Comparison of Congener Patterns and TEQs in environmental and human samples

Marianne Rappolder, Nina Brüders, Christa Schröter-Kermani

Introduction

WHO has initiated the re-evaluation of toxic equivalency factors (TEFs) for dioxins and related compounds based on recent studies. New TEFs do not only improve the risk assessment for humans. The TEF-concept is also used in samples from other matrices. Results published for environmental samples are given as concentrations of homologues, 2,3,7,8 substituted congeners or TEQs calculated with factors of different TEF-concepts and with different approaches for the limit of quantification. For this reason it is very difficult to compare the data from published studies.

For decades PCDD/PCDF have been subject of intensive monitoring programmes in Germany. The analytical results of these programmes are documented in the German POP-DIOXIN DATABASE on congener-specific basis including metadata with compartment specific information. This allows flexible assessment of data. Here, we critically compare the results of environmental and human samples calculated as concentrations, WHO-TEQ and I-TEQ.

Materials and Methods

All data are from investigations of environmental and human samples stored at the German POP-DIOXIN DATABASE. Analytical results of 2,3,7,8 substituted congeners from ambient air and deposition, soil, conifer shoots, cow milk and human blood were calculated with WHO-TEFs and I-TEFs and compared with the original concentration of the congeners. Results below the limit of detection were calculated with half of this limit (half bound approach). Details for methods and results are described elsewhere (air and deposition[1,2], soil[3], biota[4], cow milk[5], human blood[6]). For ambient air and deposition, samples were chosen from a background station in Hesse. Data from 1990, 1995 and 2000 to 2002 (air n=101, deposition n=56) were selected and the annual median for each congener was calculated. The data from soil samples are based on a survey at background stations all over Germany by the Federal Environmental Agency in 1990 and 1997. The samples were differentiated in forest (n=147), grassland (n=56) and agriculture use (n=56). Data for conifer shoots are from the German Environmental Specimen Bank (ESB) and were taken from a station in Saarland for the years 1985, 1991, 1995, 2001 and 2004 (n=5). Cow milk was collected in many parts of Germany within the food monitoring programme. Results from 1990, 1995 and 2000 to 2002 were selected (n=333) and the median from each congener of the periods was calculated. Blood samples from 1985, 1990, 1995 and 1999 originating from the ESB were analysed (n=80) and medians of the 2,3,7,8 substituted congeners of each year were calculated.

Results:

All sums are applied to the seventeen 2,3,7,8 substituted congeners. The sum of the concentration data (PCDD/F) does not include homologues; the WHO-TEQ is only calculated for dioxins and furans. OCDD dominates in all samples. The main contribution to the WHO-TEQ and to the I-TEQ is with the exception of human blood from 2,3,4,7,8-PeCDF. Details are shown in table 1. In Fig 1 the congener patterns of the concentration in environmental and human samples are shown, in Fig 2 the contribution to the WHO-TEQ is demonstrated.

Soil: The main congener OCDD is followed by OCDF with about 15 %. Calculation with TEFs changes these relations, depending on applied factors. The different congener pattern in soils leads to different TEQ proportions. While in forest soil the WHO-TEQ is 17 % higher than the I-TEQ , the WHO-TEQ in grassland is 20 % and in field soil about 43 % lower than the I-TEQ.

Ambient Air: Between 1990 and 2002 PCDD/F concentration in ambient air decreased from 1100 fg/m³ to 330 fg/m³ (63 %). When calculated as TEQ, the diminution is only 57 %. The congener pattern in ambient air exhibited nearly no changes in this period. Due to the high OCDD-concentration and a low TEF, dioxin congeners contribute with 80 % to the total sum, while the share to WHO-TEQ is only 41 %. The WHO-TEQ is about 7 % higher than the I-TEQ.

Deposition: Between 1990 and 2002 the deposition of PCDD/F decreased from 212 pg/m²d to 50 pg/m²d (77 %). The congener patterns remained stable over this period. The calculation of the TEQs results in large differences depending on concentrations below the limit of quantification (LOQ) since most of the congeners below LOQ are calculated with relatively high factors (e.g. 2,3,7,8-TCDD). Therefore, the margin of the share to total TEQ is very large with 40 to 72 % for WHO-TEQ and 36 to 58 % for I-TEQ. Thus, the LOQ of congeners highly influences their contribution to total TEQ. The WHO-TEQ is about 8 % higher than the I-TEQ.
Conifer shoots: Between 1985 and 2004 PCDD/F concentration decreased from 57 ng/kg dm to 12 ng/kg dm (80 %), Calculated in WHO-TEQ the decrease was about 76 % at the same time. The congener pattern varies only little in this period. The WHO-TEQ is about 10 % higher than the I-TEQ.

