PCDD/F PROFILES IN EMISSIONS, FEEDING STUFF AND FOOD

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Introduction

The dioxin scandal in Belgium for sure attracted attention and led to a new sensitivity regarding the everyday addition of persistent organic pollutants (POPs), especially polychlorinated dibenzo(p)dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) to the human organism. Finally the substantial investigations and analyses of foodstuffs and animal-feed samples contributed to the fast clearing up of reasons and apart from the already known impact of emissions, they identified additions in mineral animal feed (such as kaolinite clay) and contaminations of animal feed by hydraulics or transformer oil as causal.[1]

Only a rough estimation concerning the number of dioxin analyses which have been made by private institutes in Germany within the acute period from mid to end 1999 can be made. In our view it must come up to ca. 2,500, 50 % of which from abroad. On the basis of roughly 600 feeding stuff and food samples analysed by the GfA during this time, mainly two things became clear:

- in more than 80 % of the samples, dioxins and furans were detected
- in more than 95 % of the samples, the guide and intervention values were not exceeded

This explains that the "dioxin scandal" in other words became the "Belgian chicken dioxin contamination problem".[2] At the same time, it makes clear that we cannot and must not evade the problem of the, in the truest sense, everyday, encounter with POPs. This we are going to clarify in the following by means of selected examples of presentations of "dioxin and furan profiles".

Methods and Materials

The PCDF/Ds are extracted by means of fat extraction. The contaminants are then separated from the fat and other interfering components and finally analysed by gas chromatography/mass spectrometry (GC/MS). For PCDF/D analysis, seventeen $^{13}C_{12}$-labelled PCDF/D congeners were added to the fat extract of each sample as internal standards. For each native PCDF/D congener to be determined, the corresponding $^{13}C_{12}$-labelled PCDF/D standard was added (isotope dilution). For the separation of the PCDF/Ds from the fat, the total fat extract was dissolved in hexane and then percolated through a mixed silica and an alumina column by means of different solvents (hexane, benzene and methylene chloride).

The PCDF/D fraction was further cleaned-up by liquid chromatography using a Florisil column and two solvents (hexane and methylene chloride). Prior to the instrumental analysis, another PCDD standard ($^{13}C_6$-1,2,3,4-TetraCDD) was added to the PCDF/D fraction to determine the recovery of the $^{13}C_{12}$-labelled internal PCDF/D standards through the clean up.

For the PCDF/D determination, a capillary gas chromatograph (HRGC, HP 5890) equipped with a PTV injector and connected to a high resolution mass spectrometer (HRMS, VG AutoSpec) was used.

Results and Discussion

Since the 1980ies, mechanisms of the formation of new dioxins and furans in exhaust fumes of high-temperature processes have been discussed under the collective term "de novo synthesis".[3-6] Only recently the postulation of a variant as so-called "thermostat synthesis" on the basis of semi-empirical quantum-mechanical calculations was added.[7-9]

The effect of dioxins on the environment resulting from these mechanisms of new formation which are causally responsible for emissions of PCDD/F is therefore obvious. The profiles of congeners i.e. the percentages of the individual 2378-chlorine-substituted furans or dioxins in comparison with the respective sum of the examined furan or dioxin congeners are characteristic.

Figure 1: D/F profiles from different combustion processes as well as the percentage evaluation of the difference in heat of formation among the PCDD/F-congeners, calculated by means of MOPAC (HOF MOPAC)[8,10]

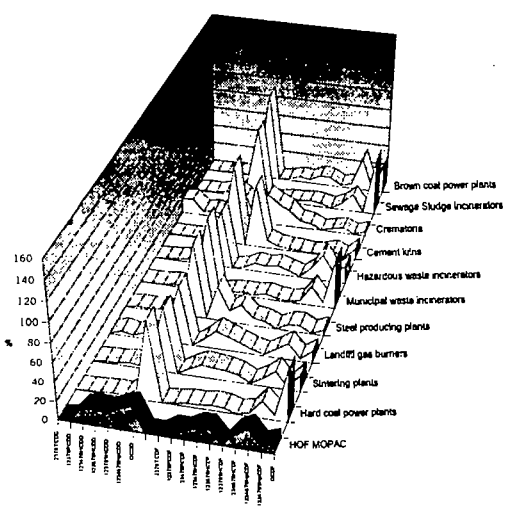
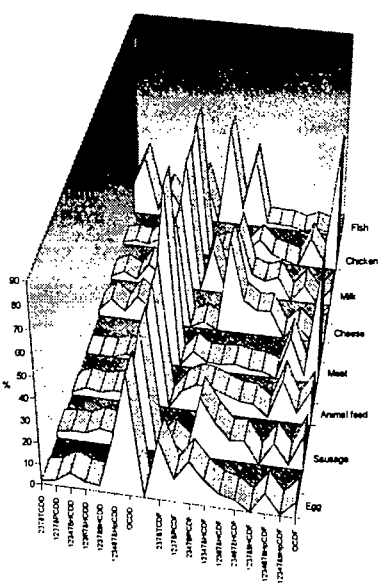


