THREE CASE STUDIES FROM THE DANISH CONTROL PROGRAM FOR DIOXINS AND PCB IN FOOD AND FEED.

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Introduction

EU limits for dioxins in food and feed came into force 1st of July 2002. Commission's recommendation concerning the reduction of levels of dioxins and PCB in food also provides action levels at a level equivalent to 75% of ML. When the ML or action level is exceeded, the authorities recommend to undertake studies to identify the source of contamination and to take measures to reduce or eliminate the source of contamination. In Denmark the necessary follow-up effort involves the cooperation of several authorities: The Danish Veterinary and Food Administration (DVFA) takes action on food items, The Danish Plant Directorate (DPD) on feed items, The Danish Environmental Protection Agency (DEPA) about environmental problems and the National Food Institute (NFI) as NRL for food and feed. This paper describes the tasks of those authorities with three cases from the Danish control program 2009.

Experimentals

PowerPrep from Fluid Management System and **MAT95** from Thermo are used for sample cleanup and detection of dioxins and PCB in fat from pig, egg and beef. Soil samples were extracted with toluene and cleaned up with Dioxin Prep System (Supelco); analysis was performed with GC-HRMS (DFS, Thermo Scientific).

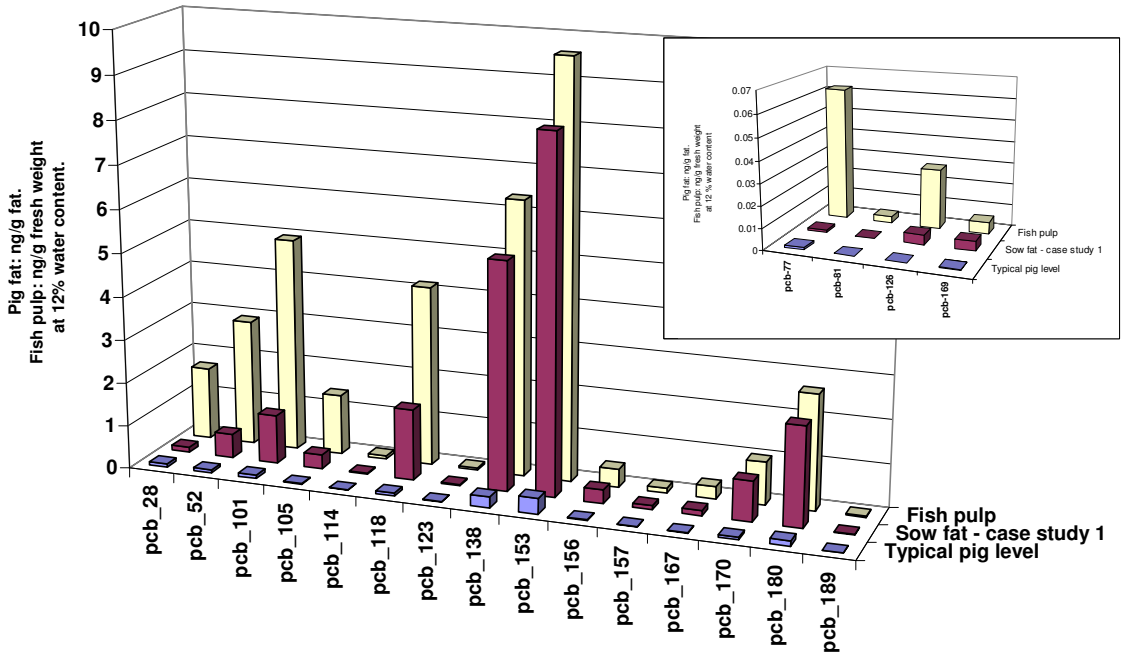
Results and Discussion

Case study 1. Sow fat exceeding the action limit for PCB.

During the Danish 2009 control program on pig fat (100 samples per year) one sample from a sow was found with levels of PCB exceeding the action level, but not significantly the ML. The levels normally found in Danish pig fat are extremely low for both dioxins and PCB (see table 1)[1]. Further investigations by DVFA and DPD on the farm, which was a large sow herd with more than 1000 sows, brought the attention to the feed used for pigs. The farmer said he uses grain mixed with 10% fish pulp on a daily base. The content of dioxins and PCB in the fish pulp sample did not exceed the ML or action level. However the mono- and di-ortho PCB congener patterns for the sow sample and the fish pulp, show good correlation which indicates that the feed might be the source of the PCB contamination (see figure 1). Only the congener pattern for the non-ortho PCB does not correlate in the two samples (see insert in figure 1). The dominant PCB-77 is completely missing in the pork fat, where PCB 126 and 169 are the dominant congeners. The fish pulp is stored in a large silo, which is filled from the top at regular intervals and the contents of PCB may have changed through mixing of fresh fish pulp during the three months period that have elapsed since the sow was slaughtered. Further, the portion of fish pulp could have been larger than 10% on a daily base. DPD has contact to both farmer and the company producing the fish pulp to prevent further contaminations.

