PCDD/F IN KAOLINITIC CLAYS AND ITS RELEVANCE FOR FEEDINGSTUFF, FOOD AND COSMETICS

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Introduction

As result of an intense program to control feedstuff for its dioxin content during the Belgium crisis, the Austrian Ministry of Agriculture reported in June 1999 the finding of a new dioxin source: Kaolinitic clay was found with a high dioxin contamination (174 pg I-TEQ/g) and an unknown pattern (raising content from TCDD to OCDD; no PCDF detectable). It turned out that the clay came from a region in Germany with volcanic activities in its geological history (region of Westerwald in the German state Rheinland-Pfalz). After intense studies it is assumed that this clay contains „naturally" produced PCDD (1). A very similar contamination was found in „ball clay" from the Mississippi basin which led to a contamination of feed for fish and poultry (2, 3, 4) and in sediments from coastal areas in Australia (5). All these findings support the discussion of a natural formation (6).

Kaolinitic clays are used as additives to feedingstuff and belong to the group of „binders, anti-caking agents and coagulants" according to EU regulations. As it became clear that contaminated clay had been sold to many other states, many clay and feedstuff samples were analyzed. Then, a possible transfer to food was checked. Later, also cosmetic products had to be included.

Methods and materials

Samples of clay, feedstuff, food and cosmetic products were collected between summer 1999 and January 2000. The samples were analyzed according to methods which were tested succesfully in collaborative studies and optimized for the individual matrices (7, 8, 9).

Results and Discussion

Table 1 summarizes the results of the analysis 67 samples of mineral feed or additives for mineral feed. These samples can be divided in two groups:

1. kaolinitic clay samples from the highly contaminated Westerwald area and mineral feeds with use of such clays,
2. additives and mineral feeds without contaminated kaolinitic clay.

31 samples had a link to use of highly contaminated clay. Four samples were „pure" kaolinitic clay from the Westerwald area, with a dioxin content of 64,400, 111,000, 339,000 and 479,000 pg WHO-TEQ/kg showing a wide range of contamination. The other samples were mineral feeds with different amounts of caolinitic clay showing even a wider range of contamination.

The majority of not contaminated samples had a dioxin content below 100 pg WHO-TEQ/kg. Most samples were analyzed shortly after the first reports about the new detected dioxin source. At that time, some manufacturers of mineral feed had different stocks of raw material. Thus, mineral feeds from the market from the same producer could have a wide range of contamination. As a result, samples below 500 pg WHO-TEQ/kg were considered „not contaminated". However, it is possible that after elimination of the dioxin source, the frequency distribution in the range between 100 and 500 pg WHO-TEQ/kg would change to lower dioxin values. Specific aspects to derive the background contamination are discussed in a separate paper (10).

Table 1: Results of clay and mineral feed samples (in pg WHO-TEQ/kg, as upper bound determination limit)

	clay samples	samples containing contaminated clay	samples without contaminated clay
number of samples	4	27	36
	pg WHO-TeQ / kg	pg WHO-TeQ / kg	pg WHO-TeQ / kg
mean	248,000	14,250	103
median	225,000	11,120	70
minimum	64,400	414	15
maximum	479,000	69,700	483
90 % percentile		29,500	254
95 % percentile		37,130	315

When it was clear that contaminated mineral feed had been used in the food chain, immediately food samples were taken to check the extent of a possible food contamination. 15 food samples from 12 farms were collected where the use of mineral feed with PCDD/F contaminated kaolinitic clay was proven or very likely. However, none of these samples had a dioxin content significantly above the normal background contamination. At one selected farm, two food samples and the mineral feed were analysed. Table 2 gives the results. Although the mineral feed had a high dioxin content, neither the milk nor the veal sample had significantly increased values for WHO-TEQ or the most important congeners which had to be expected to be detectable at elevated levels in the food as result of the dioxin pattern of the clay. The low effect on the produced food was explained by low consumption rates: Mineral feed contributes only to about 0.5 to 2 % of the daily feed ration.

Table 2: Results of food and mineral feed samples collected on a selected farm (food: in pg/g fat; mineral feed: as pg /kg, all values as upper bound determination limit)

sample	WHO-TeQ	2378-TCDD	12378-PeCDD	OCDD
milk	0.65	0.14	0.25	0.92
veal	1.37	0.35	0.53	3.67
mineral feed	31,812	8,040	1,480	2,306,225

The situation is completely different if the clay is used as anticaking agent (as in the ball clay case). The reason is that then the possibly contaminated compound feed can be fed as only feedstuff for a long period and contribute to 100 % of the daily intake. In our supervision district, we found such an application on a poultry farm where we had detected considerably elevated dioxin levels in eggs and meat from turkey. Table 3 summarizes selected results.

Table 3: Results of selected food and compound feed samples (food: in pg /g fat; mineral feed: as pg /kg, all values as upper bound determination limit)

sample	WHO-TeQ	2378-TCDD	12378-PeCDD	OCDD
eggs (herd no. 337)	6.96	2.10	4.14	4.16
eggs (herd no. 104)	41.65	17.03	21.23	8.88
turkey breast (herd no. 337, female)	11.15	5.14	5.35	4.39
turkey breast (herd no. 337, male)	48.18	23.22	22.32	14.87
turkey breast (herd no. 104, female)	42.78	18.62	21.86	10.70
turkey breast (herd no. 104, male)	63.58	30.66	29.27	15.70
compound feed	9,536	4,133	2,871	627,352

The use of a high contaminated feedstuff over months had a considerable effect on the dioxin content: Egg and turkey breast samples exceeded the dioxin tolerances which were set during the Belgium crisis (for eggs and poultry: 5 pg WHO-TEQ/g fat as upperbound detection level) (11). Even long withdrawal periods did not show quickly decreasing dioxin levels to meet the requirements of the dioxin tolerances. Female turkeys had a significant lower dioxin than male turkeys.

The European Community fixed a tolerance of 500 pg WHO-TEQ/kg (upper bound determination limit) for additives belonging to the group of binders, anti-caking agents and coagulants in feedingstuffs (12).

Finally it was discovered that kaolinitic clays are an important raw material also for cosmetic products. Thus, 12 raw products and 8 cosmetic products from the market were analyzed. All raw materials had a dioxin content in the range between 50 and 300 pg WHO-TEQ/kg which is considered to be background. Also, goods from the market did not have any elevated dioxin levels.

Acknowledgement

I'd like to thank Mrs. Tritschler and Mr. Huber for their reliable preparation of the samples and Mr. Winterhalter for running the high resolution mass spectrometer.

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