PREDICTION OF TOTAL TCDD EQUIVALENTS (TEQs) IN ENVIRONMENTAL BIOTIC MATRICES USING 2,2',4,4',5,5' HexCB (PCB 153) AS A MARKER COMPOUND

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INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls are widespread contaminants of the global environment[1]. Due to the lipophilicity and metabolic stability of the 2,3,7,8- substituted PCDD/Fs and many PCB congeners, these compounds tend to accumulate in organisms at different trophic levels[2,3]. The 2,3,7,8- substituted PCDD/Fs and non- or mono-ortho PCBs all act at least in part via a common mechanism of action. As a result all these congeners have a different potency, but qualitatively cause the same effects[4]. Congeners potencies are expressed in Toxic Equivalence Factors (TEFs), in which $TEF_X = ED_{50\text{-}TCDD} / ED_{50\text{-}X}$. By multiplying a congener concentration with its specific TEF a concentration expressed in 2,3,7,8-TCDD equivalents (TEQs) is obtained. Assuming additivity of the compounds, the total toxicity of the mixture is calculated by summation of the TEQs. Until recently, most risk evaluations of exposition to dioxin-like compounds were confined to the 2,3,7,8-substituted PCDD/Fs only. However, there is growing evidence for a major contribution to total dioxin-like toxicity of some non- and mono-ortho PCBs which are approximate stereoisomers of 2,3,7,8-TCDD. These compounds are generally less potent than the 2,3,7,8- substituted PCDD/Fs[4,5,6], but are present in much higher concentrations in environmental biological matrices[7,8,9]. For risk assessment, the analysis of all the different "dioxin" like compounds is needed. In general, data for the calculation of the total TEQs are obtained by congener specific analysis of PCDD/Fs and non-ortho PCBs by using high resolution gas chromatography combined with high- or low resolution mass spectrometric detection (HRGC- HR/LRMS). The analysis of

mono- and di-ortho PCBs is usually performed by gas chromatography with electron capture detection (GC/ECD). Especially congener specific analysis of 2,3,7,8-substituted PCDD/Fs and the three non-ortho PCBs (# 77, #126 and #169) is a very time consuming and costly process. The aim of the studies presented in this paper was to investigate whether or not an accurate prediction of the total TEQs in biological samples is possible using the analysis of a single PCB which is present in high concentrations and easy to analyze in biotic matrices. To investigate this, samples from wildlife and human matrices were analyzed and checked for a consistent qualitative pattern of the compounds.

EXPERIMENTAL

PCDD/F and/or PCB patterns were determined in samples from yolksac tissue of Common tern hatchlings and in human milk. Common tern hatchlings were originating from eight different locations and human milk samples from three different locations throughout the Netherlands. All samples were extracted with dichloromethane for 24 hours. The extract was divided in two fractions. One fraction (5 v/v) was used for mono- and di-ortho PCB analysis on GC-ECD. The other fraction (95 v/v) was used for non-ortho PCB and PCDD/F analysis. Non-ortho PCBs were separated from the PCDD/Fs by a carbosphere column based on the methods of Liem *et al.*[10]. For the PCDD/Fs an additional clean up with a Al_2O_3 column was used. For the non-ortho PCBs in Common tern samples, the additional clean up with an Al_2O_3 column was followed by high performance liquid chromatography using a pyrenyl ethyl column based on the methods described by Haglund *et al.*[11]. For the human milk samples the Al_2O_3 column was followed by a Bio Beads SX3 column. Detailed descriptions of the methods used for PCDD/F, mono- and di-ortho PCB analysis in Common tern samples have been published earlier[8]. Detailed description of the methods used for non-ortho PCB analysis will be published elsewhere. Total TEQs of the samples were calculated by multiplying the concentrations with the TEFs as proposed by Safe[4]. Contributions to the total TEQs of the different groups are calculated. The different groups are: 1) all 2,3,7,8-chlorine substituted PCDD/Fs; 2) non-ortho PCBs (nos. #77, #126, #169); 3) mono-ortho PCBs (nos. #105, #118, #156, #157, #167); 4) di-ortho PCBs (nos. #52, #101, #138, #153, #180). Relations of single PCB congeners toward total TEQs and between individual congeners are analyzed with linear regression.