Table 1	Sow fat	Pig fat (normal level)[1]	ML[3] Pig fat	Fish pulp	ML[4] Fish pulp
	pg/g fat	pg/g fat	pg/g fat	ng/kg (12% water)	ng/kg (12% water)
WHO-PCDD/F-TEQ	0.35	0.19	1.0	1.4	2.25
WHO-PCB-TEQ	0.91	0.04	0.5	3.7	7.0
WHO-PCDD/F-PCB-TEQ	1.27	0.23	1.5	5.1	11.0

Figure 1. Congener patterns for PCB in pig fat and fish pulp - Case study 1



Case study 2. Beef fat exceeding the ML for the sum of dioxin and PCB.

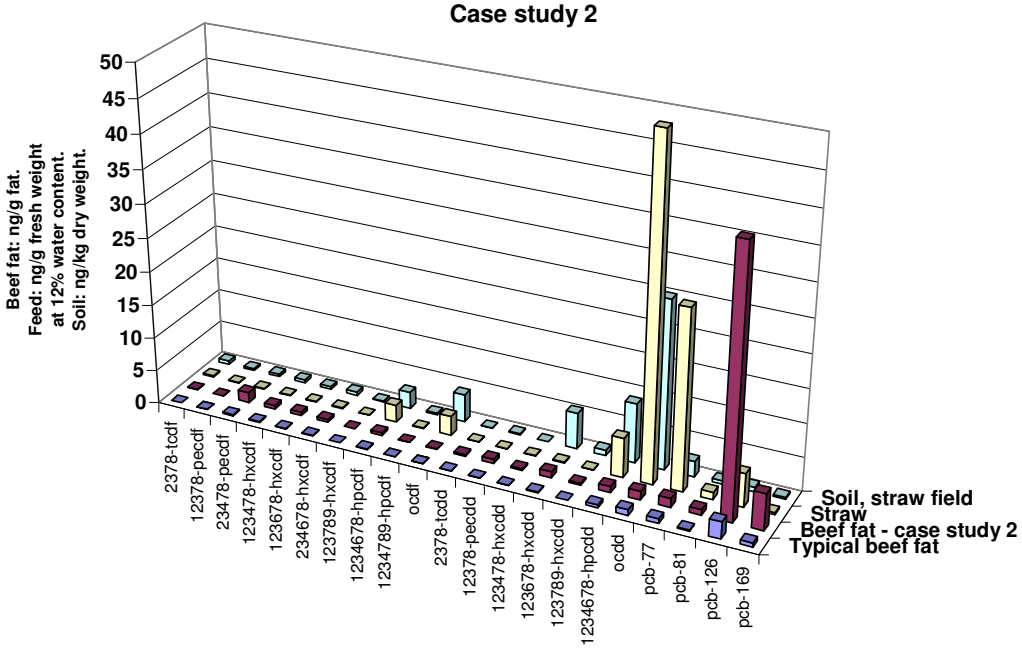
A bovine fat sample taken during the Danish 2009 control program (100 samples of bovine fat samples per year) exceeded the ML for the sum of dioxins and PCB (see table 2). Two local officers from DVFA and DPD visited the farm to look for possible sources of dioxins and PCB in the herd. It was a small biological farm with only a few animals, but recently they had slaughtered a bull and a pig and they still had some roasts (a loin roast and a sirloin) lying in the freezer, which could be used as samples. Further, 6 feed samples were taken (grass, straw, soy meal, beets, barley and mineral compound feed).

Table 2	Beef fat	Beef fat (normal level)[1]	ML[3] Beef fat	Straw	ML[4] Straw
	pg/g fat	pg/g fat	pg/g fat	ng/kg (12% water)	ng/kg (12% water)
WHO-PCDD/F-TEQ	2.0	0.23	3.0	0.35	0.75
WHO-PCB-TEQ	4.6	0.31	1.0	0.63	0.35
WHO-PCDD/F-PCB-TEQ	6.6	0.54	4.5	0.98	1.25

The fat from the bull had exactly the same congener composition as the original sample, but in somewhat lower concentration (only the PCB-TEQ level exceeded the action level), whereas for the pig fat it was only the mono- and di-ortho PCB congener pattern that were consistent with the original sample. All feed samples were compliant except the straw, which had PCB content exceeding the action lever for PCB (see table 2). The DEPA were contacted to look for possible environmental problems at the farm. No obvious problems were observed. They took some soil samples from different places on the farm. The same dioxin congener pattern is observed in the straw and the soil where the straw was grown (see figure 2), but no correlation could be observed for the PCB. In the beef fat, the PCB

126 is the dominant non-ortho PCB, which is almost always the case for beef fat. In the straw PCB 77 is the dominant congener, which indicates that the straw is not an important source for dioxins and PCB in the beef. The investigations on the farm haven't finished yet and further studies of the soil carried out by DEPA may lead to clearer indications of the source of the contamination.

