

Dioxins and PCBs in German meat and meat products – Results of a monitoring study with a specific focus on poultry meat

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Introduction

Since 4 November 2006 new maximum residue levels (MRLs) for dioxins and dioxin-like PCBs in animal fats from ruminants, poultry and pigs entered into force in the European Union [1]. The new EU regulation lists maximum residue levels for the sum of dioxins and furans (WHO-PCDD/F-TEQ) and maximum levels for the sum of dioxins, furans and dioxin-like PCBs (WHO-PCDD/F-PCB-TEQ). Furthermore in 2006 the European Commission (DG Sanco) provided a maximum level for the sum of the 6 marker PCBs of 50 µg/kg fat for meat and meat products [2]. Because of a lack of representative data concerning the actual contents of dioxins (17 WHO-PCDD/Fs), dioxin-like PCBs (12 WHO-PCBs) and non-dioxin-like PCBs (6 marker PCBs) in feed and food originating from animals in Germany a project financially supported by the Federal Ministry of Food, Agriculture and Consumer Protection (BMELV) was carried out at the Federal Research Centre for Nutrition and Food (BfEL). In the location of the BfEL in Kulmbach, which coordinates the project, more than 200 samples of feed and about 300 samples of meat/meat products were analyzed until now. The investigation of 200 samples of eggs will follow. In the BfEL locations in Kiel and Hamburg milk/milk products and fish were investigated.

In order to get a representative overview of the contamination levels of these toxicologically relevant substances about 300 representative samples of German meat and meat products were analysed in the years 2005 and 2006. Samples were collected in consideration of the different geographic regions and the actual food pattern in Germany. Approximately 50 percent of the samples were meat and 50 percent were meat products.

Materials and methods

Samples

Meat samples of beef, pig and poultry were taken in small butcheries in Germany. Samples of meat products (pork sausage, liver sausage, salami and bacon) were taken at quality competitions of the German Agricultural Society (DLG).

Analytical procedures

The analytical procedure followed the method described by Kleinhenz et al. [3]. Accelerated solvent extraction (ASE), GPC, chromatography with florisil and a final chromatography on activated charcoal were used as clean-up steps before determining the analytes in the samples with GC-High-Resolution MS (GC-HRMS).

Accelerated solvent extraction (ASE)

The extraction cells (33 mL) were filled with freeze-dried sample material, drying substance and sea sand. Extractions were performed by ASE 200 from Dionex: For extraction, n-hexane was used at a pressure of 100 bar and a temperature of 100°C. The samples were extracted in two cycles with a static time of 10 min each. The solvent of the extraction was removed with nitrogen in a water bath at 40°C.

Gel permeation chromatography (GPC)

To the extract of ASE (4 g fat) the internal standards with ¹³C₁₂-labeled PCDD/F (17 WHO-PCDD/F), dioxin-like PCBs (12 WHO-PCBs) and non-dioxin-like PCBs (6 marker PCBs) were

added. The GPC was done to remove higher molecular weight compounds from the sample (about 1 g fat/injection). Wasting times of 0-28 min and collecting times of 28-38 min were selected. For GPC, a LC glass column with an inner diameter of 25 mm was filled with 60 g Bio-Beads S-X3. GPC (Abimed Gilson, Langenfeld, Germany) was carried out with a solvent mixture of cyclohexane:ethyl acetate (1:1) and a flow rate of 5mL/min.

Clean-up with florisil

The samples were evaporated under reduced pressure, carefully brought to dryness with nitrogen and dissolved in 1 mL toluene. Florisil, calcined for 12 h at 550°C, was deactivated with 4% water, and 3 g were filled into commercial disposable 8-mL SPE columns (id 12 mm). After conditioning of the columns with 10 mL toluene, the samples were applied and eluted with 60 mL toluene to remove more polar compounds.

Clean-up with activated charcoal

An LC glass column with an id of 12.5 mm was filled with 250 mg activated charcoal (Supelclean ENVI-Carb). For conditioning of the column, one blank run was made with a flow rate of 5 mL/min following program: (1) 20 mL solvent mixture 1 (n-hexane/toluene; 99:1); (2) 20 mL solvent mixture 2 (n-hexane/toluene; 75:25); (3) 60 mL toluene (back-flush mode); and (4) cleaning and conditioning of the column with toluene and solvent mixture 1 in both flow directions to use the column material again for a new sample.

Samples were concentrated to a volume of 1 mL and fractionated with the mentioned program. In the first fraction (20 mL n-hexane/toluene; 99:1) the di- and mono-ortho-substituted PCBs, and in the second fraction (20 mL n-hexane/toluene; 75:25) the non-ortho-substituted PCBs were collected. In the third fraction (60 mL toluene) the PCDD/Fs were collected in back-flush mode.

