FIRST EXPERIENCES WITH NEW EU-LIMIT VALUES FOR PCDDs/PCDFs AND DL-PCBs IN FOOD AND FEEDING STUFF

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Abstract
Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are unwanted by-products in a variety of industrial and thermal processes. Because of their many sources, PCDDs and PCDFs are ubiquitously distributed. Polychlorinated biphenyls (PCBs) were widely used in various technical processes (e.g. as transformer oil, capacitor oil, softening agent) and thus are ubiquitously distributed as well.

More than 90 % of the human exposure to PCDDs/PCDFs ("dioxins") and dioxinlike PCBs ("DL-PCBs") are referred to food consumption [1]. Especially food of animal origin contributes about 80 % to this uptake. For this reason the European Union designed a strategy to decrease the concentration of PCDDs/PCDFs and DL-PCBs in food and feeding stuff. First experiences made with the application of the new EU limit values for DL-PCBs in food and feeding stuff samples originating from the routine analytical service of ERGO are available and will be reported in the following.

Introduction
In 2001 the European Union developed a strategy to support protecting the environmental and human health by reducing the concentration of dioxins and PCBs in both - the environment and food and feeding stuff. Especially food of animal origin counts as an important source for the human exposure to dioxins and PCBs. As the contamination of food is in direct relation to the contamination of feeding stuff, the *Community strategy for dioxins, furans and polychlorinated biphenyls* [2] enforced regulations for both – food and feeding stuff - regulations which are based on three key principles:

- Determination of limit values on a low, but practicable level, which will be gradually reduced, so that unacceptable high contaminated products will then no longer be used.
- Determination of so called action levels aimed to trigger „early warning" in case of concentrations that exceed EU limit values for food and feeding stuff: In consequence, the sources and pathways of the specific contamination will be investigated and actions to reduce the amount of contamination be taken.
- Determination of target values which – when finally reached – ensure that a great majority of the European population will be exposed to less than 14 pg WHO-TEQ/kg bodyweight of dioxins and dioxinlike PCBs per week by means of food.

Since as early as the 1st of July 2002 Europe-wide applicable limit values for dioxins in food and feeding stuff have been effective (Council Regulation (EC) No. 2375/2001 [3] and Directive 2002/32/EC [4]). Even if, from a toxicological point of view limit values are not only needed for dioxins but also for dioxinlike PCBs, initially only limit values for dioxins were established. The reason was, that until then little was known about the occurrences of dioxinlike PCBs. Mainly the so called Marker-PCBs (non-dioxinlike PCBs), which do not include dioxinlike PCBs, have been analysed so far. With considerable delay (at the beginning of February 2006) the European Commission first published limit values and action levels for dioxinlike PCBs in food and feeding stuff which became effective in November 2006 (Commission Regulation (EC) No. 199/2006 [5] and Directive 2006/13/EC [6]). In addition, the so called action levels for food and feeding stuff were revised. The regulations for food and feeding stuff became simultaneously effective and have been part of national legislation since 4th November 2006. The following aspects are especially important for the application of those specific limit values:
The limit values for dioxins only will stay effective for a transition period until at least end of 2008.
Additionally, new limit values for the sum of dioxins plus dioxinlike PCBs were established. Thus, the determination of dioxinlike PCBs is now mandatory. As sources and pathways for dioxins and dioxinlike PCBs differ, action levels for both groups were - unlike those new limit values above - determined separately.

The requirements concerning the quality of analysis for the determination of dioxinlike PCBs do not differ from those for the determination of dioxins. Directives 2002/69/EC [7] and 2002/70/EC [8] remain unaltered valid.

Limit values and action levels will be examined carefully until end of 2008 at the latest. Up to now, no target values have been defined by the EU (projected for 2008).

In the following we would like to present first experiences with the new EU-limit values for PCDDs/PCDFs and DL-PCBs in feeding stuff (fish oil, fish meal and fish feed) and food (milk).

Materials and Methods

Fish oil samples were dissolved in hexane (crude oil was slightly warmed and homogenized before solving). Fish meal and fish feed samples were soxhlet extracted for 20h by means of n-hexane/aceton (v:v, 1:1). Milk samples were treated by liquid/liquid extraction by means of n-hexane (after addition of potassium oxalate). Before extraction or solving, a mixture of ^{13}C-labelled internal standards (17 2.3.7.8 substituted PCDDs/PCDFs, 12 dioxin-like PCBs) was added to the sample. All ^{13}C-labelled internal standards were delivered by Cambridge Isotopes Laboratories (USA) or Wellington Laboratories (Canada). After solvent evaporation a gravimetric lipid determination was performed. A multicolumn clean-up including silica gel, different treated silica gel (H_2SO_4-SiO_2, CsOH-SiO_2), activated carbon and alumina oxide followed. $^{13}C_{12}$-1.2.3.4-TCDD and $^{13}C_6$-1.2.3.4.6.7.8- HeptaCDF were added to the final extract as recovery standards.
The measurement was performed by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) on a HP 5890 II GC coupled with a Micromass AutoSpec mass spectrometer (ionisation mode: Electron impact (EI), resolution: 10,000). A DB 5 column was used for gas chromatographic separation. Quantification was done by means of isotope dilution method using a five-point calibration.
TEQ data was calculated by using WHO-TEFs and by taking into account the whole detection limit for non-detected compounds (upperbound procedure).

