Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Smoked Meat Products

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Introduction

In industrialized countries polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) are widespread in the environment. Due to their bioaccumulation potential PCDD/F are accumulated in the food chain. Consequently food is the main source of human PCDD/F exposure [1, 2]. In Germany the average daily PCDD/F intake via food has decreased significantly within the past few years as a result of improvements in emission control measures [3, 4].
Besides the transfer of toxic compounds from environment to food, a direct contamination of food during production and processing can occur. Smoke utilized for curing of meat and fish is considered be an important source of carcinogenic polycyclic aromatic hydrocarbons (PAH) ingested by humans [5]. PAH are formed during the incomplete combustion of wood in smoke generators. Since PCDD/F can also be formed during combustion, the treatment of food with curing smoke could be a source of PCDD/F contamination. To investigate the relevance of this route of exposure, 41 smoked ham samples produced in southern Germany were analyzed. Results were compared to PCDD/F levels determined in untreated pork samples.

Material and Methods

All samples were analyzed within the framework of official food monitoring in the federal state Bavaria in southern Germany. Smoked ham samples, including so-called black smoked hams were collected directly at the producers. Prior to analysis non-edible parts were removed and weight and size of the products were determined. For sample preparation only the outer parts of the products (outer layer of about 1 cm thickness) were used because it was assumed that PCDD/F derived from curing smoke should be concentrated at the surface of the products. The weight of the separated parts was determined and the material freeze-dried. Fat was isolated by extraction with n-hexane/acetone (2+1). After addition of a mixture of 15 $^{13}C_{12}$-labeled standards a clean-up with three chromatographic steps (mixed acid-base-silica, charcoal,

florisil) was carried out. Determination of PCDD/F was performed by HRGC/HRMS on a AutoSpec Ultima mass spectrometer at a resolution of 10,000 in the selected ion mode. Isomeric specific separation of PCDD/F was carried out on a DB5-ms capillary column. For calculation of I-TEQ values TEFs according to NATO/CCMS were used [6]. Results were expressed on fat basis for comparative purposes and on basis of the edible parts for assessment of dietary intake.

Results and Discussion

In table 1 fat based PCDD/F contents of the outer parts of smoked ham samples and PCDD/F contents of pork samples are compared.

Table 1: PCDD/F in smoked ham samples compared to pork [pg I-TEQ/g fat]

	n	min.	max.	mean	median
smoked ham (outer parts)	41	0.08	85	6.2	0.33
untreated pork	21	0.09	1.2	0.31	0.31

Almost all pork samples showed low contamination levels below 0.5 pg I-TEQ/g fat. Only two samples had slightly increased levels exceeding 1 pg I-TEQ/g fat.
61 % of the analyzed smoked ham samples also revealed very low contamination levels below 0.5 pg I-TEQ/g fat. This situation was reflected by identical median I-TEQ values of smoked ham samples and pork samples. On the other hand the mean I-TEQ value of smoked ham samples was clearly elevated compared to the mean I-TEQ value of pork due to high contamination levels of several smoked ham samples. The maximum value of 85 pg I-TEQ/g fat was equivalent to the 270-fold of the background contamination of pork.
Although fat based I-TEQ results of the outer parts of smoked samples are not suitable for assessment of dietary intake, they indicate that the surface of smoked food can be contaminated with high amounts of PCDD/F.

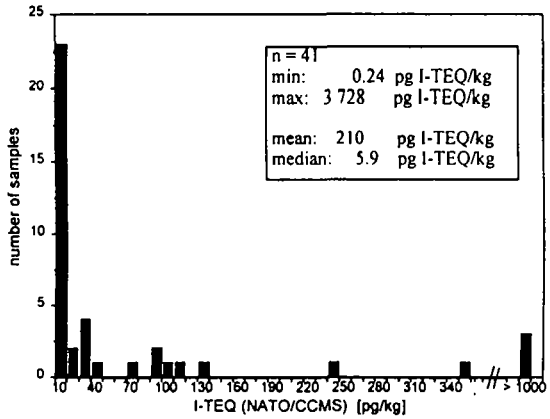

Figure 1: PCDD/F in the edible part of smoked ham samples

Figure 1 shows the distribution of I-TEQ results based on the edible parts of smoked ham samples. Considerable variations in PCDD/F levels ranging from 0.2 to 3700 pg I-TEQ/kg were observed. Three groups of contamination levels can be distinguished in the frequency histogram. The majority of samples (73 %) was weakly contaminated with I-TEQ values below 40 pg/kg. Eight samples showed increased PCDD/F levels between 60 and 350 pg I-TEQ/kg and three samples revealed high contamination ranging from 1700 to 3700 pg I-TEQ/kg.

