Review

Dioxins and PCBs in feed and food — Review from European perspective

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ABSTRACT

During the 1990s, a number of adverse contamination incidents focussed the attention of the media and the general public on food safety. This led to the evaluation of safety measures with regard to dioxin intake from food. Important aspects regarding dioxins and PCBs in the food chain are reviewed here, allowing a contextual understanding of the present situation through its chronological developments. About 90–98% of the average exposure of humans to dioxins and PCBs results from dietary intake, with food of animal origin being the predominant source. Therefore, animal feed contributes considerably to the presence of these compounds in food.

The detection of the “real” source of a contamination event in the food chain is a complex scientific problem and requires specific knowledge on production processes and changes of patterns during bioaccumulation. This is demonstrated by complex investigations performed in three studies on two continents to identify the source (e.g. from contamination of cow’s milk in Germany, to citrus pulp pellets from Brazil as an ingredient in feed, then to contaminated lime for neutralization and finally to a landfill with residues of vinyl chloride monomer production). This example shows also the substantial economic losses resulting from incidents in the food chain and the consequences to global trade.

In 2001, the EU Scientific Committee on Food established a group tolerable weekly intake (TWI) of 14 pg WHO-TEQ/kg body weight and concluded that a considerable proportion of the European population would exceed this TWI. On the global level, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) provides scientific advice to the Codex Alimentarius Commission and therefore contributes to harmonized international food standards. In its evaluation of 2001, JECFA derived a provisional tolerable monthly intake (PTMI) of 70 pg TEQ/kg body weight. The sum of the median intake of PCDD/F-TEQ and PCB-TEQ exceeded the PTMI in Western European countries, was in the PTMI range in North America, but lower in Japan and New Zealand. The 90th percentile of PCDD/F-TEQ exceeded the PTMI in Western European countries and North America, the 90th percentile of coplanar PCBs in Western European countries.

Therefore, in 2001 the EU Commission developed a strategy to reduce the presence of dioxins and PCBs in the environment and in the food chain. The legislative measures comprised maximum levels and action levels for feed and food, and a Rapid Alert System for detected incidents was introduced. The network of the EU Reference Laboratory and National Reference Laboratories contributes to harmonization within the EU Member States and developed analytical criteria for screening and confirmatory methods for control of feed and food.

After all these efforts it is of general interest to see whether these measures had an effect. The 2012 evaluation of the European Food Safety Authority (EFSA) based on comprehensive monitoring data of 26 European countries shows a general decrease in dietary exposure of dioxins and DL-PCBs between 2002–2004 and 2008–2010, estimated to be between 16.6% and 79.3% for the different population groups. A smaller decrease was observed for NDL-PCBs. The percentage of individuals exposed above the TWI of 14 pg TEQ/kg b.w. was estimated to be between 1.0 and 52.9%. Toddlers and other children were the most exposed groups (being at the upper end of these ranges). Fish, meat and dairy products appeared to be the highest contributing food groups to dietary exposure.

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1. Introduction

“Dioxins” (polychlorinated dibenzo-p-dioxins [PCDDs] and polychlorinated dibenzofurans [PCDFs]) can be formed as unintentional by-products in a number of chemical processes as well as in almost every combustion process. Polychlorinated biphenyls (PCBs) are intentionally produced chemicals, that were manufactured for decades before the ban in marketing and use was adopted in 1985. In the 1980s/early 1990s, a number of measures were taken to detect possible sources for these contaminants and to stop or reduce their release into the environment. During the 1990s, a number of adverse contamination incidents focussed the attention of the media and the general public on food safety. This led to the evaluation of the safety of food with regard to the dioxin intake. Important aspects regarding dioxins and PCBs in the food chain are reviewed allowing a contextual understanding of the present situation, through its chronological developments, particularly from a European perspective.1

2. Incidents in the food chain and the investigative efforts to identify the source of a contamination

The interest in levels of dioxins and PCBs in the food chain was particularly triggered by incidents which were uncovered in the late 1990s. Generally, a complex scientific detective work and specific knowledge on production processes are necessary to identify the source of a dioxin contamination. Only in a limited number of contamination cases it is possible to identify the “real” source. Two examples are selected to show the difficulties and efforts.

2.1. The “citrus pulp pellets” case

The first example of the late 1990s is selected to show the comprehensive work which in the end had to be performed in three studies on two continents after the first findings of elevated dioxin levels in cow’s milk in Germany to the final identification of the source in Brazil.

2.1.1. From contaminated milk in Germany to citrus pulp pellets from Brazil

The incident was found as a result of programmes to monitor the PCDD/F contamination of food. In Germany, since 1989 numerous measures were taken to reduce the exposure humans and the environment with respect to dioxins. Subsequent surveys showed a decrease of the dioxin burden in food and breast milk in the following years. Thus, concerns were raised when the State Institute for Chemical and Veterinary Analysis of Food (CVUA) Freiburg found a reverse of the decreasing trend in milk and butter samples beginning gradually in September 1997. Butter samples collected randomly in south-western Germany in January and February 1998 showed about double the usual PCDD/F content compared with August 1997. It soon became clear that this increase was not a local incident, but concerned samples also from other parts of Germany and The Netherlands (showing increased I-TEQ-values with the same pattern: significantly elevated levels of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD) (Malisch, 1998).

For confirmation and as part of the necessary quality control, four other dioxin laboratories of the official food control in Germany were asked to analyse four butter samples as an “emergency collaborative study”. The results confirmed the initial findings (Malisch et al., 2000).

