	0.011
2,3,4,6,7,8-HxCDF	0.01	0.066	0.01	0.01	0.01	0.031
1,2,3,7,8,9-HxCDF	0.01	0.01	0.01	0.01	0.01	0.01
1,2,3,4,6,7,8-HpCDF	0.0010	0.001	0.001	0.001	0.0012	0.0026
1,2,3,4,7,8,9-HpCDF	0.001	0.001	0.001	0.001	0.001	0.001
1,2,3,4,6,7,8,9-OCDF	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
Sum of PCDD&PCDF	0.52	5.1	0.34	0.65	0.52	0.70
Fat content, %	9.2	100	0.5	7.1	10.2	6.3
Origin	animal	fish oil	plant	animal	animal	animal

bl. sub. = blank reduction
fw =fresh weight
dw = dry weight
nd = not determined
Animal Origin normally related to sea animal products

Table 1, continues.
"Upper bound limit"

Dioxins and furans	Sample G bl. sub. pg/g fw	Sample H bl. sub. pg/g fw	Sample I bl. sub. pg/g fw	Sample J bl. sub. pg/g fw	Sample K bl. sub. pg/g fw	Sample L bl. sub. pg/g fat
2,3,7,8-TCDD	0.1	0.1	0.1	0.1	0.1	0.1
1,2,3,7,8-PeCDD	0.1	0.19	0.1	0.1	0.1	0.81
1,2,3,4,7,8-HxCDD	0.01	0.01	0.01	0.01	0.01	0.01
1,2,3,6,7,8-HxCDD	0.01	0.01	0.01	0.01	0.01	0.059
1,2,3,7,8,9-HxCDD	0.01	0.01	0.01	0.01	0.01	0.01
1,2,3,4,6,7,8-HpCDD	0.0043	0.0021	0.003	0.0044	0.0029	0.011
1,2,3,4,6,7,8,9-OCDD	0.00011	0.000092	0.00021	0.00013	0.000037	0.00011
2,3,7,8-TCDF	0.01	0.31	0.049	0.087	0.01	0.53
1,2,3,7,8-PeCDF	0.005	0.025	0.014	0.0061	0.005	0.054
2,3,4,7,8-PeCDF	0.05	0.35	0.050	0.25	0.05	1.4
1,2,3,4,7,8-HxCDF	0.01	0.01	0.01	0.01	0.01	0.04
1,2,3,6,7,8-HxCDF	0.01	0.01	0.01	0.01	0.01	0.033
2,3,4,6,7,8-HxCDF	0.01	0.01	0.01	0.01	0.01	0.040
1,2,3,7,8,9-HxCDF	0.01	0.01	0.01	0.01	0.01	0.01
1,2,3,4,6,7,8-HpCDF	0.0029	0.0034	0.001	0.00096	0.00058	0.001
1,2,3,4,7,8,9-HpCDF	0.001	0.001	0.001	0.001	0.001	0.001
1,2,3,4,6,7,8,9-OCDF	0.000062	0.000086	0.000065	0.00001	0.0000083	0.00001
Sum of PCDD& PCDF	0.34	1.1	0.39	0.62	0.34	3.1
Fat content, %	0.5	10.6	13.5	0.5	0.5	100
Origin	plant	animal	plant	plant	plant	fish oil

bl. sub. = blank reduction
fw =fresh weight
dw = dry weight
nd = not determined
Animal Origin normally related to sea animal products

Table 1, continues.
"Upper bound limit"

Dioxins and furans	Sample M bl. sub. pg/g fw	Sample N bl. sub. pg/g fw	Sample O bl. sub. pg/g fw	Sample P bl. sub. pg/g fw	Sample Q bl. sub. pg/g fw	Sample R bl. sub. pg/g ka
2,3,7,8-TCDD	0.1	0.1	0.1	0.1	0.1	0.01
1,2,3,7,8-PeCDD	0.1	0.1	0.1	0.1	0.1	0.01
1,2,3,4,7,8-HxCDD	0.01	0.01	0.01	0.01	0.01	0.001
1,2,3,6,7,8-HxCDD	0.01	0.01	0.01	0.01	0.01	0.001
1,2,3,7,8,9-HxCDD	0.01	0.010	0.010	0.010	0.01	0.001
1,2,3,4,6,7,8-HpCDD	0.0025	0.0010	0.0010	0.0040	0.0094	0.00042
1,2,3,4,6,7,8,9-OCDD	0.000045	0.00001	0.00030	0.00012	0.000013	0.000049
2,3,7,8-TCDF	0.099	0.01	0.045	0.010	0.15	0.001
1,2,3,7,8-PeCDF	0.011	0.005	0.005	0.005	0.005	0.0005
2,3,4,7,8-PeCDF	0.05	0.05	0.10	0.05	0.05	0.005
1,2,3,4,7,8-HxCDF	0.01	0.010	0.010	0.010	0.01	0.001
1,2,3,6,7,8-HxCDF	0.01	0.01	0.01	0.01	0.01	0.001
2,3,4,6,7,8-HxCDF	0.01	0.01	0.01	0.01	0.01	0.001
1,2,3,7,8,9-HxCDF	0.01	0.01	0.01	0.01	0.01	0.001
1,2,3,4,6,7,8-HpCDF	0.0019	0.0010	0.00091	0.0021	0.0015	0.0001
1,2,3,4,7,8,9-HpCDF	0.001	0.001	0.001	0.001	0.001	0.0001
1,2,3,4,6,7,8,9-OCDF	0.00001	0.00001	0.000024	0.000048	0.000016	0.000014
Sum of PCDD&PCDF	0.44	0.34	0.43	0.34	0.49	0.034
Fat content, %	9.2	0.5	9.7	0.5	8.6	nd
Origin	animal	plant	animal	plant	animal	limestone

bl. sub. = blank reduction
fw =fresh weight
dw = dry weight
nd = not determined
Animal Origin normally related to sea animal products

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