# BACKGROUND CONTAMINATION OF FRUIT AND VEGETABLES WITH PCDDs, PCDFs, DIOXIN-LIKE PCBs AND NON-DIOXIN-LIKE PCBs IN GERMANY

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## Introduction

The determination of PCDDs, PCDFs (PCDDs/Fs) and PCBs in fruit and vegetables represents an analytical challenge as levels of those compounds prove to be very low in that sort of food and therefore are hardly detectable. Consequently respective data are scarce, especially when the complete spectrum of those compounds has to be taken into account. Notwithstanding the complexity of the task, reliable data about background contamination are necessary in general and in particular to support positions and protective provisions of the Commission of the European Union such as setting of maximum levels, action levels and target levels.[1,2]

## Materials and Methods

One hundred samples of vegetables, fruit and grain were collected between July and October 2004 in equal measure in all parts of Germany, north, east, south, west and centre, in purely rural areas as well as in regions with higher population density. Within the four fruit and vegetable categories mentioned below, ten samples of every kind were analyzed for PCDDs/Fs, dioxin-like PCBs (dl-PCBs) and non dioxin-like PCBs (ndl-PCBs): below ground growing vegetables (carrots, potatoes), above ground growing vegetables and fruit (cauliflower/kohlrabi, zucchini, strawberries), leafy vegetables at ground level (lettuce, white cabbage) and vegetables and fruit growing far above ground level (beans, apples, grain).

Methods of sampling and analysis were performed in compliance with Commission Directive 2004/44/EC.[3] The PCDDs/Fs and dl-PCBs results were summarized as WHO-PCDD/F-TEQ and WHO-PCB-TEQ concentrations by using the toxic equivalent factors (TEFs) from WHO and expressed in pg/g on a fresh weight basis.[4] The total TEQ (WHO-TEQ) concentration in a sample is the the sum of both WHO-PCDD/F-TEQ and WHO-PCB-TEQ concentrations. For ndl-PCBs, concentrations of the congeners PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180 were measured and summed up to Σ6PCB concentration in pg/g on a fresh weight basis. For calculating TEQs and Σ6PCB all non-quantified congeners contribute with the limit of quantification (upper bound).[5]

The analysis concentrated on the edible parts only. Adherent matter such as soil, fouly parts, non-edible leaves or stems were removed manually or exceptionally by slight brushing. Peeling and washing were performed only where these methods are generally applied: peeling of potatoes and kohlrabi, washing of strawberries and lettuce. Edible parts of the samples were freeze dried and extracted by using soxhlet (toluene). $^{13}C_{12}$-labeled internal standards for PCDDs/Fs and PCBs were added prior to the extraction. Cleanup (following the method in accordance with the German Sewage Sludge Ordinance (Appendix 1)) was based on mixed silica column and aluminium oxide column methods.[6] Non-ortho and mono-ortho PCBs were separated into two different fractions on another aluminium oxide column. Gelpermeation chromatography with Bio-Beads S-X3 presented the final clean-up step. Measurements of PCDDs/Fs, dl-PCBs and ndl-PCBs were performed by using HRGC/HRMS: Varian 3400 gas chromatograph equipped with a cold injection system (Gerstel KAS), a DB-Dioxin column, and a DB-5 column for PCDDs/Fs and PCBs, respectively; Finnigan MAT 90 HRMS at a resolution 8,000 – 10,000. The surrogate standards for quantification included one PCDD/F and three dl-PCB congeners. Typical limits of quantification (LOQ) were in the range of 0.003 - 0.004 pg WHO-PCDD/F-TEQ/g, 0.001 – 0.002 pg WHO-PCB-TEQ/g and 0.6 – 2.0 pg Σ6PCB/g. This corresponds to most PCDD/F, non-ortho PCB, mono-ortho PCB and ndl-PCB congeners with LOQs in the range of 0.001 - 0.002, 0.002 - 0.015, 0.03 - 0.3 and 0.1 – 0.3 pg/g, respectively. Recovery rates were in-between 60 and 120 %. A self-imposed blank level criteria of below 0.002 pg WHO-TEQ/g for the whole method could be met over the entire measuring period. Variation of a project specific reference sample, representing a typical contamination level was below the 15 % criteria at that time. The differences between upper and lower bound levels were below 30 % at a contamination level of approximately 0.02 pg WHO-TEQ/g and consequently can be considered as fulfilling the requirements of EU food legislation concerning PCDDs/Fs and PCBs.[3,5]

**Results and Discussion**

The concentrations (upper bound[5], on a fresh weight basis) of WHO-PCDD/F-TEQs, WHO-PCB-TEQs, (total) WHO-TEQs and Σ6PCB found in the respective ten fruit and vegetable items were detailed and summarized in terms of minimum, mean, maximum, median (50$^{th}$ percentile), 25$^{th}$ and 75$^{th}$ percentile in Table 1.

