PCDDs, PCDFs, PCBs, and other Organochlorine Compounds in Human Milk Levels and their Dynamics in Germany

Lutz Alder, Hans Beck, Wolfgang Mathar, Richard Palavinskas
Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin (bgvv),
Postfach 33 00 13, D-14191 Berlin, Germany

INTRODUCTION

The body burden from PCDDs, PCDFs, PCBs and other organochlorine compounds (OCs) of the German population living in the western part of the country is well known since more than 2000 samples of human milk (including pooled samples) were analyzed for PCDDs and PCDFs and more than 10000 for PCBs and OCs. In the former German Demokratic Republic (GDR) very limited or no data on these substances were available. After the reunification of Germany it was therefore necessary to gain knowledge of the situation in the new eastern part of the country by analyzing individual and pooled human milk samples. In Western Germany, human milk samples were analyzed for PCDDs and PCDFs (PCDDs/Fs) since 1985. The dynamics of their levels were established for the years from 1985 to 93.

EXPERIMENTAL

SAMPLES

Eastern Germany: Sampling period for all samples was 1990-91.
From the 13 districts of the former GDR, individual samples were selected and combined on an equal volume basis to form a representative sample. Only samples from mothers nursing their first child between week 4 and 12 after delivery were selected.
43 samples from mothers of 5 areas nursing between week 4 and 12 including a few samples from mothers having their 2nd or 3rd child were selected for individual analyses.
Except for the mothers of Ilsenburg, no special point source responsible for an elevated body burden was assumed. Further details are listed in Table 1.

Western Germany: 115 randomly collected individual samples and three pooled samples from 73 mothers nursing their first child between week 4 and 12 after delivery were analyzed for PCDDs/Fs, classified by year and subsequently averaged. To obtain a broader basis, these data were combined with other data published on human milk in Germany [1-7].

EXTRACTION AND CLEAN-UP

Fat extraction was performed using the AOAC method [8].

PCDDs/Fs: The clean-up was carried out according to the procedure by Smith et al. [9], with minor modifications [10,11]. The final extract was concentrated by evaporation to 30 µl.

PCBs and OCs: 0.7 g milk fat dissolved in 5 ml cyclohexane/ethyl acetate (1/1=v/v) was introduced via sample loop for gel permeation chromatography [12] with Bio Beads SX 3. A further clean-up step with deactivated silica [12] resulted in an extract of 1 ml.

PCBTOX

DETERMINATION

PCDDs/Fs: Quantitation was performed by HRGC-HRMS with a VG 7070 or Finnigan MAT 95 instrument (resolution 10000) on the basis of ^{13}C-labelled internal standards [10,11].

PCBs and OCs: These compounds were quantified by HRGC-ECD with a DB-5 column [13].

RESULTS AND DISCUSSION

PCDDs AND PCDFs

Samples from Eastern Germany: The mean PCDD/F concentrations of samples from 17 regions of Eastern Germany have been listed in Table 2. Altogether, the differences of the body burden at the various places of residence are irrelevant: typically, the maximum concentrations are 2-3 times higher than the minimum concentrations. Nevertheless, such regional differences were not recognized for samples from Western Germany where food is of wide-spread origin in contrast to Eastern Germany where food was of a more or less local origin. Compared to data from Western Germany obtained in the same period [14,15] (Table 2), the congener levels were relatively similar with the exception that, for some samples from Eastern Germany, 2,3,7,8-TCDD was higher whereas 2,3,4,7,8-PeCDF and 2,3,7,8-substituted HxCDDs were lower resulting in slightly lower I-TEq levels. Since the age of the mothers from Eastern Germany was about 3-4 years lower than that of mothers from Western Germany and the levels are increasing with age, these differences for I-TEq levels are of minor importance.
The concentrations in samples from Ilsenburg - an area contaminated by emissions from a copper plant - are distinctly higher (Table 4): Their minimum levels for 2,3,4,7,8-PeCDF and 2,3,7,8-substituted HxCDFs are higher and for 1,2,3,7,8-PeCDD and 2,3,7,8-substituted HxCDDs are equal compared to the maximum levels of the 17 representative samples from Eastern Germany (Table 2). The differences of remaining congener levels are not striking. This means that the mean I-TEq level for the samples from Ilsenburg (59 ppt) is twice as high as the maximum concentration of the 17 representative samples from Eastern Germany and as the mean of the reference samples from Western Germany in the same period (Table 2). On the other side, even the highest I-TEq concentration in the human milk samples from Ilsenburg is in the range of that of the reference samples from Western Germany in that period [15].