Effective efforts to identify the source required the identification of samples with high dioxin levels from central points in this food chain. In March 1998 a sample was found with an alarming 7.4 pg I-TEQ/g fat in milk from a road tanker (collecting milk from 70 farms on tours to the dairy). The highest PCDD/F content on one of the 12 biggest farms of this tour was 4.8 pg I-TEQ/g fat. Here, a comprehensive search for the PCDD/F source was conducted. All kinds of possibilities were considered (disinfectants, detergents, pesticides [insecticides, herbicides], drugs used in veterinary medicine, paint used for the grain silos and all kinds of feed) and 11 samples were analysed. As result, a compound feed for milk production was identified as having a considerably higher PCDD/F contamination than other feeds or vegetable food. In the absence of maximum or action levels for feed in the 1990s, and based on laboratory data, the background contamination of feeds or vegetable food was concluded to be in the range of about 0.1 to 0.3 ng I-TEQ/kg dry weight. This particular compound feed (with six components) had about 1.8 ng I-TEQ/kg. Whereas five of these single components were in the range of the normal background contamination, citrus pulp pellets (CPP) had about 5.6 ng I-TEQ/kg. These high levels were also found in a second sample taken for confirmation (7.1 ng I-TEQ/kg) (Malisch, 2000a).

As circumstantial evidence, milk and feed from 9 farms were checked. The highest dioxin contamination of milk was found on a
farm where cows were fed up to 8 kg per day of a certain compound feed containing 25% contaminated CPP. Other farms with lower CPP contaminated feed intake per cow had lower dioxin levels in the milk. Four farms had a dioxin contamination in the milk below 0.9 pg I-TEQ/g fat. Two of these farms didn’t feed any compound feed at all; two farms fed a compound feed without contaminated CPP. Thus, the likely source for the dioxin contamination of the milk was evident.

### 2.1.2. Dioxin patterns and transfer factors

The congener pattern of the citrus pulp pellets was unknown: The predominant congener, by far, was OCDF at about 450 ng/kg, followed by 1,2,3,4,6,7,8-HpCDF at about 40 ng/kg. OCDD which is usually much higher than OCDF was determined at about 10 ng/kg. Within the PCDD group, the content decreased from OCDD to hepta- and hexacongeners, but in contrast to the typical pentachlorophenol-related pattern, increased again for TCDD and PeCDD. In contrast, in the milk samples elevated levels of 2,3,4,7,8-PeCDF, HexaCDF and even the milk production in the high performance phase, (up to about 28 to 30 kg compound feed per cow for an increase of the pattern found in the milk. They were calculated based on feeding of a copper substitute had severe supply problems.

Thus, the use of the compound feed could result in the congener pattern found in the milk. They calculated based on feeding of a maximum of up to 8 kg compound feed per cow for an increase of the milk production in the high performance phase, (up to about 28 to 30 kg with 4% fat) as follows:

\[
\text{transfer factor} = \frac{c_{mf}}{c_{cf}} = \frac{pmf}{f}
\]

where

- \(c_{mf}\) concentration in milk fat (pg/g),
- \(c_{cf}\) concentration in feed (pg/g),
- \(pmf\) daily production of milk fat (g),
- \(f\) daily amount of feed intake (g).

The resulting transfer factors for the predominant congeners of the citrus pulp pellets were in line with the findings of Schuler et al. (1997) for bioaccumulation from grass to milk (Table 1). Generally, the transfer depends on the congener and on the matrix. Thus, a relatively wide range of transfer factors is observed. Even in the Schuler study with feeding of grass over a period of two years with four sampling dates, for example a range between 0.06 and 0.7 was observed for 2,3,7,8-TCDD, with an average of 0.3. Therefore, a transfer rate for TEQ-values can be calculated only for the specific situation.

As a result, bioaccumulation from feed to food of animal origin changes the dioxin patterns considerably. Without consideration of the transfer factors, comparison of patterns between feed and food would cause wrong conclusions. In this case, the transfer factors provided further evidence for the identification of the source.

### 2.1.3. Economic and legal consequences on a global scale

Immediately after the discovery of the dioxin source, other federal states of Germany and the European Union were informed. It turned out that an important market was concerned: Citrus pulp pellets were said to be produced at a volume of about 1.5 million tonnes/year, worth about 100 to 150 million US-$. From this huge amount, about 250,000 t were said to have been imported annually into Germany.

The contaminated citrus pulp was removed from the market. In the EU about 92,000 t was blocked (worth about 10 million $) and had to be discarded or destroyed. 12 member states were affected. In some countries of the European Union the CPP market collapsed because its use was stopped completely.

CPP makes up to 25% in compound feed for ruminants and therefore is an important ingredient in such feed. Thus, due to the huge volumes necessary to substitute the blocked citrus pulp, the market for these substitutes had severe supply problems.

Brazil dominates the world market for the production of citrus pulp where the season is from September to February. About 60% of the import into Germany originated there – including the contaminated product. The U.S. is the next most dominant supplier (analysis of a limited number of samples showed background contamination). Thus, many countries were involved either as producers or customers.

The European Union evaluated the use of this contaminated citrus pulp from Brazil as a feed material as a possible risk to human health. Therefore, it was decided in July 1998 to fix a temporary tolerance for dioxins in citrus pulp of 0.5 ng I-TEQ/kg (Commission Directive 98/60/EC). It became the first legally binding maximum level for dioxins in all

### Table 1

Factors for transfer of dioxins from contaminated compound feed to milk and comparison with factors reported for transfer from grass to milk.