The median PCDD/F and dl-PCB levels were very low and similar to each other with values between 0.004 and 0.012 pg WHO-PCDD/F-TEQs/g and between 0.001 and 0.005 pg WHO-PCB-TEQs/g. Most of the respective maximum levels were not even distinctly higher. Partly because of many congener concentrations being close to LOQs, WHO-PCDD/F-TEQ and WHO-PCB-TEQ concentrations in some cases just slightly exceeded 0.010 pg/g except for zucchini and lettuce. The highest levels found in the latter two vegetables were respectively 0.056 and 0.022 pg WHO-PCDD/F-TEQs/g, and 0.040 and 0.011 pg WHO-PCB-TEQs/g. Even these relatively higher concentrations were distinctly lower in comparison to action levels of 0.4 pg WHO-PCDD/F-TEQ/g and 0.2 pg WHO-PCB-TEQs/g fixed by the EU (Commission recommendation) to stimulate the identification of sources of contaminations above average in order to take measures for reduction or elimination.[2]

Since soil-plant transfer of PCDDs/Fs was found to be highest in the cucumber family (Cucurbitaceae), the very high levels in some zucchini were not surprising[7]. In comparison to food of animal origin, relatively distinct concentrations of non-2,3,7,8-substituted PCDD/F congeners were found in food of vegetable origin. The respective levels were up to twice as high as those of the 2,3,7,8-substituted congeners. Regarding PCDDs/Fs, the congeners 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD and regarding PCBs, the two congeners PCB 126 and PCB 118 contributed most to the respective TEQs. OCDD, 2,3,4,7,8-PeCDF, 2,3,7,8-TCDF, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF were found to be the most abundant PCDD/F congeners.

Considering WHO-PCDD/F-TEQ, WHO-PCB-TEQ and WHO-TEQ, the mean level of all 100 samples amounted to 0.006, 0.004 and 0.01 pg/g, respectively. Based on an assumed daily average consumption of approximately 400 g of fruit and vegetables (excepted vegetable oil) per person, respective intakes of about 2 and 3 pg/person/day corresponding with 0.04 pg WHO-PCDD/F-TEQ and 0.07 pg WHO-TEQ/kg person/day were calculated. Such intakes through fruit and vegetables (excepted vegetable oil) are estimated to represent a share of approximately 5 % of the total intake of WHO-PCDD/F-TEQs and WHO-TEQs in food.[8]

WHO-PCB-TEQ contribution to WHO-TEQs was generally minor except for beans and apples (growing far above ground level) where it was higher than the contribution of WHO-PCDD/F-TEQ. Since many congener levels were close or equivalent to LOQs, we cannot deduce more comprehensively from the data in Table 1. For the same reason expected variety of levels depending on agglomeration (rural or more urban-like) could not be confirmed. Geographical differences (northern, eastern, southern, western and central Germany) did not seem to play any role at all. Finally, emphasis must be placed on the fact that the number of analyzed samples was deemed unsufficient to allow for extensive conclusion. Alternatively, while no differences were found, yet one could presume that those are relatively low, especially when referring to the action levels in EU legislation.[2]

The overall median and mean Σ6PCB level (n=100) amounted to 54 and 72 pg/g, respectively. Similarly to TEQs, in apples, lettuce and especially zucchini the highest Σ6PCB levels were found (zucchini: maximum 1230 pg Σ6PCB/g). Even though the dominating PCB 138 and PCB 153 were found highest in concentration, their contribution to Σ6PCB was not as high as in food of animal origin.[9] In some samples, especially apples, PCB 28 was the dominating congener in Σ6PCB.

The total PCB concentration (ΣPCB, considering tri- to heptachlorinated PCB congeners) was found to be about 2 to 2.5 times as high as that one of Σ6PCB. Presuming a daily average consumption of fruit and vegetables (see details given above), an intake of about 65 ng ΣPCB/person/day corresponding with 1 ng ΣPCB/kg person/day was calculated. In parallel to PCDDs/Fs and dl-PCBs an estimation showed that those intakes through fruit and vegetables (without vegetable oil) represent a share of roughly 5 % of the total intake of ΣPCB in food.[9] The con-

**Table 1**: Concentrations (pg/g fresh weight, upper bound) of PCDDs/Fs, dioxin-like PCBs (each expressed as WHO-TEQs), total TEQs (WHO-TEQ) and Σ6PCB in different fruit and vegetables (minimum, maximum, mean, 25$^{th}$, 50$^{th}$ and 75$^{th}$ percentile)

