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# Dioxins: now it's time for action

*Dr. Peter Luthardt, of GfA Gesellschaft für Arbeitsplatz- und Umweltanalytik explains what the latest dioxins regulation mean for food manufacturers*

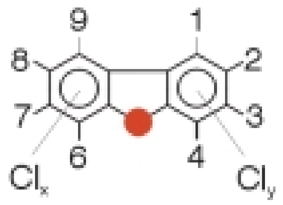
The recent dioxin scandal in Belgium attracted considerable attention and has led to a new sensitivity regarding the everyday addition of Persistent Organic Pollutants (POPs), especially Polychlorinated Dibenzo(p)dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) to the human body. Substantial investigations and analyses of foodstuffs and animal-feed samples contributed to the fast determination of the sources of contamination. It also identified additions in mineral animal feed (such as kaolinite clay) and contamination of animal feed by hydraulics or transformer oil as causal (Ref. 1).

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

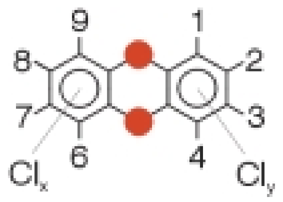
- In more than 80% of the samples, dioxins and furans were detected
- In more than 95% of the samples, the guide and intervention values were not exceeded.

However concerns remained, finally leading to EC directives for the restriction of dioxin contents in feedingstuff and food coming into force on July 1st, 2002.