<table>
<thead>
<tr>
<th>Dioxin</th>
<th>Milk pg/g fat</th>
<th>Compound feed pg/kg</th>
<th>Transfer factor feed — milk fat</th>
<th>Transfer factor Schuler et al. <em>a, b</em></th>
<th>Mean</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,3,7,8-TCDD</td>
<td>2.39</td>
<td>614</td>
<td>0.58</td>
<td>0.3</td>
<td>0.06-0.7</td>
<td></td>
</tr>
<tr>
<td>1,2,3,4,7,8-HpCDF</td>
<td>1.70</td>
<td>524</td>
<td>0.49</td>
<td>0.2</td>
<td>0.08-0.3</td>
<td></td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDF</td>
<td>0.52</td>
<td>153</td>
<td>(0.51)</td>
<td>0.08</td>
<td>0.05-0.1</td>
<td></td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDF</td>
<td>0.43</td>
<td>85</td>
<td>(0.77)</td>
<td>0.02</td>
<td>nd-0.03</td>
<td></td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDF</td>
<td>0.29</td>
<td>126</td>
<td>(0.35)</td>
<td>0.02</td>
<td>0.004-0.02</td>
<td></td>
</tr>
<tr>
<td>OCDD</td>
<td>0.84</td>
<td>689</td>
<td>(0.18)</td>
<td>0.02</td>
<td>nd-0.03</td>
<td></td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDD</td>
<td>0.97</td>
<td>3960</td>
<td>(0.037)</td>
<td>0.02</td>
<td>0.01-0.04</td>
<td></td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDD</td>
<td>0.13</td>
<td>688</td>
<td>(0.037)</td>
<td>0.02</td>
<td>0.01-0.04</td>
<td></td>
</tr>
<tr>
<td>1,2,3,4,7,8-PeCDF</td>
<td>0.08</td>
<td>325</td>
<td>(0.038)</td>
<td>0.02</td>
<td>0.02-0.05</td>
<td></td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDF</td>
<td>1.09</td>
<td>440</td>
<td>(0.58)</td>
<td>0.5</td>
<td>nd-0.7</td>
<td></td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDF</td>
<td>2.33</td>
<td>1053</td>
<td>0.33</td>
<td>0.07</td>
<td>0.04-0.1</td>
<td></td>
</tr>
<tr>
<td>2,3,4,6,7,8-HxCDF</td>
<td>1.04</td>
<td>515</td>
<td>0.30</td>
<td>0.5</td>
<td>nd-0.7</td>
<td></td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDF</td>
<td>2.23</td>
<td>1724</td>
<td>0.19</td>
<td>0.5</td>
<td>nd-0.7</td>
<td></td>
</tr>
<tr>
<td>1,2,3,4,7,8,9-HpCDF</td>
<td>0.07</td>
<td>&lt;150</td>
<td>–</td>
<td>0.01</td>
<td>0.004-0.02</td>
<td></td>
</tr>
<tr>
<td>1,2,3,4,7,8,9-HpCDF</td>
<td>2.35</td>
<td>11,298</td>
<td>0.031</td>
<td>0.01</td>
<td>0.004-0.02</td>
<td></td>
</tr>
<tr>
<td>OCDF</td>
<td>3.25</td>
<td>133,880</td>
<td>0.004</td>
<td>0.01</td>
<td>0.009-0.02</td>
<td></td>
</tr>
</tbody>
</table>

*a: Dioxin contamination in milk (pg/g fat) of a farm, in the compound feed used on this farm (pg/kg) and the resulting transfer factors.

b: Transfer factors from Schuler et al. (1997).

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Member States. As a consequence, also Brazil set a maximum level of 0.5 ng l-TEQ/kg for dioxins/furans for CPP.

Additionally, the concept of tolerances “including upper bound detection limits” was introduced (Hoogerbrugge and Liem, 2000): The maximum level was set as “upper bound concentration”. That means that, if individual congeners are not detectable, they must be included with the full detection limit for the calculation of the TEQ-level. In this way, inappropriate analytical methods with too high limits of detection would be excluded.

2.1.4. Consequences of this contamination for dioxin intake in Germany

Between autumn 1997 and spring 1998, i.e. for about half a year, distinctly elevated dioxin levels up to a factor of 10, accompanied by characteristic changes in the congener pattern were observed in cow’s milk, milk products, beef and veal in Germany. These products accounted for about 50% of the dietary dioxin intake in Germany. Therefore, the extent of this food contamination with regard to bioaccumulation in humans was checked in four federal states of Germany where data from human milk and cow’s milk were available. The concentrations of single congeners in human milk and blood before (1996/97) and after (1998, 1998/99) the contamination event were compared (Vieth et al., 2002). In conclusion, it was presumed that the use of highly contaminated citrus pulp as a feeding component resulted in an increase of the dioxin body burden of humans in two federal states of Germany, a situation which did not support the federal policy on preventative health care, and on control of exposure to breast-fed babies.

2.1.5. Measures in Brazil to identify the source for the contamination of citrus pulp

The reason for the contamination of the citrus pulp was unknown for a long time. CPP is a by-product from orange juice production: The remaining peels, seeds and pulp are pH-adjusted by the addition of lime, followed by the removal of water via pressing and drying, and are then sold as pellets. The particular PCDD/F pattern did not match any previously established contamination pattern. The production process for CPP identified three possibilities for the route of contamination:

• pesticides in the orange peel,
• fuel oil containing perchloroethylene as additive,
• ingredients such as lime.