| Food | | Min | P25 | P50 | Mean | P75 | Max |
|---|---|---|---|---|---|---|---|
| Potatoes | WHO-PCDD/F-TEQ | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 | 0.006 |
| (n=10) | WHO-PCB-TEQ | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.002 |
| | WHO-TEQ | 0.004 | 0.004 | 0.005 | 0.005 | 0.005 | 0.008 |
| | Σ6PCB | 7.9 | 12.5 | 18.0 | 18.6 | 21.0 | 37.7 |
| Carrots | WHO-PCDD/F-TEQ | 0.004 | 0.004 | 0.005 | 0.005 | 0.007 | 0.009 |
| (n=10) | WHO-PCB-TEQ | 0.002 | 0.002 | 0.002 | 0.003 | 0.003 | 0.004 |
| | WHO-TEQ | 0.005 | 0.006 | 0.008 | 0.008 | 0.009 | 0.012 |
| | Σ6PCB | 13.1 | 33.0 | 43.3 | 55.6 | 88.8 | 105 |
| Cauliflower | WHO-PCDD/F-TEQ | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 |
| /kohlrabi | WHO-PCB-TEQ | 0.001 | 0.001 | 0.001 | 0.001 | 0.002 | 0.002 |
| (n=10) | WHO-TEQ | 0.004 | 0.004 | 0.005 | 0.005 | 0.005 | 0.006 |
| | Σ6PCB | 12.1 | 20.6 | 35.0 | 39.0 | 44.5 | 115 |
| Zucchini | WHO-PCDD/F-TEQ | 0.004 | 0.008 | 0.012 | 0.020 | 0.018 | 0.056 |
| (n=10) | WHO-PCB-TEQ | 0.002 | 0.002 | 0.005 | 0.009 | 0.009 | 0.040 |
| | WHO-TEQ | 0.006 | 0.011 | 0.020 | 0.029 | 0.023 | 0.096 |
| | Σ6PCB | 26.0 | 62.4 | 82.6 | 219 | 206 | 1230 |
| Strawberries | WHO-PCDD/F-TEQ | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 | 0.005 |
| (n=10) | WHO-PCB-TEQ | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.005 |
| | WHO-TEQ | 0.004 | 0.005 | 0.005 | 0.005 | 0.005 | 0.009 |
| | Σ6PCB | 10.6 | 14.6 | 16.1 | 24.9 | 22.7 | 98.0 |
| Lettuce | WHO-PCDD/F-TEQ | 0.004 | 0.005 | 0.006 | 0.008 | 0.009 | 0.022 |
| (n=10) | WHO-PCB-TEQ | 0.003 | 0.003 | 0.005 | 0.006 | 0.007 | 0.011 |
| | WHO-TEQ | 0.007 | 0.009 | 0.012 | 0.014 | 0.014 | 0.033 |
| | Σ6PCB | 73.6 | 86.3 | 108 | 125 | 150 | 217 |
| White cabbage | WHO-PCDD/F-TEQ | 0.003 | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 |
| (n=10) | WHO-PCB-TEQ | 0.001 | 0.001 | 0.002 | 0.002 | 0.002 | 0.006 |
| | WHO-TEQ | 0.004 | 0.005 | 0.005 | 0.005 | 0.005 | 0.009 |
| | Σ6PCB | 5.9 | 19.5 | 24.1 | 28.0 | 29.2 | 74.6 |
| Beans | WHO-PCDD/F-TEQ | 0.004 | 0.004 | 0.004 | 0.004 | 0.005 | 0.005 |
| (n=10) | WHO-PCB-TEQ | 0.003 | 0.003 | 0.004 | 0.005 | 0.005 | 0.011 |
| | WHO-TEQ | 0.007 | 0.007 | 0.008 | 0.009 | 0.009 | 0.016 |
| | Σ6PCB | 28.0 | 35.8 | 47.5 | 55.4 | 67.8 | 119 |
| Apples | WHO-PCDD/F-TEQ | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 | 0.005 |
| (n=10) | WHO-PCB-TEQ | 0.003 | 0.004 | 0.005 | 0.006 | 0.007 | 0.012 |
| | WHO-TEQ | 0.007 | 0.008 | 0.009 | 0.010 | 0.011 | 0.017 |
| | Σ6PCB | 59.6 | 78.2 | 99.4 | 113 | 120 | 238 |
| Grain | WHO-PCDD/F-TEQ | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 | 0.007 |
| (n=10) | WHO-PCB-TEQ | 0.002 | 0.003 | 0.004 | 0.004 | 0.004 | 0.006 |
| | WHO-TEQ | 0.005 | 0.007 | 0.007 | 0.008 | 0.010 | 0.010 |
| | Σ6PCB | 19.6 | 32.0 | 40.1 | 44.1 | 53.7 | 78.8 |
| All samples | WHO-PCDD/F-TEQ | 0.003 | 0.003 | 0.004 | 0.006 | 0.005 | 0.056 |
| (n=100) | WHO-PCB-TEQ | 0.001 | 0.001 | 0.003 | 0.004 | 0.004 | 0.040 |
| | WHO-TEQ | 0.004 | 0.005 | 0.007 | 0.010 | 0.010 | 0.096 |
| | Σ6PCB | 5.9 | 22.3 | 41.7 | 72.2 | 86.0 | 1230 |

tribution of WHO-PCB-TEQs to ΣPCB was about 25 µg/g and consequently similar to Aroclor 1254 (find reference data compiled in Lit.).[9]

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