**TABLE 1: STRUCTURE OF THE PCDFS AND PCDDS NUMBER OF POSSIBLE ISOMERS PER DEGREE OF CHLORINATION**




PCDFs
Polychlorinated Dibenzofurans

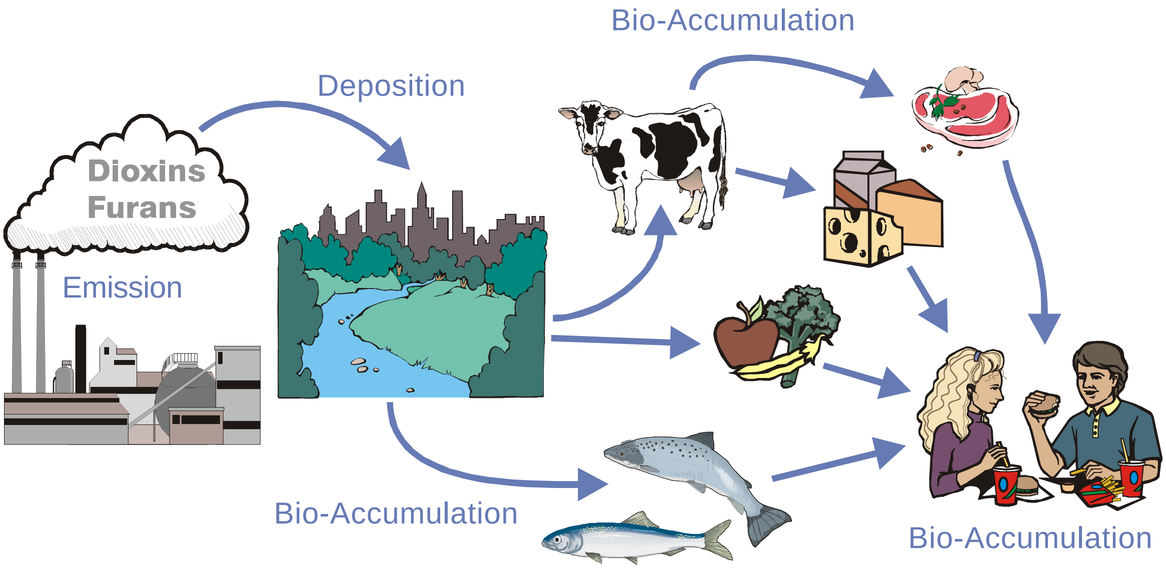



PCDDs
Polychlorinated Dibenzo(p)dioxins

$x = 0 - 4;\ \ y = 0 - 4;\ \ 1 \leq x + y \leq 8$

| Homologue group of PCDF/Ds | Number of Chlorine atoms | Number of PCDF Isomers (2,3,7,8-subst. Congeners) | Number of PCDD Isomers (2,3,7,8-subst. congeners) |
|---|---|---|---|
| MonoCDF/Ds | 1 | 4 (-) | 2 (-) |
| DiCDF/Ds | 2 | 16 (-) | 10 (-) |
| TriCDF/Ds | 3 | 28 (-) | 14 (-) |
| TetraCDF/Ds | 4 | 38 (1) | 22 (1) |
| PentaCDF/Ds | 5 | 28 (2) | 14 (1) |
| HexaCDF/Ds | 6 | 16 (4) | 10 (3) |
| HeptaCDF/Ds | 7 | 4 (2) | 2 (1) |
| OctaCDF/Ds | 8 | 1 (1) | 1 (1) |
| | Congeners | 135 (10) | 75 (7) |

**FIGURE 1: ACCUMULATION PATHWAY OF DIOXINS AND FURANS**




The food industry as well as feed manufacturers are now responsible to ensure that the products put into circulation meet these requirements.

## TOXICOLOGIC AND ECOTOXICOLOGIC ASPECTS

Dioxins and furans belong to the so-called Persistant Organic Pollutants (POPs). These two substance classes are usually described under the collective term 'dioxins'. All in all these two substance classes include 210 individual compounds (congeners), which derive from their different substitution pattern (Table 1).

'Dioxins' are characterised by a strong chemical and

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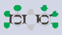
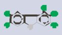
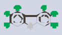
**TABLE 2: TOXIC EQUIVALENT FACTORS BLANK (TEFS) FOR POLYCHLORINATED DIBENZODIOXINSAND DIBENZOFURANS ACCORDING TO THE PROPOSAL OF THE NATO/CCMS AND THE WHO**

| PCDF/D | Structure | NATO/CCMS 1988 | WHO 1997 |
|---|---|---|---|
| 2378-TetraCDD |  | 1,0 | 1,0 |
| 12378-PentaCDD |  | 0,5 | 1,0 |
| 123478-HexaCDD |  | 0,1 | 0,1 |
| 123678-HexaCDD |  | 0,1 | 0,1 |
| 123789-HexaCDD |  | 0,1 | 0,1 |
| 1234678-HeptaCDD |  | 0,01 | 0,01 |
| OctaCDD |  | 0,001 | 0,0001 |
| | | | |
| 2378-TetraCDF |  | 0,1 | 0,1 |
| 12378-PentaCDF |  | 0,05 | 0,05 |
| 23478-PentaCDF |  | 0,5 | 0,5 |
| 123478-HexaCDF |  | 0,1 | 0,1 |
| 123678-HexaCDF |  | 0,1 | 0,1 |
| 123789-HexaCDF |  | 0,1 | 0,1 |
| 234678-HexaCDF |  | 0,1 | 0,1 |
| 1234678-HeptaCDF |  | 0,01 | 0,01 |
| 1234789-HeptaCDF |  | 0,01 | 0,01 |
| OctaCDF |  | 0,001 | 0,0001 |

The TEQ-value of a sample is calculated by multiplying the concentration of each PCDF/D congener with the corresponding TE factor and adding up the products.

biological stability and a high enrichment potential (the half-life value for the 2,3,7,8 TCDD-'Seveso-dioxin' comes up to six-10 years). Mussels, fish and humans accumulate dioxins in fatty tissue and the liver, while more than 90% of the daily dioxin absorption of humans results from nutrition. The main sources of dioxins in foodstuffs are animal fats, e.g. milk, eggs, meat and fish. Here the dioxin absorption from foodstuffs of plant origin is of minor relevance.

The main source for the background contamination of foodstuffs is the atmospheric deposition (Figure 1). This ,however, is causally related to emissions from combustion processes.

High-temperature processes (>800°C) result in almost complete destruction of dioxins and furans brought in via the input (Ref.2). The fact that these classes of substances can nevertheless be detected in exhaust fumes of incinerating plants is based on different (re-) formation mechanisms. (Ref. 3, 4, 5, 6), such as:

- The formation of PCDD/F from related, chlorinated precursor compounds (e.g. polychlorinated biphenyls (PCBs), polychlorinated phenols (PCPhs) and polychlorinated benzenes (PCBzs) at a temperature between 300 and 700°C),
- The formation of PCDD/F from non-chlorinated organic carbon compounds in the presence of a chlorine source and catalytically effective metals ( especially Cu) at a temperature between 450 and 250°C ('de novo synthesis').