Research work on peel containing chlorinated pesticides presented by the Brazilian industry and authorities showed that PCDD/F were not generated during the drying process with detection limits far below the range needed to account for the highly contaminated CPP. The addition of perchloroethylene to fuel oil which was burnt for drying of the pulp was considered as a possible source. The particular PCDD/F pattern did not match any previously established contamination pattern. The production process for CPP identified three possibilities for the route of contamination:

• pesticides in the orange peel,
• fuel oil containing perchloroethylene as additive,
• ingredients such as lime.

In July 1998, the main source was identified as coming from lime (Louis Dreyfus Citrus, 1998; Carvalhaes et al., 2002), which is added to wet peels, seeds and pulps of oranges in order to raise the pH from between 2 and 3 up to between 6 and 7, and constitutes about 2% of the dried CPP. The lime was very highly contaminated: up to 2500 ng l-TEQ/kg was reported as first findings. The dioxin pattern of the lime and of the contaminated CPP showed strong similarities.

The contaminated lime came from one supplier who sourced the lime from the landfill of a chemical company. The lime was primarily used for civil construction. It passed the quality control procedures of the supplier (with quality parameters such as heavy metal content and colour). Therefore, the lime from the landfill site was sold also to the CPP market — without knowledge of the dioxin contamination. More information on sorts of lime and its production was provided for the mission of experts of the European Union which took place in January 1999 to collect information on the progress of the Brazilian competent authorities regarding the investigation on the source of the contamination and to evaluate the established control system (Malisch et al., 1999).

2.1.6. Identification of the source for the contamination of lime

Details about the origin of the PCDD/Fs in the contaminated lime were not revealed until 2008 when Torres et al. presented results of their investigations (Torres et al., 2008, 2013). They had found the link between the dioxin contamination of the lime milk and the chemical processes of a chlorine/organochlorine industry which disposed of waste at the landfill site.

The landfill site was used for more than 30 years for the disposal of lime milk from the vinyl chloride monomer (VCM) production process (for PVC production) and other residues from the company. The factory operated at least two processes with potentially high PCDD/PCDF releases, namely the oxychlorination process for production of ethylene dichloride (EDC) and the chloro-alkali process. The main landfill waste was lime milk (1.4 million tons) from the vinyl chloride monomer production (via the acetylene process) along with residues from other processes. The PCDD/PCDF fingerprint revealed that most samples from the chemical landfill showed an EDC-type PCDD/PCDF pattern with a characteristic octachlorodibenzo-furan dominance.

2.2. From elevated levels found by a bioassay to brominated dioxins

The second example of a forensic examination shows the complex work from first findings of elevated levels in bioanalytical screening to physico-chemical identification of brominated contaminants. So far, it is the only known case where non-chlorinated dioxins and furans could be identified as a source of the contamination, and resulted from comprehensive investigations after bioanalytical screening.

In The Netherlands, RIKILT had tested several samples of the feed additive chlorine chloride as positive in the DR CALUX assay. However, GC/MS analysis could not confirm the presence of PCDD/PCDFs or dioxin-like PCBs. Examination by GC–TOFMS revealed the presence of various brominated flame retardants (BFRs), such as PBDEs and 2,4,6-tribromophenol, but also the new brominated flame retardant octabromo-1,3,3-trimethylphenyl-1-indan (OBIND). These compounds could not explain the positive CALUX-result but indicated the presence of brominated dioxins. This was confirmed by GC/MS analysis, showing in particular 2,3,7,8-TBDF (Traag et al., 2009).

This case shows that the follow-up of well validated “false-positive” samples in the CALUX bioassay by comprehensive analyses (in particular with GC–TOFMS) may actually result in the detection of novel emerging risks, in this case the presence of brominated flame retardants and brominated dioxins in a widely used feed additive. This included a novel BFR, OBIND, that was not detected in feed or food before.

It must be stressed that the bioanalytical screening result has to be well validated, so as not to promote any unconfirmed (by confirmatory HRMS) elevated result as arising from a novel contaminant. There are a number of factors which can cause apparently elevated results. These factors were carefully controlled by RIKILT before the conclusion was drawn to check for brominated contaminants.

Although the levels observed in this case may not directly present a risk for the animals and the consumers, it was evident that during the production or handling of this material it became contaminated with industrial chemicals whose introduction in the food chain was highly undesirable.

2.3. Other major contamination incidents in the food chain at the end of the 1990s

2.3.1. Belgian PCB incident

The Belgian PCB incident occurred at the end of January 1999 when a mixture of polychlorinated biphenyls contaminated with dioxins was accidentally added to a stock of recycled fat used in the production of animal feeds. Although signs of poultry poisoning were noticed by
February 1999, the source and the extent of the contamination were discovered only in May 1999, when it appeared that more than 2500 farms could have been supplied with these contaminated feedstuffs. This resulted in a major food crisis, which rapidly extended to the whole country and could be resolved only by the implementation of a large PCB/dioxin food monitoring programme. At the end of December 1999, the database contained the results of more than 55,000 PCB and 500 dioxin analyses. The total amount of PCBs added to recycled fats was estimated at 50 kg (sum of the seven markers) or approximately 150 kg total PCBs, which corresponds to about 100 l of PCB oil. This PCB mixture contained about 1 g TEQ dioxins (more than 90% contributed by PCDFs) and about 2 g TEQ dioxin-like PCBs (Bernard et al., 2002). In September 1999, the direct costs for Belgium were estimated to be about 1 billion ECU (European Currency Unit; replaced on 1 Jan 1999 by Euro with the conversion ratio 1:1), the indirect costs about 3 billion ECU. In comparison to this, the costs for analyses were negligible (De Poorter, 1999).