Cow Milk: Between 1990 and 2002 PCDD/F concentration in cow milk decreased from 7 ng/kg lipid to 3 ng/kg lipid (55 %). Due to relatively low concentration of OCDD and greater share of congeners with higher TEFs (1,2,3,7,8-PeCDD, 2,3,7,8-TCDD) to the TEQ, the decreasing trend of both TEQs over this period is higher (70 %). The congener patterns varies only a little over this period. The WHO-TEQ is about 15 % higher than the I-TEQ.
Human blood: Between 1985 and 1999 PCDD/F concentration in human blood diminished from 60 pg/g lipid to 30 pg/g lipid (50 %). For WHO-TEQ and I-TEQ, the decrease amounted to 67 %. For the sum of PCDD/F concentration the main congener is OCDD with 60 to 67 %, followed by 1,2,3,4,6,7,8-HpCDD with a decreasing share trend from 11 to 7 % and OCDF with an increasing share trend from 4 to 8 %. At the same time the share of the furan congeners increased from 15 to 24 %. Also the contributions of the congeners to the WHO-TEQ changed. The rise of 2,3,7,8-TCDD in 1999 is maybe caused by contaminated citrus pulp in cow feed at this time. The WHO-TEQ is 21 % higher than the I-TEQ.

Table 1: Relatively contribution to sum of PCDD/PCDF concentration, to PCDF/PCDD-WHO-TEQ and to I-TEQ in environmental and human samples, share of furan congeners in concentration and TEQs. Source: German POP-DIOXIN-DATABASE

Matrices (number of samples)	Main contribution to sum of PCDD/F	Furan % share in PCDD/PCDF concentr.	Main contribution to PCDD/F WHO-TEQ	Furan % share in PCDD/F WHO-TEQ	Main contribution to I-TEQ	Furan % share in I-TEQ
Forest soil (n=147)	OCDD 43 %	55 %	2,3,4,7,8-PeCDF 44 %	82 %	2,3,4,7,8-PeCDF 45 %	85 %
Grassland soil (n=56)	OCDD 52 %	66 %	2,3,4,7,8-PeCDF 29 %	65 %	2,3,4,7,8-PeCDF 31 %	69 %
Field soil (n=56)	OCDD 52 %	65 %	2,3,4,7,8-PeCDF 24 %	56 %	2,3,4,7,8-PeCDF 26 %	62 %
Ambient air (n=101)	OCDD 51 – 60 %	19 -26 %	2,3,4,7,8-PeCDF 35 – 41 %	58 - 60 %	2,3,4,7,8-PeCDF 38 - 44 %	63 - 64 %
Deposition (n=56)	OCDD 54 – 61 %	19 - 27 %	2,3,4,7,8-PeCDF 30 - 34 %	40 - 72 % (LOQ!)	2,3,4,7,8-PeCDF 31 - 36 %	42 - 64 % (LOQ!)
Biota conifer shoots (n=5)	OCDD 36 - 49 %	32 - 40 %	2,3,4,7,8-PeCDF 33 - 39 %	62 – 69 %	2,3,4,7,8-PeCDF 36 - 43 %	69 – 75 %
Cow milk (n=333)	OCDD 20 – 31 %	34 - 41 %	2,3,4,7,8-PeCDF 33 - 39 %	44 - 50 %	2,3,4,7,8-PeCDF 39 – 46 %	52 - 59 %
Human blood (n=80)	OCDD					
1985, 1990:	64 – 67 %	15 - 16 %	1,2,3,7,8-PeCDD 29%	36 - 41 %	2,3,4,7,8-PeCDF 29 %	39 - 44 %
1995:	64 %	20 %	2,3,4,7,8-PeCDF 27 %	46 %	2,3,4,7,8-PeCDF 32 %	49 %
1999: (Citrus pulp?)	60 %	24 %	2,3,7,8-TCDD 29 %	30 %	2,3,7,8-TCDD 29 %	32 %