Results and Discussion

Miscellaneous samples of food and feeding stuff originating from various sources have been analysed by the analytical service of ERGO so far – most of the times dioxins were determined in the past. In food, dioxinlike PCBs exist in distinctly lower concentration than non-dioxinlike PCBs („Marker-PCBs“) – however, in the range of pg/g to ng/g their amounts are commensurable to dioxins. Therefore, a precise analysis is essential. The analysis of dioxins and dioxinlike PCBs was carried out according to Directives 2002/69/EC [7] and 2002/70/EC [8] concerning the determination of contaminants in food and feeding stuff by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Animals are mainly exposed to dioxins and dioxinlike PCBs by feeding stuff and the greatest amounts of contaminants in feed materials [9] can be found in fish oil, fish meal and fish feed – samples which are most frequently analysed by ERGO.

Figures 1 to 3 show the amounts of dioxins and DL-PCBs determined in 2006/beginning of 2007 in fish oil (application as feeding stuff), fish meal and fish feed compared to current limit values for dioxins as well as limit values for the sum of dioxins and dioxinlike PCBs.

A general chart for milk samples, which are also affected by the new limit values, will be shown by way of example, too (Figure 4).

It can be clearly seen that the percentage of untradeable products do not rise significantly. Most of the analysed samples show results which are clear below the limit values for PCDDs/PCDFs and also for PCDDs/PCDFs plus dioxinlike PCBs.

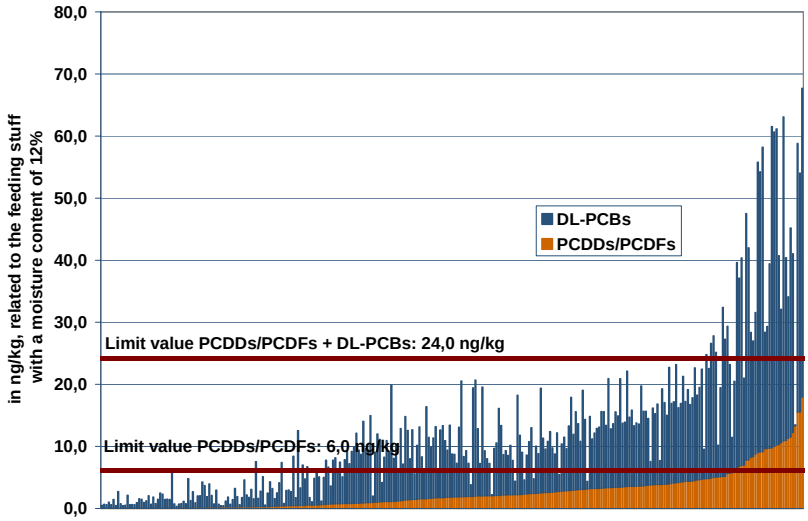

Figure 1: PCDDs/PCDFs and DL-PCBs in fish oil - application as feeding stuff (n=301)

In the case of fish oils – independent of application (for human or animal consumption) - it has to be taken into account that their contamination can be reduced by, for example, a cleaning by the means of activated carbon. Because of the absorptive characteristics of activated carbon, the amount of dioxins and of so-called non-ortho PCBs (which belong to the group of dioxinlike PCBs) can be reduced significantly. However, this procedure will hardly alter the amount of so-called mono-ortho PCBs in fish oils. Thus, especially in the case of originally highly contaminated fish oils, the amount of dioxins might actually drop below the limit value for dioxins after being cleaned by the means of activated carbon, whilst the product might remain not tradeable because of a remaining content of PCBs.