Dynamics in samples from Western Germany: Fürst et al. were the first who recognized a decline of PCDDs/Fs in human milk since 1990 [1]. This finding is confirmed by our own data (Fig. 1). On the basis of all averaged mean I-TEq levels in human milk reported by 5 laboratories (including ours) [1-7,15] for each year, a 40 % decline in 1993 in comparison with data of 1985-89 was found.

PCBs AND OTHER ORGANOCHLORINE COMPOUNDS

Mean concentrations of PCBs and other OCs in samples from 17 regions of Eastern Germany and the mean concentrations in milk samples from Western Germany [16] collected in the same period have been listed in Table 3. Levels of hexachlorobenzene (HCB) and ß-hexachlorocyclohexane (ß-HCH) are very similar and no significant difference can be observed whereas the levels of p,p'-DDE and p,p'-DDT are higher in the samples from Eastern Germany. Differences in levels of α-HCH, Lindane, cis-Heptachlor epoxide and Dieldrin are of minor importance because of their low levels. HCB was found to be highest in the samples from Ilsenburg. This is probably due to emissions from the copper plant.
For the PCBs, the congener pattern of the samples from East and West is very similar but their levels in the samples from Eastern Germany are lower by 60 %.
Altogether, the differences in the body burden at the various places of residence are irrelevant: typically, the maximum concentrations are 2-3 times higher than the minimum concentrations. For PCBs the lowest differences were found.

Table 1: Basic data of human milk samples from Eastern Germany

Region	Abb.	p/i	No.	Age	In.	Description of region	Land
Güstrow	Gü	p	27	23	1	rural	M
Rostock	Ro	p	37	25	1	city at Baltic Sea	M
Berlin (East)	Be	p	30	25	1	city, industry	Be
Neuruppin	Neur	p	43	24	1	rural	Bg
Bautzen	Bau	p	40	23	1	rural	S
Magdeburg	Ma	p	38	25	1	city, industry	St
Jena	Je	p	35	23	1	city, industry	T
Hoyerswerda	Ho	p	37	22	1	town, power plants	S
Eisenach	Ei	p	38	23	1	town, small industry	T
Neubrandendburg	Neub	p	35	24	1	rural	M
Halle	Ha	p	31	23	1	town, chemical plants	St
Schwedt	Sch	i	5	22	1	town, paper industry, refinery	M
Senftenberg	Se	i	10	26	1,9	industrial, power plants	Bg
Borna	Bo	i	8	26	1,7	industrial, chemical plants	S
Merseburg	Me	i	10	25	1,4	industrial, chemical plants	St
Freiberg	Fr	p	36	24	1	town, nonferrous metal plants	S
Ilsenburg	Il	i	10	27	1,7	rural, copper plant	St
Leipzig	Lei	p	39	24	1	city in the vicinity of chemical industry	S

Abb., abbreviation for region; p, pooled; i, individual; No., number of samples in pool or of individual samples; Age, mean age of mothers; In., number of infants (mean); Land, federal land; M, Mecklenburg-Western Pomerania; S, Saxony; St, Saxony-Anhalt; Be, Berlin; T, Thuringia; Bg, Brandenburg