3. Exposure assessments carried out before 2001 and tolerable intakes as estimated by scientific committees that are still valid today

It is generally accepted that about 90–98% of the typical exposure of humans to PCDD/F and PCBs results from food, except where there is a history of occupational or other exposure. In different studies, the uptake from ambient sources (ingestion of soil and inhalation of air or dust, water ingestion) and miscellaneous non-food (transfer from paper; cigarette smoking) was estimated to be only in the range of up to 10% of the total average exposure of the adult. Due to bioaccumulation in fatty tissues, food of animal origin is the predominant source of the intake. However, different dietary habits of subpopulations and various cultural, religious and ethnic groups across the world lead to variations in the relative contributions of food groups. When normalized with respect to body weight, exposure is highest for children, in particular babies (Bund-Länder-Arbeitsgruppe DIOXINE, 1992; Wesp and Rippen, 1996; IARC, 1997; liem et al., 2000; Canady et al., 2002).

In contrast to the clear dominance of food to the average exposure of PCDD/F and PCBs, for the brominated flame retardants hexabromocyclododecanes (HBCDDs) and polybrominated diphenyl ethers (PBDEs) and for perfluoralkyl compounds (PFCS) the review of Harrad et al. (2010) underlines the importance of indoor air and dust as a pathway of human exposure. Similar elevation can be expected also for other chemicals arising from the use of household products. Particular concern is raised for young children (frequent hand-to-mouth contact, also of non-food items).

A comprehensive assessment of dietary intake of dioxins and related PCBs by the population of EU Member States was performed as a specific task to provide the European Commission with information on dietary exposure to PCDDs, PCDFs and dioxin-like PCBs in participating countries (EU Scientific Co-operation [SCOOP] Report, 2000). The SCOOP task resulted in a comprehensive database with information on concentrations of PCDDs, PCDFs and dioxin-like PCBs in samples of food products and human milk. Samples were taken from various sites, including rural and industrial sites, and were collected in different years covering the period 1982–1999. The data resulting from some studies were considered representative for the country and suitable for use in intake estimates.

Based on the available data, the EU Scientific Committee on Food (SCF) performed risk assessment of dioxins and dioxin-like PCBs in food (European Commission — Scientific Committee on Food, 2000, 2001). In order to give examples for risk management, the frequency distributions of dioxin and dioxin-like PCB contamination levels in a number of foods of animal origin were derived on the basis of the estimated weighted mean and standard deviation figures. The toxicity of dioxins and dioxin-like PCBs was evaluated. The Committee established a group tolerable weekly intake (TWI) of 14 pg WHO TEQ/kg body weight (bw) for all 2,3,7,8-substituted PCDDs and PCDFs and the dioxin-like PCBs, expressed as WHO TEQ (van den Berg et al., 1998). The Committee wished to stress that, given the average dietary intakes of dioxins and dioxin-like PCBs in the European countries of 1.2–3.0 pg/kg bw per day, a considerable proportion of the European population would exceed the TWI derived by the Committee.

A World Health Organization (WHO) consultation held in 1998 established a tolerable daily intake (TDI) of 1–4 pg/kg body weight, applicable to the toxic equivalents of PCDDs, PCDFs and coplanar PCBs (Van Leeuwen and Yonnes, 2000). Exposure was addressed from different aspects: background, accidental and occupational. It was acknowledged that breast-fed infants are exposed to higher intakes of these compounds on a body weight basis, although for a small proportion of their lifespan. However, breastfeeding is associated with beneficial aspects, in spite of the contaminants present. The subtle effects were found to be associated with transplacental, rather than lactational, exposure. Therefore, conclusions and recommendations of previous WHO meetings were reiterated which promote and support breastfeeding.

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The Joint FAO/WHO Expert Committee on Food Additives (JECFA) is an international scientific expert committee that is administered jointly by the Food and Agriculture Organization of the United Nations (FAO) and WHO. It provides scientific advice to the Codex Alimentarius Commission and was established in 1963 to develop harmonized international food standards and guideline codes of practice to protect the health of the consumers and ensure fair practices in the food trade. The reference made to Codex food safety standards in the World Trade Organizations' Agreement on Sanitary and Phytosanitary measures (SPS Agreement) means that Codex has far reaching implications for resolving trade disputes. WTO members that wish to apply stricter food safety measures than those set by Codex may be required to justify these measures scientifically (Codex Alimentarius Commission, 2014). Therefore, JECFA evaluations are of particular importance at the global level.

In its evaluation in 2001, JECFA derived a provisional tolerable monthly intake (PTMI) of 70 pg/kg of body weight per month for intake of PCDDs, PCDFs and coplanar PCBs expressed as TEQs (Joint FAO/WHO Expert Committee on Food Additives [JECFA], 2002). As the long half-lives of these compounds mean that each daily ingestion has a small or even negligible effect on the overall intake, the total or average intake should be assessed over a longer period, and tolerable intake should be assessed over a period of at least one month. That was the rationale behind expressing the provisional tolerable intake on a monthly basis.