Figure 2. Congener patterns for dioxin and non-ortho PCB for beef, feed and soil - Case study 2



Case study 3. Egg exceeding the action limit for dioxin.

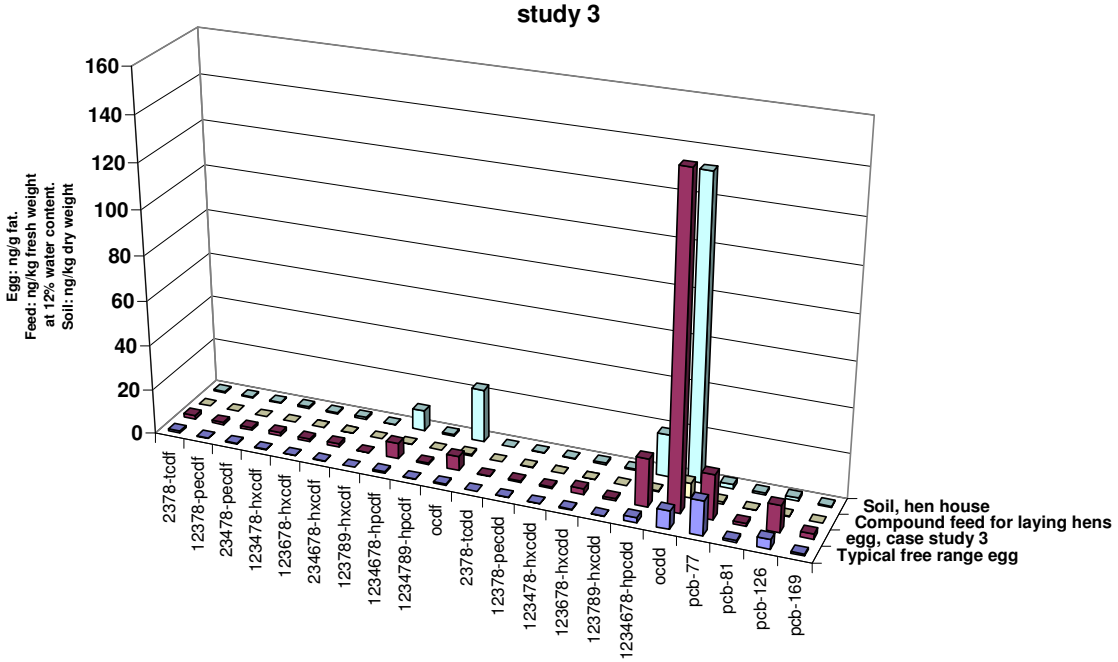
The Danish control program for eggs contains 20 samples per year. One of these had a very special congener pattern with a very high OCDD content (140 pg/g of fat) and increased levels of most other dioxins and furans, especially the higher chlorinated congeners. The action level was not significantly exceeded (see table 3), but because of the special congener pattern it was agreed to follow up and make a visit to the farm. During this visit the following samples were taken for analysis: 1 egg sample (12 yolks), 3 feed samples (wheat, oats and compound feed for laying hen) and 5 soil samples from the chicken cage and surrounding areas.

Table 3	Egg yolk	Egg yolk (normal level)[1]	ML[3] egg	Soil, hen house
	pg/g fat	pg/g fat	pg/g fat	ng/kg (dry weight)
WHO-PCDD/F-TEQ	2.7	0.7	3.0	1.2
WHO-PCB-TEQ	1.4	0.6	2.0	0.2
WHO-PCDD/F-PCB-TEQ	4.2	1.3	6.0	1.4

The feed samples showed no particular content of dioxins and PCB, except for a minor contribution of OCDD in the compound feed (see figure 3). All soil samples showed the same congener pattern of dioxins and furans with a dominant OCDD peak and minor contributions from the HpCDD/F and OCDF, but the content was clearly higher

within the chicken cage compared to the surrounding fields and the congener pattern matched nicely with the contaminated egg. This indicates that the contamination of the eggs with the higher chlorinated congeners is due to the hen pecking in the soil near the hen house. The PCB pattern for soil and egg seems not to match each other. This is consistent with other studies, where only the profile for dioxins and furans found in eggs matched the profile of the contaminated soil where the hens were pecking[2].

Figure 3. Congener patterns for dioxin and non-ortho PCB in egg, feed and soil - case study 3



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References:

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