RESULTS AND DISCUSSION

Complete results of all the analyses will be published elsewhere. In this paper only the

2,3,7,8-TCDD equivalents per group of congeners and correlations among fractions will be presented. The highest concentrations were found for PCB 153 (71 ± 45 µg/g lipid and 128 ± 50 µg/g lipid for respective tern and human tissue). PCB 153 showed relatively high and well separable peaks in all GC/ECD chromatograms. For these reasons PCB 153 was chosen as a marker compound to determine correlations with other compounds. Concerning total 2,3,7,8-TCDD equivalents present in Common tern yolksac, highly significant relationships were found between PCB 153 and $TEQ_{NO\text{-}PCB}$ as well as $TEQ_{MO\text{-}PCB}$ and $TEQ_{DO\text{-}PCB}$. No relationship was found between PCB 153 and $TEQ_{PCDD/F}$. However, due to the very low contribution of PCDD/Fs to the total amount of TEQs in this tissue (< 1%), a highly significant relationship between PCB 153 and TEQ_{TOT} could be established (see figure 1). Except for the PCDD/Fs, which were not analyzed in the milk samples, the same highly significant relationships were found in human tissue (see figure 2). Average PCDD/F concentrations of 41 pg TEQ/g lipid are reported for human milk in the Netherlands[12]. If these data are combined with the results from our study, PCDD/Fs will contribute 33 % to the total amount of TEQs present in human milk in the Netherlands. In both human milk and bird tissue the mono-ortho PCBs were by far the most important group of congeners with respect to contribution to total TEQs in a sample ($TEQ_{MO\text{-}PCB}$ respective 51% and 76% of TEQ_{TOT}). In both matrices the non-ortho PCBs counted for 11% to 14% of the TEQ_{TOT}. Despite the very low Ah-mediated potency of the di-ortho PCBs, a contribution to TEQ_{TOT} of 5% to 12% was found due to the high concentrations of these congeners in both type of samples.

figure 1. Relationships between PCB 153 and $TEQ_{NO\text{-}PCB}$, $TEQ_{MO\text{-}PCB}$, $TEQ_{DO\text{-}PCB}$, $TEQ_{PCDD/F}$ and TEQ_{TOT} in the Common tern yolksac. Equations were determined by linear regression and can be described as follows: PCB 153 vs:

□ $TEQ_{NO\text{-}PCB}$: Y= 1.4 + 0.015 X (r=0.594)
\+ $TEQ_{MO\text{-}PCB}$: Y= 2.9 + 0.3 X (r=0.976)
◇ $TEQ_{DO\text{-}PCB}$: Y= 0.01 + 0.053 X (r=0.994)
△ $TEQ_{PCDD/F}$: Y= 0.134 + 0.00053 X (r=0.187)
○ TEQ_{TOT} : Y= 4.46 + 0.35 X (r=0.979)

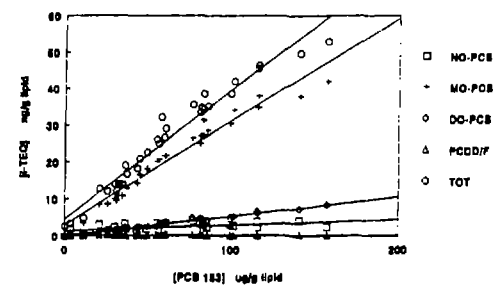
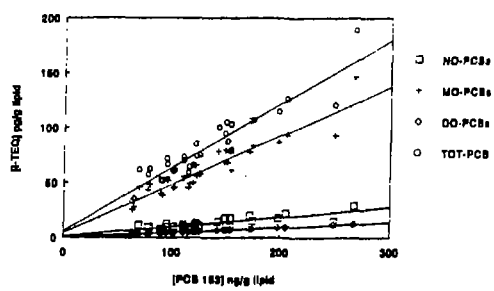


figure 2. Relationships between PCB 153 and $TEQ_{NO\text{-}PCB}$, $TEQ_{MO\text{-}PCB}$, $TEQ_{DO\text{-}PCB}$ and $TEQ_{\Sigma PCB}$ in human milk. Equations were determined by linear regression and can be described as follows: PCB 153 vs:

□ $TEQ_{NO\text{-}PCB}$: Y=1.5 + 0.089 X (r=0.838)
\+ $TEQ_{MO\text{-}PCB}$: Y= 4.4 + 0.44 X (r=0.935)
◇ $TEQ_{DO\text{-}PCB}$: Y=0.25 + 0.047 X (r=0.997)
○ $TEQ_{\Sigma PCB}$: Y = 6.1 + 0.58 X (r=0.937)



CONCLUSIONS

Our studies showed that once a consistent qualitative PCB pattern is established in a certain area and species a single PCB congener can be used to predict the total TEQs in the different PCB fractions as well as in the whole matrix. In all samples PCB 153 was easy to detect and quantify. PCB 153 showed good correlations with all other higher chlorinated PCBs analyzed in the sample. Our results show that these relationships can be of use for monitoring purposes within one species and as such be highly cost effective.

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