As a conclusion, both of the still valid tolerable intakes (EU SCF: tolerable weekly intake of 14 pg WHO TEQ/kg bw; JECFA: provisional tolerable monthly intake of 70 pg WHO TEQ/kg bw) are comparable (at about 2 pg WHO TEQ/kg bw if expressed on a daily basis).

JECFA also evaluated levels and patterns of contamination of food commodities and calculated the weighted mean and derived median for six food groups, expressed as pg TEQ/g whole food, for North America, Western Europe, Japan and New Zealand. Based on regional diets of the Global Environment Monitoring System — Food Contamination Monitoring and Assessment Programme (GEMS/Food) of WHO and based on national food consumption habits, the median and 90th percentile values of estimated long-term intake of PCDDs, PCDFs and coplanar PCBs were calculated. As a result, the contribution of coplanar PCBs to the total TEQ was similar to the contribution of PCDD/F in European countries and Japan, lower in New Zealand and considerably lower in North America. The sum of the median intake of PCDD/F-TEQ and PCB-TEQ exceeded the PTMI in Western European countries, but was in this range in North America, and lower in Japan and New Zealand. The 90th percentile of PCDD/F-TEQ exceeded the PTMI for the sum of dioxins and dioxin-like PCBs in Western European countries and North America, the 90th percentile of coplanar PCBs in Western European countries.

In 2012, US Environmental Protection Agency (EPA) derived an oral reference dose (RFD) for TCDD of $7 \times 10^{-10}$ mg/kg-day (US Environmental Protection Agency [EPA], 2012).

4. EU Strategy for PCDD/F and PCB and legislative measures concerning feed and food

The incidents in the food chain of the late 1990s triggered a deep concern from the international community for reduction and control of dioxins and PCBs. Moreover, there was considerable public, scientific and regulatory concern over the negative effects on human health and on the environment of long-term exposure to even the smallest amounts of dioxins and PCBs. In particular with regard to the conclusion of EU SCF that the dietary exposure to dioxins and dioxin-like PCBs exceeded the recommended tolerable intake values for a considerable part of the European population, the EU saw a pressing need for further action to avoid environmental and adverse health effects from dioxins and PCBs. The goal was to secure better protection of human health and of the environment from the effects of dioxins and PCBs and to reduce the sources of environmental contamination by these compounds to the lowest possible amounts. This was seen as the best way to reduce human exposure. Therefore, the EU Strategy as an integrated and systematic approach for dioxins and PCB control was developed (Commission of the European Communities, 2001) based on two pillars:

1) to reduce the presence of dioxins and PCBs in the environment;
2) to reduce the presence of dioxins and PCBs in feed and food.

For reduction of these contaminants in the environment, a set of actions was identified for the short- to medium-term (Hazard Identification, Risk Assessment, Risk Management, Research, Communication to the public and Cooperation with third countries and international organisations) and for the long-term (Data Collection, Monitoring and Surveillance, Identification of Measures).

Food of animal origin is a predominant source of human exposure to dioxins and PCBs. As food contamination is directly related to feed contamination, an integrated approach was followed to reduce dioxin/PCB incidence all along the food chain, i.e. from feed materials through food-producing animals to humans. The legislative measures concerning feed and food were proposed to consist of three pillars:

- the establishment of maximum levels at a strict but feasible level in food and feed,
- the establishment of action levels acting as a tool for “early warning” of higher than desirable levels of dioxin in food or feed,
- the establishment of target levels, over time, to bring exposure of a large part of the European population within the limits recommended by the Scientific Committees.

Maximum limits allow the exclusion of highly contaminated products. The establishment of such a limit is a necessary tool for risk management and to ensure uniform application across the EU.

Permanent monitoring of the presence of dioxins and PCBs in feed and food was considered necessary. In the case of an abnormal increase in the level of these compounds, sources and/or pathways of contamination have to be identified. Once identified, appropriate measures to prevent or reduce contamination from the source could be determined and applied. In order to determine what has to be considered as an abnormal increased level, action levels were set. Action levels were designed to trigger a proactive approach from competent authorities and operators to identify sources and pathways of contamination and to take measures to eliminate them. To summarise these legal consequences: whereas samples exceeding maximum limits are discarded from the market, samples exceeding action levels can still be sold on the market, however, measures should be taken to identify and eliminate the source.

Target levels were seen as levels to be achieved in food and feed whereby it can be reasonably assumed that the dietary exposure of a large majority of the European population will be within the tolerable weekly intake for dioxins and dioxin-like PCBs. However, these levels were never established, and later it was decided to remove the target levels and to limit the monitoring strategy to maximum and action levels.

A report summarised the main progress over the first two years (end of 2001 to end of 2003) with the actions for the environment and the actions for feed and food (Commission of the European Communities, 2004).

Based on the statistical descriptors of dioxin concentrations in European food as derived by the EU Scientific Committee on Food (see Section 3), the first maximum levels were established in 2001 for levels of PCDD/F (determined as pg WHO-PCDD/F-TEQ/g fat or product) for meat, meat products and liver, for fish and fishery products, for milk and milk products, for hen eggs and egg products, and for oils and fats (Council Regulation [EC] No 2375/2001). Amendments comprise also other food categories and regulations for PCBs: The recent regulations for food set maximum levels for WHO-PCDD/F-TEQ, WHO-PCDF/F-PCB-TEQ and the sum of 6 indicator PCBs (Sum of PCB 28, PCB 52, PCB...

