PCDD/PCDF Formation in Smoked, Fried and Broiled Meat and Fish

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Introduction

According to our knowledge no investigations were made as to whether the process of smoking, frying or charcoal-grilling of meat and fish leads to additional accumulation of polychlorinated dibenzodioxins and dibenzofurans in these products.

We therefore analyzed several samples of smoked meat, sausage and fish, charcoal-grilled meat and fat that had been used for deep frying fish.

Analytical procedure

After homogenisation, freeze drying and addition of $^{13}C_{12}$-PCDD/PCDF-standards the samples were extracted with hexane. The extracts were treated with conc. H_2SO_4. Up to 60 g of fat could be removed in this way. After chromatography on Alumina B Super I and a carbon column, analysis by HRGC/LRMS was carried out. For the isomer-specific analysis, capillary columns with a polar GC-phase (CP-Sil 88) and a Finnigan MAT 8230 were used.

Results

PCDD/PCDF in cold smoked meat

In all 5 samples of cold smoked pork and sausages measured, we were able to detect non-2,3,7,8-substituted PCDD/PCDF in addition to the normally found 2,3,7,8-substituted PCDD/PCDF. The analytical result of a representative salami sample is shown in table 1.

The patterns were characteristic for PCDD/PCDF formation under conditions of incomplete combustion as illustrated in figure 1a for the Cl_4DF isomer pattern of a bacon sample.

The PCDD/PCDF concentrations in the cold smoked samples (expressed as 2,3,7,8-TCDD-equivalents (TEQ)), are, on an average, about twice as high as those of the four raw pork and fat samples analyzed (figure 2).

PCDD/PCDF in hot smoked fish

In 4 samples of hot smoked fish, non-2,3,7,8-substituted PCDD/PCDF were found only for Cl_4DF and Cl_5DF as shown in table 1 for the meat of a mackerel. This can be explained by the comparatively short duration of smoking (about 20 min).

Figure 3 shows that significantly increased amounts of (all) PCDD/PCDF were detected only in meat and skin of a trout which had fallen into the fire during smoking.

PCDD/PCDF in charcoal-grilled meat

3 pork chops were broiled for 20 min on a charcoal grill to a well done state. Temperatures between 125 and 215°C were measured under the grill.

2 samples showed PCDD/PCDF concentrations as in the raw meat (R1 in figure 1). In the third sample, which was salted (1% salt) before broiling, the isomer patterns of incomplete combustion of non-2,3,7,8-substituted PCDD/PCDF were detected in comparatively high concentrations (table 1). Figure 1b shows the isomer pattern of the Cl_4DF of this pork chop.

PCDD/PCDF in pan fried meat

In a steel pan four times 2 pork chops were fried in coconut oil free of PCDD/PCDF to a very well done state. Some of the pieces were salted. The temperatures in the pan ranged from 140 to 264°C. No distinct difference in PCDD/PCDF concentration before and after frying could be detected. In the gravy of two samples only low concentrations of Cl_8DF were found.

PCDD/PCDF in fat used for deep frying fish

150 salted carps were fried within one day in 15 l of pork fat at 180-200°C. The PCDD/PCDF content of the fat expressed as TEQ (NATO/CCMS) increased about 7-fold as a result of enrichment of 2,3,7,8-substituted PCDD/PCDF from the carps. In addition, a de novo formation of Cl_4DF and Cl_5DF was noticed (table 1). Figure 1c shows the isomer pattern of the Cl_4DF.

Conclusions

According to this preliminary study the additional uptake of PCDD/PCDF from **smoked, fried and charcoal-grilled** meat and fish is marginal compared to the PCDD/PCDF already present in raw fish and meat.

The additional uptake through the consumption of **cold smoked meat** is calculated to about 3% of the total average daily uptake of PCDD/PCDF via food (table 2).

The additional uptake through smoked fish and fried meat and fish is not measurable.

In the case of (salted) charcoal broiled meat further investigations are necessary.

Table 1: PCDD/PCDF concentrations of some characteristic smoked, charcoal-grilled and fried samples

Sample	Salami cold smoked pg/g fat	Mackerel hot smoked pg/g fat	Pork Chop charcoal-grilled pg/g fat	Used Fat deep frying pg/g fat
Sum non-2,3,7,8-TetraCDD	0.22	n.n.	3.13	n.n.
2,3,7,8-TetraCDD	*0.07*	*0.48*	*0.13*	*0.07*
Sum non-2,3,7,8-PentaCDD	0.51	n.n.	7.42	n.n.
1,2,3,7,8-PentaCDD	*0.34*	*0.76*	*0.77*	*0.16*
Sum non-2,3,7,8-HexaCDD	1.00	n.n.	4.92	n.n.
1,2,3,4,7,8-HexaCDD	*0.84*	*(<0.20)*	*0.33*	*0.14*
1,2,3,6,7,8-HexaCDD	*1.07*	*(<0.20)*	*0.42*	*0.33*
1,2,3,7,8,9-HexaCDD	*0.30*	*(<0.20)*	*0.28*	*0.06*
1,2,3,4,6,7,9-HeptaCDD	2.59	n.n.	3.84	0.26
1,2,3,4,6,7,8-HeptaCDD	*7.91*	*(<0.56)*	*6.41*	*2.23*
OctaCDD	55	(<4.4)	35	18
Sum PCDD	**70**	**1.24**	**62**	**21.4**
Sum non-2,3,7,8-TetraCDF	0.92	5.12	22.6	2.18
2,3,7,8-TetraCDF	*0.08*	*16.7*	*0.78*	*1.76*
Sum non-2,3,7,8-PentaCDF	0.94	2.15	14	2.02
1,2,3,7,8-PentaCDF	*0.15*	*0.43*	*1.17*	*0.42*
2,3,4,7,8-PentaCDF	*0.85*	*1.25*	*0.91*	*0.69*
Sum non-2,3,7,8-HexaCDF	1.05	n.n.	3.41	n.n.
1,2,3,4,7,8-HexaCDF	*0.60*	*(<0.07)*	*0.92*	*0.16*
1,2,3,6,7,8-HexaCDF	*0.61*	*(<0.07)*	*0.65*	*0.16*
1,2,3,7,8,9-HexaCDF	*(<0.05)*	*(<0.03)*	*(<0.22)*	*(<0.03)*
2,3,4,6,7,8-HexaCDF	*0.47*	*(<0.03)*	*0.22*	*0.07*
Sum non-2,3,7,8-HeptaCDF	0.57	n.n.	n.n.	0.13
1,2,3,4,6,7,8-HeptaCDF	*6.83*	*(<0.12)*	*2.01*	*0.53*
1,2,3,4,7,8,9-HeptaCDF	*0.20*	*(<0.05)*	*(<0.16)*	*0.02*
OctaCDF	3.67	(<0.40)	(<1.4)	0.31
Sum PCDF	**17**	**26**	**47**	**8.45**
TEQ BGA	**0.86**	**2.47**	**1.46**	**0.55**
TEQ NATO/CCMS	**1.28**	**3.18**	**1.51**	**0.83**