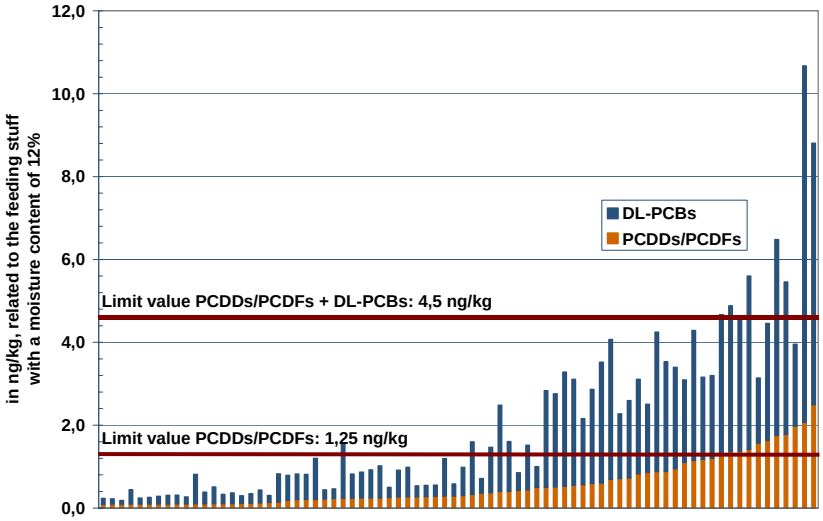

Figure 2: PCDDs/PCDFs and DL-PCBs in fish meal (n=78)

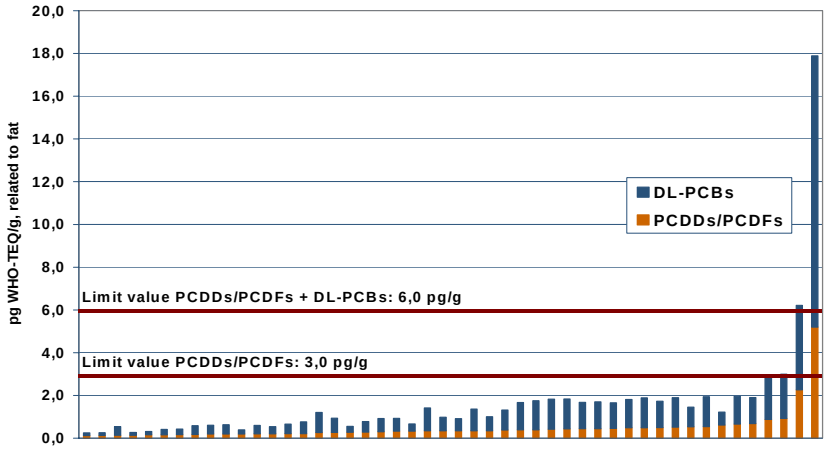

Figure 3: PCDDs/PCDFs and DL-PCBs in fish feed (n=43)

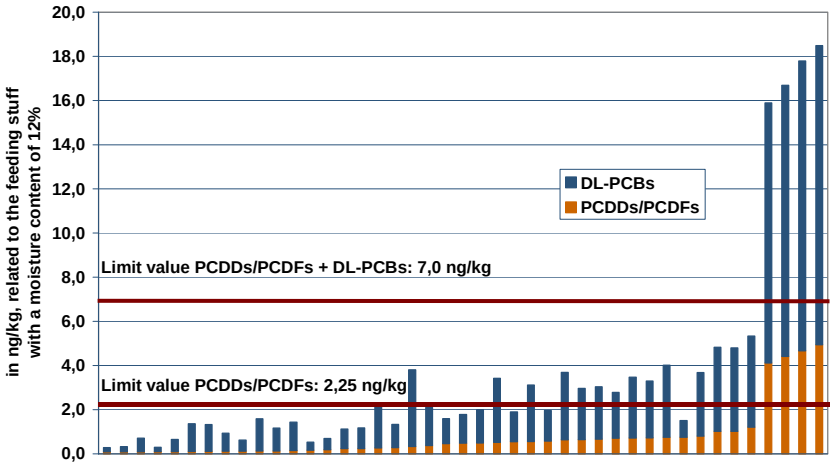

Figure 4: PCDDs/PCDFs and DL-PCBs in milk samples (n=48)

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References

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[3] Council Regulation (EC) No 2375/2001 (OJ L 321, 6.12.2001, p. 1)
[4] Directive 2002/32/EC (OJ L 140, 30.5.2002, p. 10)
[5] Commission Regulation (EC) No 199/2006 (OJ. L 32, 4.2.2006, p. 34)
[6] Directive 2006/13/EC (OJ L 32, 4.2.2006, p. 44)
[7] Directive 2002/69/EC (OJ L 209, 6.8.2002, p. 5)
[8] Directive 2002/70/EC (OJ L 209, 6.8.2002, p. 15)
[9] Opinion of the Scientific Committee in Animal Nutrition (SCAN): Dioxin contamination of feeding stuffs and their contribution to the contamination of food of animal origin. Adopted on 6th November 2000