As established for food, based on the statistical descriptors of dioxin concentrations in European feed as derived by the EU Scientific Committee on Animal Nutrition (SCAN) (European Commission, Scientific Committee on Animal Nutrition (SCAN), 2000) the first maximum levels for dioxins in feed were also established in 2001 (for feed materials of plant origin, minerals, animal fat and other products of animal origin, fish oil, fish meal, and compound feeds, including fish feed) (Council Directive, 2001/102/EC). Again, amendments comprise other feed categories and regulations for PCBs: Also the recent regulations for feed set maximum levels for WHO-PCDD/F-TEQ, WHO-PCDD/F-PCB-TEQ and the sum of 6 indicator PCBs (Sum of PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180). As legal basis, Directive 2002/32/EC of the European Parliament and of the Council provides that any use of products intended for animal feed which contain concentrations of undesirable substances exceeding the maximum levels is prohibited. It furthermore sets action thresholds triggering investigations in cases of increased levels of such substances. Maximum and action levels for feed are now listed in the amendment (Commission Regulation [EU] No 277/2012; Commission Regulation [EU] No 744/2012).

5. Major incidents since 2000 and the Rapid Alert System

A selection of incidents since 2000 with identification of the source shows the wide range of possibilities, of how feed and food can be contaminated with dioxins and PCBs (Table 2). Contamination of feed and food with exceedance of maximum levels can occur at a regional level. Then, local measures are taken. For large-scale incidents, the EU has put in place the Rapid Alert System for Food and Feed (RASFF) to provide food and feed control authorities with an effective tool to exchange information about measures taken responding to serious risks detected in relation to food or feed. This exchange of information helps Member States act more rapidly and in a coordinated manner in response to a health threat caused by food or feed (Rapid Alert System for Food and Feed portal). Examples for RASSF notifications in 2013 were poultry meat from Chile, Baltic salmon from Sweden, pea seeds from Ukraine, pigeon stones from Netherlands, feed pre-mixtures from China, feed additives from USA and soya extraction grist from Italy. This again proves the need to pay attention to the dioxin contamination of feed and food by continuous control, in particular with regard to the huge volumes on the global market.

Table 2
Selection of contamination incidents with dioxins and PCBs.

<table>
<thead>
<tr>
<th>Year</th>
<th>Country</th>
<th>Product</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>Spain</td>
<td>Animal feed</td>
<td>PCP-contaminated saw dust as carrier in pre-mixed choline chloride</td>
</tr>
<tr>
<td>2003</td>
<td>Germany</td>
<td>Animal feed</td>
<td>Use of waste wood for drying of the bakery waste</td>
</tr>
<tr>
<td>2004</td>
<td>Italy</td>
<td>Eggs, meat</td>
<td>Wood-shaving litter</td>
</tr>
<tr>
<td>2004</td>
<td>Netherlands</td>
<td>Milk as result of animal feed</td>
<td>Potato-by-products contaminated by kaolinitic clay</td>
</tr>
<tr>
<td>2006</td>
<td>Netherlands</td>
<td>Pig feed</td>
<td>Waste fat contaminated by a malfunction in gelatine</td>
</tr>
<tr>
<td>2008</td>
<td>India</td>
<td>Guar gum</td>
<td>Use of pentachlorophenol</td>
</tr>
<tr>
<td>2008</td>
<td>Italy</td>
<td>Mozzarella from buffalo milk</td>
<td>Illegal waste burning</td>
</tr>
<tr>
<td>2008</td>
<td>Ireland</td>
<td>Pork and beef</td>
<td>PCB-contaminated fuel for direct drying of animal feed (bakery waste)</td>
</tr>
<tr>
<td>2008</td>
<td>Korea</td>
<td>Pork</td>
<td>Contaminated zinc oxide as feed ingredient from Chile</td>
</tr>
<tr>
<td>2008</td>
<td>Netherlands</td>
<td>Feed additive</td>
<td>Brominated contaminants including brominated dioxins</td>
</tr>
<tr>
<td>2011</td>
<td>Germany</td>
<td>Animal feed</td>
<td>Fatty acids from a biodiesel company</td>
</tr>
</tbody>
</table>

6. Exposure assessments (2012) and time trends in food

After all these efforts it is of general interest to see whether these measures had an effect. An update of the monitoring of levels of dioxins and PCBs in food and feed reflects the current situation in most European countries (European Food Safety Authority [EFSA], 2012). A total of 13,797 samples were assessed for dioxins and dioxin-like PCBs (DL-PCBs) and 19,181 samples for non-dioxin-like PCBs (NDL-PCBs). These samples were submitted between 1995 and 2010 by 26 European countries.

“Meat from eels” and “fish oil and derived products” contained the highest average contamination levels of both dioxins and PCBs. Levels of dioxins and DL-PCBs, and of NDL-PCBs were above the permitted maximum levels in respectively 10% and 3% of the food samples.

Fish, meat and dairy products appeared to be the highest contributing food groups to dietary exposure. Their relative importance depended on age and country of the consumer. The major contributor to total exposure was the food category of milk and dairy products for almost all groups of infants and toddlers, whereas it was fish and seafood for most of the groups of adolescent, adult, elderly and very elderly. Meat and meat products also contributed significantly to total exposure.