Because of the acute and chronic toxicity of dioxins for humans, the WHO in 1998 and the EU SCF (Scientific Committee on Food) in 2000 set up 'Tolerable daily or weekly intake'-values for dioxins:

- 1998 WHO: 1-4 pg WHO-TEQ/kg body weight and day (TDI).
- 2000 EC SCF: 14 pg WHO-TEQ/kg body weight and week (TWI).

## WHAT ARE TEQS?

Toxicity Equivalents (TEQs) are the usual unit for 'dioxins' in concentrations and mass flows which are expressed in limit, target and action values.

Merely 17 out of totally 210 individual substances (the so-called 'dirty seventeen') that are considered to be especially toxic are relevant. These are factorially weighted based on the so-called 'Seveso-Dioxin', the 2,3,7,8-TCDD (tetrachlordibenzodioxin) using toxicity equivalency factors (TEFs; Table 2). The most common TEF models on an international basis are at the moment the NATO/CCMS (NATO-Committee on Challenges of Modern Society) as well as the WHO (World Health Organisation). The TEF model leads to concentration units using the NATO/CCMS given in I-TEQ (International Toxicity Equivalents); the WHO-TEF model leads to concentration units in WHO-TEQ.

As can be seen from Table 2 the TEFs of both models slightly differ because of the different TE factors of the weighing the 1,2,3,7,8-PentaCDD and OctaCDDs.

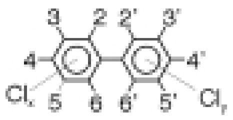
## NEW EC REGULATIONS FOR DIOXINS IN FEEDINGSTUFFS AND FOOD

Since the strong contamination of a Belgian feeding stuff with polychlorinated dibenzo(p)dioxins (PCDDs) and dibenzofurans (PCDFs) in 1999 which led to the contamination of a number of foodstuffs of animal origin all over Europe, the problem of dioxins in foodstuffs found its place in the centre of the public discussion (Ref. 7, 8). As

**TABLE 3: RELEVANT EC DIRECTIVES, REGULATIONS AND RECOMMENDATIONS**

| | food | feeding stuff | valid from | actions if exceeded | cited in | Internet |
|---|---|---|---|---|---|---|
| action levels | + | + | Jul 02 | source determination; reporting | commission recommendation 2002/201/EC | http://europa.eu.int |
| limit values | + | | Jul 02 | taking out of circulation | Council Regulation 2375/2001 | http://europa.eu.int |
| limit values | | + | Jul 02 | taking out of circulation | Council Directive 1999/29/EC | http://europa.eu.int |

### TABLE 4: STRUCTURE OF THE POLYCHLORINATED BIPHENYLS (PCBS) NUMBER OF POSSIBLE ISOMERS PER DEGREE OF CHLORINATION




$0 \leq x \leq 5; \; 0 \leq y \leq 5; \; 1 \leq x + y \leq 10$

| Homologue | Number of Chlorine atoms (x + y) | Number of possible PCB Isomers (PCB isomers with TEFs) |
|---|---|---|
| Monochlorobiphenyls | 1 | 3 |
| Dichlorobiphenyls | 2 | 12 |
| Trichlorobiphenyls | 3 | 24 |
| Tetrachlorobophenyls | 4 | 42 (2) |
| Pentachlorobiphenyls | 5 | 46 (5) |
| Hexachlorobiphenyls | 6 | 42 (4) |
| Heptachlorobiphenyls | 7 | 24 (1) |
| Octachlorobiphenyls | 8 | 12 |
| Nonachlorobiphenyls | 9 | 3 |
| Decachlorbiphenyls | 10 | 1 |
| | Congeners | 208 (12) |

one of the consequences of the Belgian feeding stuff scandal, the European Commission enacted a number of directives including maximum levels for PCDD/F in feeding stuff and food (Ref. 9, 10, 11) These limit values will have to be observed throughout Europe from July 1st, 2002 .