Fig. 1: Dynamics of I-TEq levels (pg/g fat) in human milk

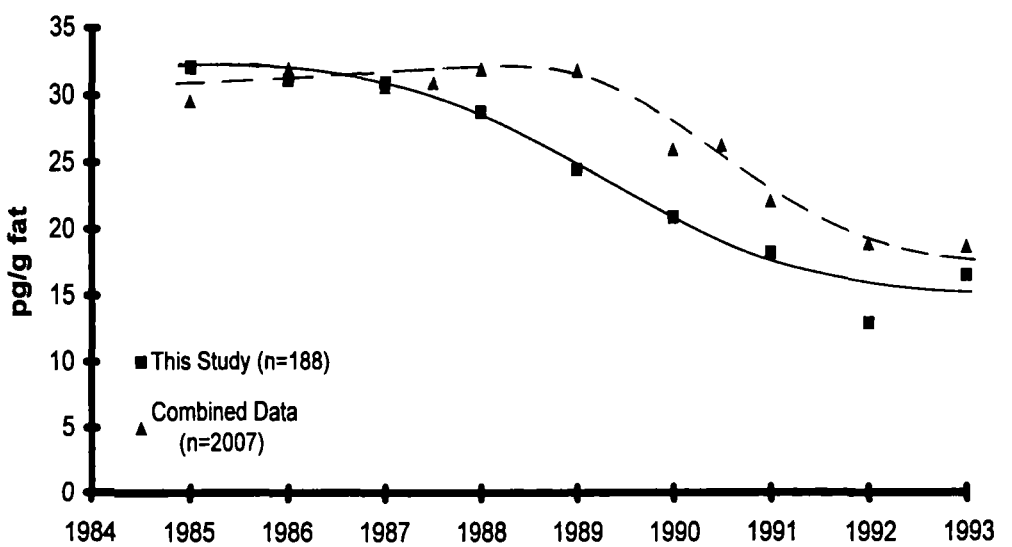

Table 2: Mean Concentrations (pg/g fat) of PCDDs and PCDFs in Human Milk Samples from 17 Regions in Eastern Germany in Comparison with Means of Reference Samples from Western Germany

Region *)	Gü	Ro	Be	Neur	Bau	Ma	Je	Ho	Ei	Fr	Lei	Neub	Ha	Sch	Se	Bo	Me	**MIN**	**MEAN** East	**MAX**	**REF** West
n	27	37	30	43	40	38	35	37	38	36	39	35	31	5	10	8	10	5	[499]	43	728
2378-TCDF	0,7	2,1	0,9	1,1	1,7	1,1	0,8	1,8	1,0	1,4	<0,5	0,8	0,7	1,6	1,2	3,3	0,7	<0,5	1,1	3,3	1,8
2378-TCDD	3,6	7,6	3,2	5,6	8,5	5,5	3,3	5,1	7,1	7,0	5,5	4,5	4,2	2,6	3,1	5,7	5,2	2,6	5,5	8,5	3,2
12378-PeCDF	<0,5	<0,5	<0,5	1,0	0,9	1,7	<0,5	0,6	<0,5	2,2	0,7	0,6	2,2	1,4	1,6	0,9	0,5	<0,5	0,9	2,2	0,6
23478-PeCDF	13	17	16	16	15	21	15	13	12	16	17	11	14	12	13	15	15	11	15	21	28
12378-PeCDD	6,1	12	7,0	9,6	12	12	9,0	7,4	5,1	12	5,7	7,5	9,7	4,1	8,7	9,1	6,3	4,1	8,8	12	10
123478-HxCDF	6,6	9,3	7,0	10	8,0	12	7,1	6,0	6,9	10,1	6,3	6,0	10,5	7,1	7,6	9,6	8,6	6,0	8,2	12	7,7
123678-HxCDF	4,4	7,7	5,4	8,3	6,8	10,3	5,4	5,2	4,3	8,8	3,5	5,1	9,1	4,7	6,4	6,4	5,5	3,5	6,5	10	7,3
234678-HxCDF	1,2	2,4	1,2	3,3	2,5	4,2	0,7	1,7	1,9	4,4	1,9	2,2	4,7	1,7	3,5	3,0	2,7	0,7	2,5	4,7	3,5
Total HxCDFs	12	19	14	22	17	26	13	13	13	23	12	13	24	13	18	19	17	12	17	26	19
123478-HxCDD	1,8	12	3,9	8,9	16	9,6	5,1	7,4	3,4	14	4,4	6,7	9,8	4,0	10,1	9,4	5,4	1,8	8,1	16	8,5
123678-HxCDD	17	23	13	21	17	21	12	16	6,8	19	11	16	18	17	14,1	16,7	10,7	6,8	16	23	38
123789-HxCDD	3,6	6,1	4,6	6,5	4,2	6,0	2,0	4,0	2,3	6,2	2,0	5,0	6,3	4,7	5,1	3,8	2,5	2,0	4,5	6,5	7
Total HxCDDs	23	41	21	36	37	36	20	28	13	39	17	28	34	26	29	30	19	13	29	41	53
1234678-HpCDF	7,2	11	7,6	8,2	5,6	6,0	5,0	5,3	4,0	7,7	3,3	7,4	10	5,7	6,4	10	4,3	3,3	6,7	11	7,3
1234678-HpCDD	18	75	16	42	39	33	15	41	22	39	21	60	44	20	50	50	25	15	36	75	47
OCDF	<1	1,7	<1	<1	<1	2,2	<1	<1	<1	2,7	<1	1,5	24	1,1	1,1	1,0	0,7	<1	2,4	24	2,2
OCDD	144	367	118	208	176	169	113	194	103	161	107	366	228	130	206	200	117	103	188	367	226
I-TEq	17	30	19	25	28	29	19	20	19	28	20	19	23	15	20	24	20	15	23	30	31