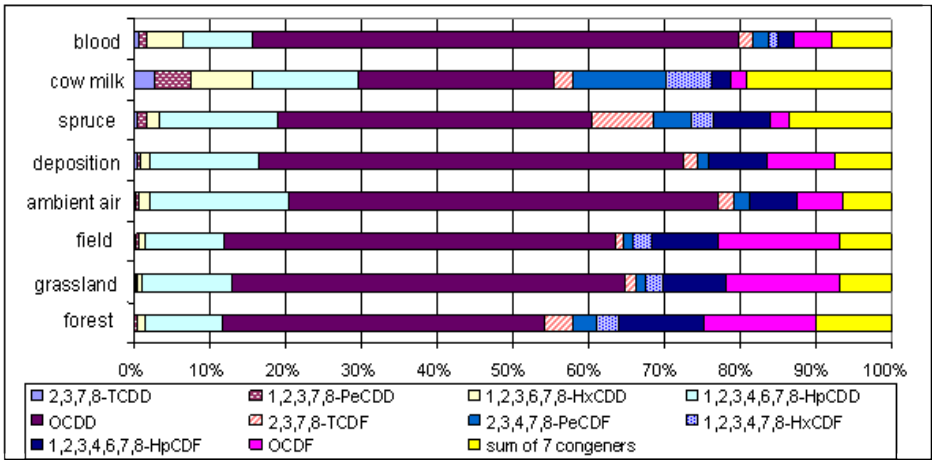

Fig 1: Contribution of 10 main congeners to the sum of 2,3,7,8 PCCD/PCDF concentrations. Low concentrations were summarized to the sum of 7 congerers (same congeners as in Fig 2)

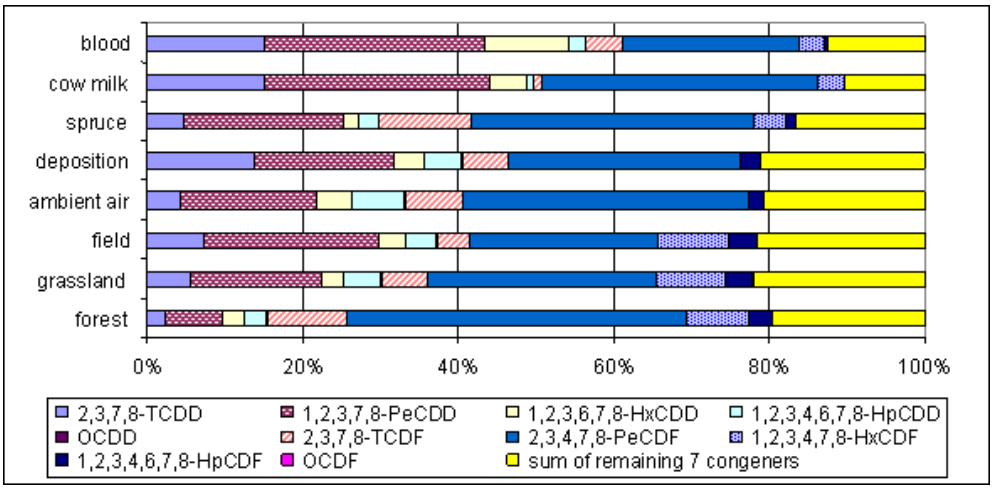

Fig 2: Contribution of 10 main congeners to the WHO-$TEQ_{PCDD/PCDF}$. Low concentrations were summarized to the sum of 7 congeners (same congeners as in Fig 1)

Discussion and Conclusion

The examples of environmental and human samples from the German POP-DIOXIN DATABASE clearly demonstrate the importance of a precise documentation of the context in which data are presented. Depending on the calculation base, huge differences may occur, resulting in different conclusions. Most of the congeners with low concentrations have high TEFs. Therefore, changing in concentrations of these congeners may produce different trends for concentrations and for TEQs. The LOQ may have also a tremendous influence on TEQs. If the dioxin content in environmental samples is low, the differences of TEQ with or without including the LOQ are high. However, the sum of the congener concentrations remains unaffected by this. For identification of sources, special impacts, trends, transfer factors and carry over rates it is important to know the concentration of the congeners.

The application of the TEF-concept is very helpful for risk assessment to evaluate the toxicity of mixtures of dioxin-like compounds to humans. For risk management regulations are based on different calculations of limit values. Emission and environment is mostly regulated with I-TEQ. In Germany, the ordinance of the prohibition of certain chemicals (1996)[7] sets limit values for all 17 2,3,7,8 chlor substituted dioxins and furans and 8 brominated dioxins/furans in substances, preparations and articles. This limit values are set for groups depending not only on the toxicity but also on the persistence of the congeners. Feed and food regulation as well as the TDI are based on

WHO-TEQ.

The TEQ is not appropriate to give information about the toxicity in environmental samples. Different TEFs are also derived for the assessment of the toxicity to fish and birds[8]. However, these TEFs may not describe toxicity adequately in other environmental samples. TEFs will be updated and new TEFs for other substances and for internal doses are under discussion[9]. With this background it is still more important to have minimum requirement and clear standards for the documentation and publication of data. These should contain at least analytical results on congener specific base with LOQ, information to the base (e.g. weight, lipid) and metadata specific to the kind of sample for a proper calculation and comparing of data according to the chosen objective. A data base like the German POP-DIOXIN DATABASE allows such flexible assessments.

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