OCCURANCE OF PCDD/F AND PCB DURING THERMAL FEED PROCESSING IN ROMANIA

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polychlorinated biphenyls (PCB) are ubiquitous environmental contaminants that were internationally recognized as persistent organic pollutants (POPs) and were included in the Stockholm Convention.

PCDDs and PCDFs are by-products of several processes such as waste incineration, metal production, bleaching of pulp using chlorine, synthesis of halogenated chemicals (e.g. pentachlorophenol), but are also known to be formed during natural processes (FERRARIO et al., 2000), natural combustions (e.g. forest fires, volcanic eruptions). PCBs are synthetic chlorinated compounds that were used in dye solvents, plasticizers, lubricants, cooling liquids for transformers, dielectric fluids for capacitors, etc., their manufacturing being banned in 1970s.

The major route by which humans are exposed to POPs is through ingestion of contaminated food, (~ 90% of the cases). The food producing animals are exposed to PCDD/Fs and PCBs through ingestion of contaminated feed (FERRARIO, 1996; PARZEFALL, 2002). PCDD/Fs and PCBs caused major problems in feed and food products during the last decades. In 1997, in US was discovered that ball clay used as anti-caking agent was the source of contamination of poultry and catfish feed. A similar contamination occurred in Europe, in 1999, when kaolinitic clay was used for the production of mineral feed (SCAN, 2000). In 2001, the use of contaminated choline chloride, originating from Spain, resulted in elevated levels of PCDD/F and PCB in certain premixtures (RIVERA et al., 2001). European Union issued in 2003 a rapid alert reporting the presence of elevated PCDD/Fs in dried German bakery waste used in animal feed, the source being the use of waste wood for the drying of bakery waste (HOOGENBOOM et al., 2004). The feed contamination incidences mentioned above demonstrate that contamination of feeding stuffs by PCDD/F and PCBs may occur at different levels of the feed chain and have very different origins.

The HRGC/HRMS method is considered the „gold" method for the analysis of dioxins and PCBs from different matrixes because it has different advantages (ABAD et al., 2006; SROGI, 2007; BIANCO et al., 2008): high sensitivity and low limits of detection; high selectivity; high specificity; high accuracy and precision.

The aim of the present study was to investigate feed processing, focused on heat treatment procedures and their impact on the level of dioxins (PCDD/F congeners) and PCBs (indicator PCBs and dioxin-like PCBs).

Materials and methods

In order to investigate the formation of dioxins and PCBs during heat treatment processes, samples - consisted of compound feed - were selected from three different compound feed production units (F1, F2 and F6), two of them located in the Central-North-West of Romania and one in the East part of the country.

For units F1, F2 and F6 the process that was investigated was the granulation (pelleting) process, used to obtain the final feed product (pellets). During the granulation process the grounded and mixed feed ingredients are treated with hot steam (at an average temperature of 70° - 80°C) which facilitates the passage through the molds and increases the hardness of the pellets. The equipment that is used in the granulation process is made of special steel and the technological steam is produced by each unit. In order to establish if this technological process influences the levels of dioxins and PCBs, samples were collected before (*input*) and after the granulation (*output*). Compound feed samples were selected for three type of animals: cattle, pigs and poultry.

The experimental design for the present study is shown in figure 1, a total of 28 compound feed samples being collected. For each sample the water content and the level of contaminant (dioxins and PCBs) were analyzed. By determining the water content we were able to report the results for the measured level of contaminat in pg/g feed or product with a moisture of 12%, as expressed in the Commission Regulation (EU) No. 574/2011, which established the maximum levels for dioxins and PCBs in feed.