Characteristic PCDD/F homolog profiles of untreated pork and of three smoked ham samples with different contamination levels are presented in figure 2. In pork samples PCDD homologs increased with the degree of chlorination and the higher chlorinated PCDD homologs clearly dominated PCDF homologs (A in figure 2). This profile represents background contamination of pork. PCDD/F homolog profiles of low contaminated smoked ham samples were very similar to profiles of pork (B in figure 2). PCDD/F levels of these samples can be attributed mainly to the body burden of the slaughtered animals. However, smoked ham samples with higher contamination revealed PCDD/F homolog profiles very different from the profiles of background contaminated samples. In these cases tetra- and pentachlorinated PCDF homologs were present in high amounts (C, D in figure 2).

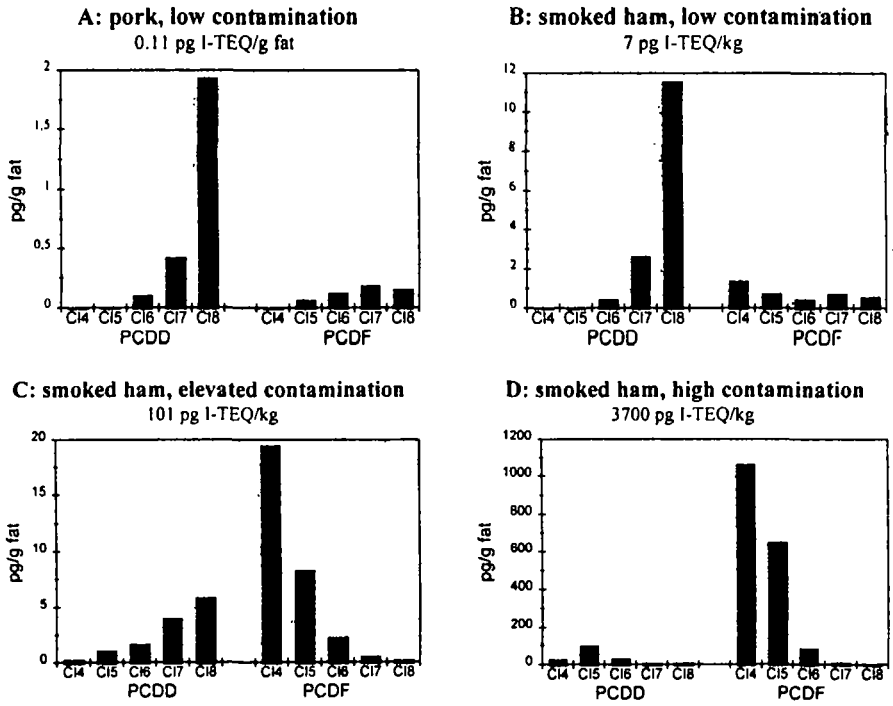

Figure 2: PCDD/F homolog profiles of pork and smoked ham samples

In contrast to pork samples, non-2,3,7,8-substituted PCDD/F were present in most smoked meat products. In smoked samples with increased contamination high concentrations of these congeners were observed and even in samples with low I-TEQ results non-2,3,7,8-substituted PCDD/F were detectable. The PCDD/F homolog profiles together with isomer patterns of homolog groups point to a thermal source responsible for increased PCDD/F levels in smoked products.

All observations together suggest that the smoking process is a potential PCDD/F source that can cause high contamination levels at the surface of the smoked goods. Smoked meat products, like so-called black smoked ham are regional food specialities in Germany and people who like this kind of food may consume these products in considerable amounts. The average daily consumption of 10 g of the smoked ham with the highest contamination level found in this study (3700 pg I-TEQ/kg) would result in a daily intake of 37 pg I-TEQ or 0.53 pg I-TEQ/kg body weight/day, respectively. This value corresponds to half of the actual average daily PCDD/F intake via food in Germany [3,4]. Consequently, the regular consumption of high contaminated smoked meat products would lead to a significant increase of dietary PCDD/F intake.

On the other hand, the results clearly shows that in most cases smoking of meat products did not produce increased PCDD/F contamination or amounts of PCDD/F derived from smoking were very low. The formation of curing smoke in the smoke generator and the transfer of the compounds to the smoking chamber are determined by a number of factors. In more detailed studies the parameters responsible for PCDD/F formation should be identified. Efforts should be undertaken to prevent this additional route of human PCDD/F exposure.

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References

1. Beck H, Droß A and Mathar W; Chemospere **1992**, 25, 1539-1550
2. Fürst P, Fürst Chr and Groebel W, Chemosphere **1990**, 20, 787-792
3. Fürst P and Wilmers K, Organohalogen Compounds **1997**, 33, 116-121
4. Malisch R, Organohalogen Compounds **1996**, 28, 277-280
5. Tóth L, Chemie der Räucherung **1983**, Verlag Chemie, Berlin
6. NATO/CCMS. *International toxicity equivalency factors (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds.* North Atlantic Treaty Organisation, Brussels, report n. 176, **1988**