Depending on the population group, defined as the combination of age class and the respective survey, average exposure to dioxins and DL-PCBs was estimated to be between 0.57 and 2.54 pg TEQWHO05/kg b.w. per day and the 95th percentile between 1.2 and 9.9 pg TEQWHO05/kg b.w. per day. The percentage of individuals exposed above the Tolerable Weekly Intake (TWI) of 14 pg TEQ/kg b.w. were estimated to be between 1.0 and 52.9%. Toddlers and other children were the most exposed groups (being at the upper end of these ranges).

Average exposure to NDL-PCB indicators was estimated to be between 4.3 and 25.7 ng/kg b.w. per day and the 95th percentile between 7.8 and 53.7 ng/kg b.w. per day.

A general decrease in dietary exposure of dioxins and DL-PCBs was observed between 2002–2004 and 2008–2010, estimated to be between 16.6% and 79.3% for the different population groups. A smaller decrease was observed for NDL-PCBs.

7. Pillars of the feed and food control and network of EU Reference Laboratory and National Reference Laboratories

The EU feed and food law is based on two pillars: (1) the principle that feed and food business operators at all stages of production, processing and distribution within the businesses under their control are responsible for ensuring that feed and food satisfy the requirements of feed and food law which are relevant to their activities; (2) the enforcement of the feed and food law by the Member States and monitoring and verification that the relevant requirements thereof are fulfilled by business operators at all stages of production, processing and distribution. Official controls are organised for that purpose (Commission Regulation [EC] No 882/2004 of the European Parliament and of the Council).

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The designation of EU and national reference laboratories is conceived to produce a high quality and uniformity of analytical results. Thus, there are three levels of public laboratories: (1) Official laboratories designated by the competent authority to carry out the analysis of samples taken during official control, (2) National Reference Laboratories (NRLs), and (3) EU Reference Laboratories (EURLs). The activities comprise organisation of comparative tests, workshops, exchange of information and technical and scientific support to the competent authorities and the Commission. Commission Regulation (EC) No 776/2006 lists all EU Reference laboratories. The list of all NRLs for dioxins and PCBs in feed and food is published at the homepage of the EURL for these tasks (http://www.eurl-dioxin-freiburg.eu/).

8. Screening and confirmatory methods for control of feed and food

As a contribution to the JECFA evaluation in 2001 (see Section 3) general acceptance criteria for dioxin analyses in feed and food samples were developed. The international harmonization of a criteria approach for control of maximum levels (which were derived at that time) was necessary to allow free trade. Quality criteria (QGs) were established for methods applying GC/MS determination (Malisch et al., 2001) and bioassays (Behnisch et al., 2001). These became the basis of the EU regulations as laid down in 2002 for control of food (Commission Directive, 2002/69/EC) and feed (Commission Directive, 2002/70/EC) with amendments as developed by the EURL/NRL network for food (at present valid: Commission Regulation [EC] No 252/2012) and feed (at present valid: Commission Regulation [EU] No 278/2012). The current amendments include the establishment of criteria for use of GC–MS/MS (Kotz et al., 2012) and some clarifications for the role and use of screening and confirmatory methods (for food: SANCO/11562/2013, for feed: SANCO/11950/2013).

Monitoring may be performed for the presence of PCDD/Fs, dioxin-like PCBS and non-dioxin-like PCBS. According to the above mentioned provisions, non-dioxin-like PCBS can be determined by Gas Chromatography/Electron Capture Detection (GC–ECD), GC–LRMS, GC–MS/MS, GC–HRMS or equivalent methods. For analysis of PCDD/Fs and dioxin-like PCBS in food, two different types of methods can be applied:

(a) Screening methods: These should allow a cost-effective high sample-throughput to identify those samples with levels of PCDD/Fs and dioxin-like PCBs that exceed the maximum levels or the action levels, thus increasing the chance to discover new incidents with high exposure and health risks of consumers. Their application should aim at avoiding false-compliant results. Screening methods compare the analytical result with a cut-off value, providing a yes/no-decision over possible exceedance of the maximum or action level. The levels in samples suspected to be non-compliant with the maximum level must be determined/confirmed by a confirmatory method.

In addition, screening methods may give an indication of the levels of PCDD/Fs and dl-PCBs. In the case of application of bioanalytical screening methods, the result is expressed as Bioanalytical Equivalents (BEQ), whereas in the case of application of physico-chemical GC–MS methods it is expressed as Toxic Equivalents (TEQ). The numerically indicated results of screening methods are suitable for demonstrating compliance or suspected noncompliance and give an indication of the range of levels in the case of follow-up by confirmatory methods. They are not suitable for purposes such as evaluation of background levels, estimation of intake, following of time trends in levels or re-evaluation of action and maximum levels.

(b) Confirmatory methods: These methods allow the unequivocal identification and quantification of PCDD/Fs and dioxin-like PCBS present in a sample and provide full information on congener basis. Therefore, these methods allow the control of maximum and action levels, including the confirmation of results obtained by screening methods. Furthermore, results may be used for other purposes such as determination of low background levels in food monitoring, following of time trends, exposure assessment of the population and building of a database for possible re-evaluation of action and maximum levels. They are also important for establishing congener patterns in order to identify the source of a possible contamination. Such methods utilize GC–HRMS. For confirming compliance or non-compliance with the maximum level, also GC–MS/MS can be used.

9. Continuing literature

The recently published book on “Persistent organic pollutants and toxic metals in food” provides valuable information in more detail on a number of different aspects (Rose and Fernandes, 2013).

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