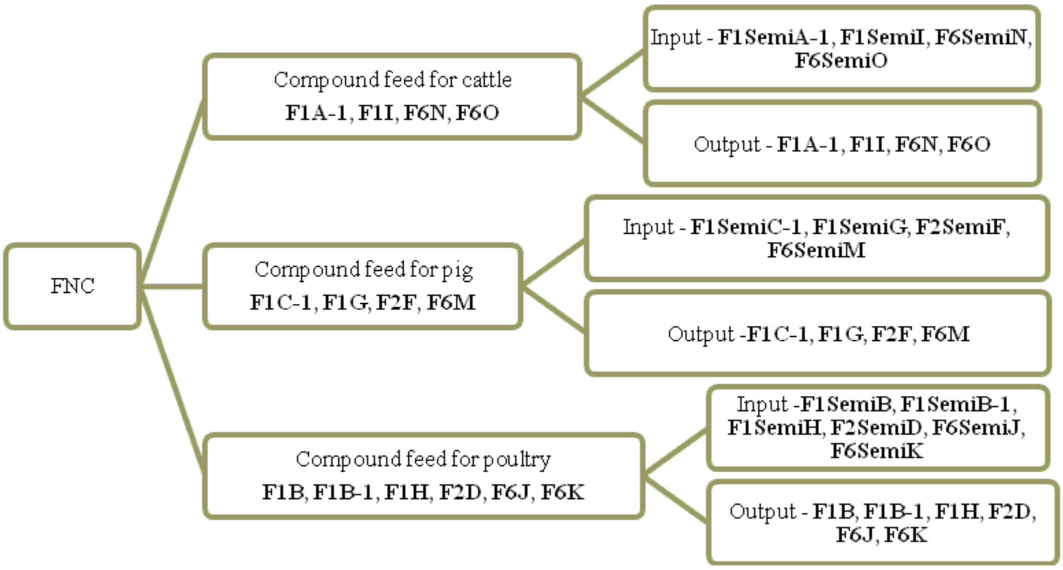

Fig. 1. Experimental design for feed samples

The separation, identification and quantification of PCDD/F and PCBs congeners was performed by high resolution gas chromatography coupled with high resolution mass spectrometry - HRGC/HRMS (CHELEMAN, 2011).

Results and discussion

Variation of PCDD/F and PCB concentration in compound feed before and after the pelleting process

Compound feed belong to the processed feed group and are complex and equilibrated mixtures of raw materials of plant, animal and mineral origin, dosed so it constitute rations with a complete value or to complete the basic rations in order to satisfy the energetic and nutrition requirements of animals (MIRCEA *et al.*, 2006).

The compound feed production consists of two important steps: first is the reception and preparation of ingredients (raw materials and other ingredients) and second the actual compound feed production. In this research it was studied the pelleting process from the second step in the feed production.

Mean concentrations, standard deviation and ranges for the analyzed PCDD/F congeners in the compound feed samples are summarized in Table 1.

Variations of PCDD/F levels in compound feed samples were also observed during the pelleting process. Only in the case of four PCDD/F congeners the concentrations in the output samples increased compared to the input samples and the congener 1,2,3,7,8-PeCDD was identified only in one input sample, but was not identified in the output samples. TCDD, the most toxic congener from the PCDD group, was identified only in one sample collected from unit F6 and the concentration increased from 0.04 pg/g feed to 0.10 pg/g feed, but these values were under the maximum accepted limits. The levels of TCDF congeners also increased in the output samples compared to the input, but without exceeding the maximum limits. In the samples from units F1 and F2, the following congeners were not identified: 2,3,7,8-TCDD; 1,2,3,7,8-PeCDD; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDD; 1,2,3,7,8,9-HxCDD which is in concordance with the results obtained by GURUGE *et al.* (2005) on the same type of samples.

After calculating the TEQ values we can notice that the levels from the input samples, which were ground and mixed feed ingredients, decreased to 0.04 pg WHO-PCDD/F-TEQ/g feed (with 12% moisture) in the output samples which were the pellets of compound feed, same results being reported by SCHWIND *et al.* (2010) for compound feed samples.