Table 3 gives a short overview of the different EC directives along with the measures which have to be taken in case the action or limit values resp. are exceeded.

At present only the substance classes of dioxins and furans are taken into consideration. On the background of a smaller data base, it is, however, already known that there are Polychlorinated Biphenyls (PCB) which carry similar characteristics. PCBs are a group of closely related chemicals and some individual PCBs named 'dioxin-like PCBs' exhibit toxicity similar to those of toxic dioxins. Partly showing relevant concentrations compared to their TEQ contribution, they will also play a role within the scope of examinations on a short to medium-term basis. Unlike dioxins, PCBs were purposely produced but by now their use should have been phased out.

It is planned to revise the EC directives in 2004 at the latest and to attach the necessary importance to the PCBs then (in the meantime the available data base is supposed set to grow). The number of congeners of PCBs amounts to 209 but merely 12 individual substances are taken into account (Table 4).

The total-TEQ of a sample is then determined by

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**TABLE 5: TOXIC EQUIVALENT FACTORS (TEFS) FOR POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS AND DIOXIN-LIKE PCBS ACCORDING TO THE PROPOSAL OF THE WHO**

| Compound | WHO-TEFs (1997) |
|---|---|
| **PCDDs** | |
| 2,3,7,8-TetraCDD | 1,0 |
| 1,2,3,7,8-PentaCDD | 1,0 |
| 1,2,3,4,7,8-HexaCDD | 0,1 |
| 1,2,3,6,7,8-HexaCDD | 0,1 |
| 1,2,3,7,8,9-HexaCDD | 0,1 |
| 1,2,3,4,6,7,8-HeptaCDD | 0,01 |
| OctaCDD | 0,0001 |
| **PCDFs** | |
| 2,3,7,8-TetraCDF | 0,1 |
| 1,2,3,7,8-PentaCDF | 0,05 |
| 2,3,4,7,8-PentaCDF | 0,5 |
| 1,2,3,4,7,8-HexaCDF | 0,1 |
| 1,2,3,6,7,8-HexaCDF | 0,1 |
| 1,2,3,7,8,9-HexaCDF | 0,1 |
| 2,3,4,6,7,8-HexaCDF | 0,1 |
| 1,2,3,4,6,7,8-HeptaCDF | 0,01 |
| 1,2,3,4,7,8,9-HeptaCDF | 0,01 |
| OctaCDF | 0,0001 |
| **PCBs** | |
| PCB 81 | 0,0001 |
| PCB 77 | 0,0001 |
| PCB 123 | 0,0001 |
| PCB 118 | 0,0001 |
| PCB 114 | 0,0005 |
| PCB 105 | 0,0001 |
| PCB 126 | 0,1 |
| PCB 167 | 0,00001 |
| PCB 156 | 0,0005 |
| PCB 157 | 0,0005 |
| PCB 169 | 0,01 |
| PCB 189 | 0,0001 |

The TEQ-value of a sample is calculated by multiplying the concentration of each congener with the corresponding TE factor and adding up the products.

multiplying the WHO toxicity factor (TEF) with the concentration of the respective individual compound (Table 5).

Both old and new literature data partly consider the total-TEQ at the example of different matrices which can be seen from Table 6.

Partly the values distinctly exceed the action and limit values (the action and limit values are in the range between 0.4 and 6 ng WHO-PCDD/F-TEQ/kg feedingstuff and between 0.6 and 6 pg WHO-PCDD/F-TEQ/g fat basis in food respectively; vide also internet references given in Table 3). The regulations are valid

## BIOGRAPHY

Dr. Peter Luthardt studied chemistry at the University of Münster, Germany, where he achieved a PhD in Organic Chemistry in 1989.

He joined the GfA mbH in 1989 and has been managing director since 1999.

The GfA is now one of Europe's leading institutes for dioxin and PCB analyses. In 2001 the GfA joined the Eurofins Scientific Group, a biotechnology company operating internationally with over 1,800 staff in more than 50 laboratories and a portfolio of around 5,000 reliable analyitical methods for proving the authenticity, origin, safety, identity and purity of biological substances.