GC/HRMS

The GC/HRMS system used was a Trace GC Ultra gas chromatograph (Thermo Fisher Scientific, Milan, Italy) with an injection in split/splitless mode and combined with a DFS High Resolution GC/MS (Thermo Fisher Scientific, Bremen, Germany). A ZB-5ms column (id 0.25 mm, film thickness 0.25 µm, 5% polysilarylene, 95% polydimethylsiloxane) from Phenomenex (Torrance, CA, USA) with a length of 60 m was used with helium purity 5.0 as carrier gas. The GC program for the PCDD/F measurement was as follows: 80°C (1 min) to 210°C (5 min) at 25°C/min, to 240°C (5 min) at 5°C/min and subsequently at 5°C/min to 320°C, then maintained for 10 min at 320°C. For PCBs the following GC program was used: 70°C (2 min) to 180°C (0 min) at 30°C/min, to 290°C (0 min) at 5°C/min and subsequently at 20°C/min to 320°C, then maintained for 10 min at 320°C. PCDD/Fs and PCBs were measured working in the electron impact (EI) positive ion mode with an electron energy of 35eV, the source temperature was set at 250°C. Data were recorded in selected ion recording mode. The resolution of the mass spectrometer was tuned up to 10000 (10% valley definition).

Results

Levels of dioxin-like and non-dioxin-like PCBs in meat samples

Within this representative study 161 meat samples (55 pork samples, 49 poultry samples and 57 beef samples) were analysed according to their contents of dioxin-like PCBs and marker PCBs. Beef showed the highest contamination levels with dioxin-like PCB, followed by poultry and pork. The median concentration of the WHO-PCB-TEQ for beef was 0.9 ng/kg fat. Poultry showed a median of 0.11 ng WHO-PCB-TEQ/kg fat and consequently more than a factor of 10 below the action level of 1.5 ng/kg fat. The action level for poultry was exceeded for only one sample. The median for the WHO-PCB-TEQ for pork was 0.06 ng/kg fat. In the group of poultry meat 35 chicken samples and 14 turkey samples were analysed. It was shown that turkey samples showed a higher content of dioxin-like PCBs (median 0.16 ng WHO-PCB-TEQ/kg fat) than chicken samples (median 0.09 ng WHO-PCB-TEQ/kg fat).

In addition to the dl-PCBs also the contents of the 6 marker PCBs (PCB 28, 52, 101, 138, 153, 180) were analysed. In 2006 the European Commission (DG Sanco) provided a maximum level for the sum of the 6 marker PCBs of 50 µg/kg fat for meat and meat products [2]. In this context there is no differentiation between the meat of ruminants, poultry and pigs. In the present study for meat of pig and poultry a median concentration of the sum of the 6 marker PCB in the range 1-2 µg/kg was found, for meat of cattle about 5 µg/kg. Consequently for poultry in Germany median concentrations for the sum of the 6 marker PCB were more than a factor of 25 below the provided maximum levels. Only one poultry sample showed a concentration above the concentration of 50 µg/kg. With respect to the marker-PCBs turkey meat (median for the sum of the 6 marker PCBs 2.1 µg/kg fat) showed higher concentrations than chicken meat (median 1.3 µg/kg fat). Within the group of meat products 133 samples (mainly produced of pig meat) were analysed. The median concentrations of the WHO-PCB-TEQ in the investigated meat products were in the range of 0.06 to 0.13 ng/kg fat and therefore comparable with the WHO-PCB-TEQ found in pork and poultry meat.

Levels of dioxins and dioxin-like PCBs in meat samples

The concentration of dioxins in poultry and pork (median of WHO-PCDD/F-TEQ 0.1 ng/kg fat each) were significantly lower than in beef (median of WHO-PCDD/F-TEQ 0.24 ng/kg fat). The maximum levels (without outliers and extreme values) for meat of pigs and poultry were 0.2 ng WHO-PCDD/F-TEQ/kg fat and about 1.3 ng WHO-PCDD/F-TEQ/kg fat for meat of cattle. The maximum levels for pork (1 ng/kg fat), poultry meat (2 ng/kg fat) and beef (3 ng/kg fat) were not exceeded for all types of meat.

Consequently the contaminations with dioxins and dioxin-like PCBs (WHO-PCDD/F-PCB-TEQ) in German meat and meat products were in median definitely below the maximum levels. Poultry meat showed a median concentration of 0.22 ng WHO-PCDD/F-PCB-TEQ/kg fat which was significantly lower than the median contamination level of beef meat (1.21 ng WHO-PCDD/F-PCB-TEQ/kg fat) and was in the range of pork (0.17 ng WHO-PCDD/F-PCB-TEQ/kg fat). With the exception of a few outliers the observed maximum concentration for poultry meat was 0.39 ng WHO-PCDD/F-PCB-TEQ/kg fat and therefore more than a factor of 10 below the maximum level (4 ng/kg fat).

Conclusions

Within the presented study it was shown that the contents of dioxins and dl-PCBs in all investigated types of meat were significantly below the maximum levels. Also the contents of the sum of the 6 marker PCBs were all far below the provided maximum level of 50 µg/kg. In comparison to a representative dioxin study in Germany about 10 years ago the dioxin concentrations especially in poultry and beef decreased significantly. This shows, that the legal regulations to reduce the emission of dioxins were successful. The concentrations of dl-PCB in feed and food originating from animals were included in the representative study for the first time. In a further study in about 10 years temporal trends of dl-PCBs in feed and food originating from animals should be investigated.

References

- [1] Commission Regulation (EC) No 199/2006 of 3 February 2006.
- [2] http://www.bfr.bund.de/cm/208/vorgeschlagene_eu_hoechtsgehalte_fuer_nicht_dioxinaehnliche_polychlorierte_biphenyle.pdf.
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Keywords

dioxins, dioxin-like PCBs, marker PCBs, meat, meat products