Table 2 presents the PCBs levels in compound feed samples before and after the granulation process. The mean concentration for two indicator PCBs (PCB 28 and PCB 52) increased in the output samples compared with the input samples, while for the other four compounds the levels decreased. From the group of dioxin-like PCBs, PCB 123 was not identified in any of the analyzed samples, while PCB 81 was only identied in two output samples collected from units F2 and F6. Higher concentrations after the granulation process were observed also in PCB 77 and PCB 126. The TEQ values calculated for the dioxin-like PCBs were very low, but comparing the input samples with the output samples, the feed pellets presented higher concentrations in dioxin-like PCBs.

Table 1

PCDD/F concentration in compound feed before and after granulation processes (pg/g feed with 12% moisture)

Comgener	***Input (n = 14)***			***Output (n = 14)***		
	Mean	**SD**	**Min-max**	**Mean**	**SD**	**Min-Max**
2,3,7,8-TCDD	0.04	-	n.d. – 0.04	0.10	-	n.d. – 0.10
1,2,3,7,8-PeCDD	0.20	-	n.d. – 0.20	n.d.	-	-
1,2,3,4,7,8-HxCDD	0.10	0.06	0.06 – 0.15	0.08	-	n.d. – 0.08
1,2,3,6,7,8-HxCDD	0.16	0.19	0.03 – 0.30	0.05	-	n.d. – 0.05
1,2,3,7,8,9-HxCDD	0.35	-	n.d. – 0.35	0.06	-	n.d. – 0.06
1,2,3,4,6,7,8-HpCDD	0.33	0.75	0.04 – 2.80	0.13	0.12	0.05 – 0.51
1,2,3,4,6,7,8,9-OCDD	1.80	3.87	0.07 – 12.90	1.39	3.04	0.06 – 9.90
2,3,7,8-TCDF	0.07	0.01	0.03 – 0.10	0.24	0.33	0.02 – 0.62
1,2,3,7,8-PeCDF	0.05	0.03	0.03 – 0.12	0.11	0.15	0.03 – 0.41
2,3,4,7,8-PeCDF	0.07	0.05	0.04 – 0.13	0.11	0.19	0.02 – 0.50
1,2,3,4,7,8-HxCDF	0.07	0.05	0.02 – 0.18	0.07	0.07	0.01 – 0.26
1,2,3,6,7,8-HxCDF	0.07	0.07	0.03 – 0.25	0.07	0.10	0.02 – 0.32
1,2,3,7,8,9-HxCDF	0.07	0.06	0.02 – 0.11	0.03	0.01	0.02 – 0.05
2,3,4,6,7,8-HxCDF	0.09	0.08	0.04 – 0.34	0.07	0.08	0.03 – 0.34
1,2,3,4,6,7,8-HpCDF	0.17	0.35	0.02 -1.30	0.10	0.14	0.03 – 0.50
1,2,3,4,7,8,9-HpCDF	0.07	0.08	0.02 – 0.25	0.03	0.01	0.02 – 0.05
1,2,3,4,6,7,8,9-OCDF	0.21	0.41	0.04 – 1.50	0.07	0.03	0.04 – 0.16
WHO-TEQ (PCDD/F)[1)]	**0.057**	**0.12**	**0.0 – 0.48**	**0.04**	**0.14**	**0.0 – 0.55**
Maximum limit (PCDD/F)[2)]	**0.75**					
Action threshold (PCDD/F)[3)]	**0.5**					

n.d. – not detected; SD – standard deviation

[1)] Values measured in the analyzed samples (pg WHO-PCDD/F-TEQ/g feed with 12% moisture).

[2)] Maximum content, according Commission Regulation (EU) No. 574/2011, expressed as pg WHO-PCDD/F-TEQ/g relative to a feedingstuff with a moisture content of 12%.

[3)] Action threshold, according Commission Regulation (EU) No. 574/2011, expressed as pg WHO-PCDD/F-TEQ/g relative to a feedingstuff with a moisture content of 12%.