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for meat, liver, fish, milk, eggs, fat and oil of animal and plant origin as well as fish oil and products thereof. Since dioxins and PCBs do not degrade easily, they have become very widespread in the natural environment and can also be found at very low concentrations in many foods, particularly fatty foods. The nature of dioxins and PCBs entails that they tend to become more concentrated along the food chain and in order to meet strict limits, control is needed in the environment, in food and in animal feed.

It is expected that even under consideration of the PCBs, these action and limit values for 2004 which are –at the time being- completely based on the TEQ value of the dioxin concentrations will not be raised considerably. ■

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## TABLE 6: DIOXIN CONTENTS IN DIFFERENT FOOD PRODUCTS (EXAMPLARY DATA)

| Matrices | Number of Samples | Location | Year | Dioxin Concentration Range | Ref. |
|---|---|---|---|---|---|
| **Fish Range** | | | | | |
| Fish | 68 | Germany | 88-91 | 31-43 pg I-TEQ/g fat basis * | 12 |
| Fish | | Germany Southwest | 91-95 | 8 pg I-TEQ/g fat basis* | |
| Eel | | Germany | bf. 96 | 12-23 pg I-TEQ/g fat basis* | |
| | | | | 75-120pg I-TEQ/g fat basis*[a] | |
| Salmon | c | Sweden | | 56pg I-TEQ/g fat basis* | 13 |
| | | | | 123pg I-TEQ/g fat basis*[a] | |
| Herring | 17 | North Sea. N. Atlantic | bf. 92 | 0.3-2.4pg I-TEQ/g fresh weight | 14 |
| Herring | 20 | Baltic Sea | bf. 92 | 0.5-13.4pg I-TEQ/g fresh weight | |
| Eel | 4 | | bf. 92 | 7.2pg I-TEQ/g fresh weight | |
| Cod / Haddock | 132 | UK and Import | | 0.3-140pg I-TEQ/g fat basis*[b] | 15 |
| Salmon / Catfish | c | USA | 98 | 0.29-1.28pg I-TEQ/g | 16 |
| Lobster / Acallopa | c | USA | 99 | 0.33-2.05pg I-TEQ/g | |
| Whale / Dolphin (blubber) | 27 | Japan | 99 | 27.1-691pg I-TEQ/g fresh weight[b] | 17 |
| Fish | c | Canada | 92-95 | 0.12-0.62pg I-TEQ/g fresh weight | 18 |
| Fish | | Poland (rivers) | 99 | 1.2-9.4pg I-TEQ/g fat basis* | 19 |
| Fish | < 400 | Poland (Baltic Sea) | 99 | 7.0-40pg I-TEQ/g fat basis* | |
| Fish oil | | Poland (Baltic Sea fish) | 99 | 11.2-50pg I-TEQ/g fat basis* | |
| Fish oil | | Brazil | 99 | 4.6pg I-TEQ/g fat basis* | 20 |
| Mussels | 70 | Catalonia (Spain) | 99 | 1.1-5.5 pgI-TEQ/g fresh | 21 |
| **Selection of food products** | | | | | |
| Eggs | 50 | Germany | 93 | 0.5-2.0pg I-TEQ/g fat basis[d] | 22, 23 |
| Poultry | 30 | Germany | 95 | 0.5-1.07pg I-TEQ/g fat basis | 22, 23 |
| Sausage | 40 | Germany | 98 | 0.15-0.21pg I-TEQ/g fat basis | 22, 1 |
| Milk and Milk products | 90 | Germany | 86-92 | 0.8-1.8pg I-TEQ/g fat basis | 22, 12 |
| Meat** | 30 | Germany | 90-92 | < 0.4 –7.42pg I-TEQ/g fat basis | 22, 23 |

a PCB-TEQ
b PCDD/F- + PCB TEQ
c Not Specified
d From hen's eggs of laying batteries; eggs from hens kept on the ground showed a wider range up to 23.4pg I-TEQ/g fat basis
* Please note that the EC maximum values are given in fresh weight
** Veal, Sheep, Beef, Pork, Goose