PCB AND PCDD/F IN BLOOD SAMPLES FROM GERMANY

Albrecht M[1], Appel M [1], Völkel W[2], Liebl B[3], Roscher E[2], Fromme H[2*]

[1] Bavarian Health and Food Safety Authority, Department of Pesticides, Contaminants, Nitrosamines, Radioactivity, Dioxins, Irradiation; Veterinaerstrasse 2, D-85764 Oberschleissheim, Germany
[2] Bavarian Health and Food Safety Authority, Department of Chemical Safety and Toxicology; Pfarrstrasse 3, D-80538 Munich, Germany
[3] Bavarian Health and Food Safety Authority, Veterinaerstrasse 2, D-85764 Oberschleissheim, Germany

Introduction

Due to their persistence in the environment and biological systems, accumulation in the food chain, and toxicological properties, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are associated with significant environmental and health concerns.

Materials and methods

In the study region of northern Bavaria, Germany, a factory for recycling of cables and electronic waste has operated since 1997. In a further environmental monitoring program air and dust deposit samples as well as soil samples were analyzed. The study results indicated no higher contamination of PCDD/Fs compared to German background levels, but in part considerably elevated immissions of dl-PCBs and PBDEs in the direct vicinity of the plant (up to 50 m; air, dust de-posit and soil samples). Additionally, a human biomonitoring was offered to the population living in a radius of one kilometer around the facility. Overall, 70 healthy subjects agreed to participate.

The analysis was described in detail by Fromme et al. (2009)[1]. Briefly, 40 g of homogenized whole blood was diluted in 30 ml of deionized water and 5 ml of ethanol and spiked with 17 $^{13}C_{12}$-labeled PCDD/Fs, 12 $^{13}C_{12}$-labeled dl-PCBs, $^{13}C_{12}$-labeled ndl-PCBs, and 10 $^{13}C_{12}$-labeled PBDEs as internal standards. Blood fat was extracted by an Isolute/sodium chloride column with a 600 ml mixture of n-hexane / 2-propanol (3/2 v:v). The crude fat extract was applied to an anhydrous sodium sulfate column and extracted with n-pentane. Fat and non-acid-stable compounds were removed on a silica gel column coated with sulfuric acid. The n-pentane fraction containing the target analytes was subsequently separated on a Carbopack / Celite column. Dl- and ndl-PCBs as well as PBDEs were eluted in the first fraction with hexane, cyclohexane and dichloromethane, followed by PCDD/Fs in the second fraction (eluted with toluene). While the PCDD/F fraction was further cleaned up on a Florisil column (1% water, rinsed with hexane, eluted with toluene), the PCB/PBDE-eluate was applied to an aluminum oxide / anhydrous sodium sulfate column to separate the mono-ortho- and ndl-PCBs (eluted with hexane / dichloromethane 98/2) from the non-ortho-PCBs and PBDEs (eluted with hexane / dichloromethane 1/1). Extracts were dissolved in 20 µl and 80 µl (mono-ortho- and ndl-PCBs) of recovery standard solution. The three final extracts were separately analyzed by double gas chromatography / high resolution mass spectrometry (2GC/HRMS) on a Thermo DFS system working at a resolution of R = 10,000. Two Agilent columns were installed in one GC, a VF-5ms of 60 m length, 0.25 mm ID and 0.25 µm film thickness (for analysis of PCDD/Fs and non-ortho-PCBs) and DB5-ms (15 m x 0,20 mm x 0,1 µm) for separation of PBDEs. In the second GC a SGE-HT8-PCB column was used to separate mono-ortho- and ndl-PCBs (60 m x 0,25 mm). All extracts were measured in single ion recordings with 4 or 5 mass optimized functions for native and labeled congeners.

Results and discussion

The 70 participants, 37 females and 33 males, were between 4 and 76 years old (median: 42 years). Results are given in Table 1. PCDD/F congener profile was dominated by OCDD (median 90.1 pg g^{-1} l.w.), followed by 1,2,3,4,6,7,8-HpCDD, 1,2,3,6,7,8-HxCDD, and 2,3,7,8-PeCDF, while the median level of 2,3,7,8-TCDD was only 0.3 pg g^{-1} l.w. The dominant dl-PCB congeners were PCB 156 (median 4325 pg g^{-1} l.w), PCB 118, and PCB 167, while PCB 126, for example, had a median concentration of only 17.3 pg g^{-1} l.w. For PCDD/Fs, a median level (95^{th} percentile in parentheses) of 4.5 pg WHO_{2005}-TEQ g^{-1} l.w. (17.9 pg g^{-1} l.w.) was determined, and the corresponding value for dl-PCB was 2.6 pg g^{-1} l.w. (13.2 pg g^{-1} l.w.). Considering the median values, the relative contribution of PCDD/F to total WHO_{2005}-TEQ was 60%. We found no significant difference between females and males or smokers and non-smokers but higher concentrations with increasing age.