Table 2

PCBs concentration in compound feed before and after the granulation processes (pg/g feed with 12% moisture)

Comgener	***Before /Input (n = 14)***			***After / Output (n = 14)***		
	Mean	**SD**	**Min-max**	**Mean**	**SD**	**Min-Max**
PCB 28	92.24	80.48	14.90 – 268.0	138.13	142.09	16.0 – 515.0
PCB 52	84.16	61.03	23.60 – 199.0	93.25	42.83	45.25 – 181.0
PCB 101	15.77	9.65	7.10 – 42.30	14.98	4.93	7.50 – 24.40
PCB 138	12.88	12.13	5.20 – 50.3	9.82	3.76	5.30 – 17.40
PCB 153	16.03	15.89	6.40 – 67.60	12.57	5.11	7.10 – 22.35
PCB 180	10.20	13.60	3.60 -55.8	7.55	3.13	4.10 – 14.05
Sum of indicator PCB	**225.94**	**96.65**	**79.4 – 363.10**	**244.87**	**86.01**	**126.5 – 688.30**
PCB 77	2.14	1.77	0.55 – 7.40	2.44	1.61	0.72 – 5.80
PCB 81	n.d.	-	-	0.32	0.12	0.24 – 0.41
PCB 105	3.37	1.98	1.60 – 9.20	3.18	1.25	1.60 – 6.45
PCB 114	0.56	0.42	0.23 – 1.80	0.48	0.18	0.25 – 0.88

PCB 118	7.03	4.28	3.40 – 19.9	6.40	2.55	3.40 – 13.0
PCB 123	n.d.	-	-	n.d.	-	-
PCB 126	0.12	0.05	0.05 – 0.18	0.17	0.21	0.06 – 0.55
PCB 156	0.98	0.88	0.42 – 3.7	0.84	0.34	0.53 – 1.60
PCB 157	0.50	0.49	0.18 – 2.0	0.36	0.12	0.19 – 0.57
PCB 167	0.55	0.34	0.23 – 1.5	0.45	0.14	0.27 – 0.76
PCB 169	0.13	0.03	0.11 – 0.16	0.13	0.05	0.08 – 0.21
PCB 189	0.20	0.19	0.07 – 0.67	0.16	0.07	0.08 – 0.27
WHO-TEQ (dl-PCB)[1)]	**0.004**	**0.007**	**n.d. – 0.02**	**0.007**	**0.017**	**n.d. – 0.06**
WHO-TEQ (PCDD/F+dl-PCB)[2)]	**0.06**			**0.05**		
Maximum limit (PCDD/F + dl-PCB)[3)]	**1.5**					
Action threshold (dl-PCB)[4)]	**0.5**					

n.d. – not detected; SD – standard deviation
[1)] TEQ values of the measured samples for 12 dioxin-like PCBs.
[2)] Sum of the TEQ values of the PCDD/F and dl-PCBs measured in the samples.
[3)] Maximum content for the sum of PCDD/F and dioxin-like PCBs, according to Reg. (EC) No. 574/2011, expresed in pg WHO-TEQ/g relative to a feedingstuff with a moisture content of 12%.
[4)] Action threshold for dioxin-like PCBs, according to Commission Regulation (EU) No. 574/2011, expressed as pg WHO-TEQ/g relative to a feedingstuff with a moisture content of 12%.

Conclusions

Regarding the granulation process applied in the production of compound feed, in 4 out of 17 analyzed PCDD/F congeners concentration increased in the granulated samples (feed pellets), same situation for the PCB congeners were in 4 out of 18 analyzed compounds was observed an increase in concentrations. From a toxicological point of view none of the samples raise any problems for the samples consist of compound feed, because the TEQ values (PCDD/F + dioxin-like PCBs) were under the accepted maximum limits: 1.5 pg-TEQ/g feed. So the mean TEQ values (PCDD/F + dioxin-like PCB) for each category of compound feed were: 0.09 pg WHO-TEQ/g feed for cattle, for poultry feed was 0.07 pg WHO-TEQ/g feed and for pigs feed 0.03 pg WHO-TEQ/g feed. These results are comparable with the ones reported by LORBER *et al.* in 2004. Refferences

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