Table 2: Estimated uptake of PCDD/PCDF by consumption of smoked meat and fish

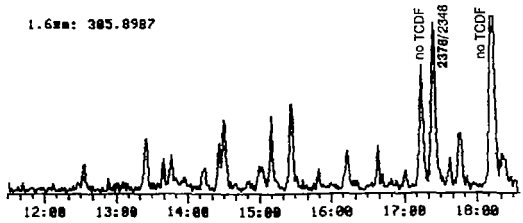
Foodstuff	Estimated intake g/day	Smoked samples TEQ NATO/CCMS pg/g fat	Raw samples TEQ NATO/CCMS pg/g fat	Additional PCDD/PCDF-intake TEQ NATO/CCMS
Cold smoked meat	5,3 (fat)	0,97 (n=5)	0,42 (n=4)	**2,9 pg/day**
Cold smoked fishes	0,2 (fat)	4,9 (n=1)	—	**ca. 0***
Hot smoked fishes		3,8 (n=3)	10,0 (n=1)	**ca. 0****
Sum of smoked meat and fishes	5,5 (fat)			**2,9 pg/day**

* Consumption very small
** Additional PCDD/PCDF-amounts negligible

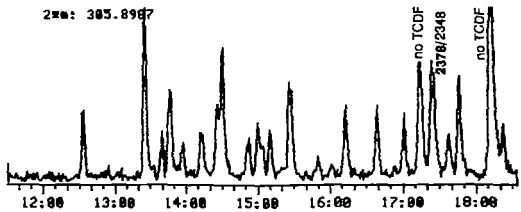
The average daily uptake of PCDD/PCDF via food is calculated by BECK et al. to about 93.5 pg TEQ (BGA) (Chemosphere 18 (1-6), 417 (1989)).

Figure 1: Comparison of the TCDF isomer patterns of cold smoked, charcoal-grilled and fried samples with those of the fly ash extract of a municipial waste incinerator

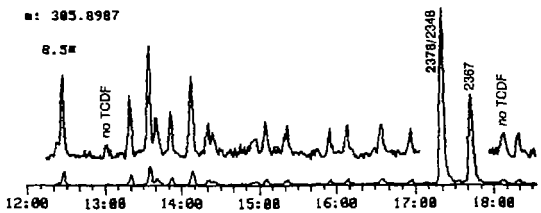
a) cold smoked bacon



b) charcoal-grilled salted pork chop



c) pork fat used for deep frying carps



d) fly ash extract of a municipial waste incinerator

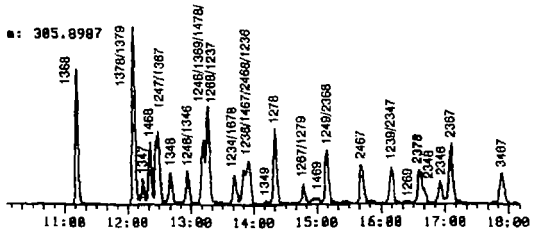


Figure 2: PCDD/PCDF concentrations of cold smoked and raw pork samples, expressed as TEQ (NATO/CCMS)

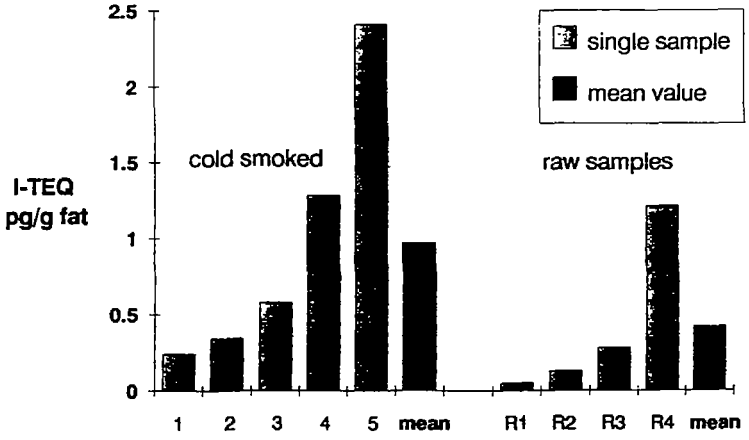


Figure 3: PCDD/PCDF concentrations of hot smoked and raw fishes, expressed as TEQ (NATO/CCMS)