Table 1: Blood levels of PCDDs, PCDFs, and dioxin-like PCBs expressed as pg WHO-TEQ g^{-1} l.w.

Compound	5th percentile	Median	95th percentile	Max	Mean
TEQ (using WHO_{1998}-TEF)					
PCDD/Fs	1.2	5.5	21.8	32.2	7.7
dl-PCBs	1.7	4.9	27.3	41.8	8.4
PCDD/Fs/dl-PCBs	3.6	10.7	47.2	74.1	16.0
TEQ (using WHO_{2005}-TEF)					
PCDDs	1.0	2.8	10.9	15.5	3.8
PCDFs	0.4	2.2	7.2	10.9	2.9
PCDD/Fs	1.1	4.5	17.9	26.2	6.3
Non-ortho PCBs	0.8	2.4	11.4	21.3	3.4
Mono-ortho PCBs	0.1	0.3	1.9	2.6	0.6
dl-PCBs	0.9	2.6	13.2	23.9	4.4
PCDD/Fs/dl-PCBs	2.6	7.5	30.7	50.1	10.7

Overall, our results are in line with results from other recent studies summarized for Europe in Table 2. In a review based on worldwide studies up to 2010, the authors stated that a significant decrease over time (1985 – 2008) could be documented for PCCDs and PCDFs, but no such significant trend was found for non-ortho-PCBs, notably PCB 126 2. Only some mono-ortho-PCBs showed a clearly significant decline. These findings were additionally supported by some more recent publications from Canada, Japan, and Spain 3,4. In a previous German study performed in 2005 the body burden of 50 subjects participating in a biomonitoring and duplicate diet study (INES) amounted to 7.7 pg WHO2005-TEQ g-1 l.w. for PCDD/Fs and 5.8 pg WHO2005-TEQ g-1 l.w. for dl-PCBs 1. Compared to these results, declines of 42% for PCDD/Fs and 55% for dlPCB are apparent in our recent study, based on median values.

Table 2: Median blood concentrations (pg WHO-TEQ g^{-1}) of PCDD/F and dl-PCB in the general population of Europe

Reference	Number	PCDD/F	dl-PCB	Age (Years)	Sampling site and year
Kiviranta et al. 2005	420	29.0	20.7	13-81	Finland, 1997-1999
Koppen et al, 2002	47 [a]	48.0	23.7	50-65	Belgium, 1999
Debacker et al. 2007	232 [b]	22.9/23.1	-	22-66	Belgium 1998/2000
De Felip et al. 2004 [c]	10	8.9	8.7 [d]	18-40	Italy, 2000/2001
	7	24.7	19.8 [d]	18-40	Belgium, 2000/2001
Reis et al. 2007	96	15.5	-	18-65	Portugal, 1999-2001
	20	9.6	-		Portugal, 2002-2004
Nadal et al. 2008	20	17.8	-	18->56	Spain, 2002
Wittsiepe et al. 2007	169	15.3	10.8	19-41	Germany, 2000-2003
Costopoulou et al. 2006	10 [e], 22 [f]	6.8	1.2-3.2	27-65	Greece, 2002-2004
Cerná et al. 2007	20	8.9	13.4	mean: 43	Czech Republic, 2003
Turrio-Baldassarri et al. 2008 [g]	94	22.0	32.0	mean: 51	Italy, 2004
De Felip et al. 2008	54 [h]	7.7-9.3	15-21	30-54	Italy, 2006
Chovancova et al. 2012	44	9.4	13.8	24-62	Slovakia, 2006-2007
Nadal et al. 2008	20	9.5	-	17-61	Spain, 2007
Fromme et al. 2009 (1998 TEF)	49	10.1	9.5	18-65	Germany, 2005
Fromme et al. 2009 (2005 TEF)	49	7.7	5.8	18-65	Germany, 2005
this study (1998 TEF)	70	5.5	4.9	4-76	Germany, 2013
this study (2005 TEF)	70	4.5	2.6	4-76	Germany, 2013

[a] females; [b] blood donors before and after an incident; [c] mean values; [d] calculated from means of non- and mono-ortho-PCB congeners; [e] urban sampling site; [f]; rural samplig site; [g] upper bound estimate; [i] number of donors, afterwards pooled; [h] serum pool

References:
1. Fromme H, Albrecht M, Boehmer S, Büchner K, Mayer R, Liebl B, Wittsiepe M, Bolte G. (2009); *Chemosphere* 76: 1457-63.
2. Consonni D, Sindaco R, Bertazzi PA. (2012); *Environ. Int.* 44: 151-62.
3. Rawn DF, Ryan JJ, Sadler AR, Sun WF, Haines D, Macey K, Van Oostdam J. (2012); *Environ. Int.* 47: 48-55.
4. Kishi R, Kobayashi S, Ikeno T, Araki A, Miyashita C, Itoh S, Sasaki S, Okada E, Kobayashi S, Kashino I, Itoh K, Nakajima S. (2013); *Environ. Health Prev. Med.* 18: 429-50.