Figure 2: Selected characteristic congener profiles of different food matrices



The matrices of Figure 2, except those of the fish or fish-product samples which naturally do have other sources of pollution, show –with all necessary caution on closer examination- some characteristics of emission samples which have their causes in thermodynamical formation

preferences (please vide HOF MOPAC in Figure 1) with regard to the origin of single congeners and sometimes shifted by the influence of different enrichment effects.[8]

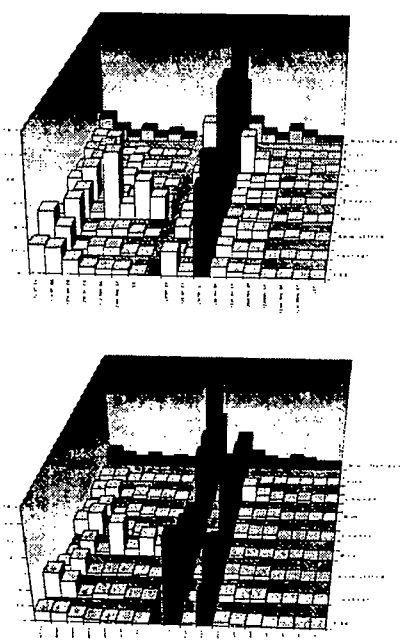
In Table 1 a selected collective of data is listed up in order unities while in Figure 2 exemplary characteristic profiles of PCDD/F congeners for single matrices are given.

Table 1: PCDD/F-levels in samples of food and animal feed

Matrice	Data Collective n=...	Concentration Unities		Comparative Data
		pg I-TEQ/g Fat Basis	pg I-TEQ/g Orig. Sample Basis	pg I-TEQ/g Fat Basis
Eggs	10	0,28 - 2,12	0,025 - 0,218	0,5 - 2,0[a][11]
Fish Products	40	0,001 - 14,8	0,0002 - 1,846	4,65 - 23,84[11]
Poultry	30	0,08 - 4,16	0,012 - 0,605	0,5 - 1,07[11]
Sausage	40	0,13 - 0,62	0,035 - 0,264	0,15 - 0,21[b][1]
Milk and Milk Products	90	0,01 - 2,67	0,002 - 0,596	0,8 - 1,8[11,12]
Animal Food	20		0,001 - 9,86	
Meat	30	0,07 - 0,82	0,006 - 0,106	< 0,4 - 7,42[11]

a. from hen's eggs of laying batteries; eggs from hens kept on the ground showed a wider range.
b. and literature cited there

Figure 3: Percentage of single 2378-Cl-substituted D/F congeners to the overall-I-TEQ- value of the respective sample.



The theme, however, remains very acute, although on a slightly smaller level than in 1999. In this context the first (after respective transfer to national law) Europe-embracing milestone for the reduction of one of the primary pathways was laid with the EC directive 94/67/EG for the restriction of PCDD/F emissions from hazardous waste incinerators (limit: 0,1 ng I-TEQ/m^3).[13] The secondary pathway shall also be continously regulated. This is expressed in a planned directive of the EC Parliament and Council concerning unwanted substances and products in animal feed. For this directive, the "Standing Committee Animal Feed" forwarded the proposals for dioxin maximum values quoted in Table 2.[14]

Table 2: Proposal of the "Standing Committee Animal Feed" for dioxin maximum values of different matrices

Matrix	Validity	Max. Value in ng I-TEQ/kg fat
Animal food of vegetable origin (except rough feed)	01.01.2002 – 31.12.2005 from 01.01.2006	0,5 0,3
Binding agent (kaolinite tone etc.) and mixtures containing these binders		1,0
Animal fats and other products from ground animals at a fat content of >25 %	01.01.2002 – 31.12.2005 from 01.01.2006	2,0 1,5
Products from ground animals at a fat content of < 25 %		0,5
Fish and fish oil, other animals from the sea and their by-products at a fat content of > 22,5 %	01.01.2002 – 31.12.2005 from 01.01.2006	6 4
Fish, other animals from the sea and their by-products at a fat content of < 22,5 %	01.01.2002 – 31.01.2005 from 01.01.2006	1,25 0,75
Vegetable oils and their by-products		0,5
Rough feed	01.01.2002 – 31.12.2005 from 01.01.2006	0,75 0,50
Mixed feed except for fish	01.01.2002 – 31.12.2005 from 01.01.2006	0,5 0,35
Fish feed	01.01.2002 – 31.12.2005 from 01.01.2006	2,25 1,25

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