*) Abbreviations see Table 1; n, number of samples; MIN, minimum; MAX, maximum; MEAN and I-TEq calculated using half the detection limits; MEANs weighted on the basis of 499 samples; REF, reference samples from Western Germany (means) [14])

Table 3: Mean Concentrations (ng/g fat) of PCBs and OCs in Human Milk Samples from 17 Regions in Eastern Germany in Comparison with Means of Reference Samples from Western Germany

Region *)	Gü	Ro	Be	Neur	Bau	Ma	Je	Ho	Ei	Fr	Lei	Neub	Ha	Sch	Se	Bo	Me	**MIN**	**MEAN** East	**MAX**	**REF** West
n	27	37	30	43	40	38	35	37	38	36	39	35	31	5	10	6	10	5	[497]	43	>1000
PCB 28	1,3	1,9	4,0	1,9	1,4	4,4	2,5	<1	3,5	2,4	2,0	1,1	<1	<1	3,1	<1	<1	<1	2,1	4,4	<10
PCB 52	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<10
PCB 101	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<10
PCB 138	80	78	101	76	60	71	80	71	85	83	80	56	57	116	75	65	77	56	75	116	199
PCB 153	120	125	131	127	102	97	101	121	115	118	97	98	104	132	111	131	124	97	112	132	247
PCB 180	50	53	52	53	40	44	39	48	45	46	39	39	40	49	49	51	50	39	45	53	130
PCB 105	6,6	5,0	7,2	6,5	5,3	4,0	4,7	6,7	5,3	5,9	4,8	4,4	5,4	12	5,9	7,1	4,2	4,0	5,5	12	n.a.
PCB 118	16	16	18	14	12	11	15	13	15	16	17	7,7	11	34	17	8,4	13	7,7	14	34	n.a.
PCB 156	15	17	18	18	14	16	13	16	15	16	13	14	14	18	16	18	18	13	15	18	n.a.
PCB 187	13	14	13	13	9,5	8,4	9,6	12	10	11	8,5	10	9,4	16	11	12	12	8	11	16	n.a.
a-HCH	<1	<1	<1	<1	<1	<1	<1	<1	<1	1,6	1,3	1,4	1,2	<1	2,6	1,8	2,7	<1	0,8	2,7	<10
ß-HCH	55	50	104	55	130	115	69	76	53	115	125	58	71	45	91	80	80	45	83	130	75
Lindane	21	7,8	11	9,0	7,1	7,2	14	7,9	5,8	11	18	6,1	4,9	12	11	13	6,6	4,9	9,8	21	16
HCB	168	126	164	116	253	241	234	129	130	122	115	215	168	158	118	80	258	80	167	258	218
HEPO	6,3	7,1	9,9	8,1	11	8,7	7,1	7,7	7,9	8,7	6,9	7,2	6,7	10	7,2	6,8	8,6	6,3	8,0	11	14
Dieldrin	6,9	4,1	5,5	2,1	4,9	1,7	4,5	4,5	4,1	6,6	5,9	<1	1,7	11	4,7	5,7	6,2	<1	4,2	11	9
p,p'-DDE	1634	1001	1216	1498	959	1130	841	996	1014	983	992	1232	1034	2621	1194	1021	1290	841	1130	2621	589
p,p'-DDD	4,3	8,3	3,2	2,3	2,6	1,9	4,2	11	4,4	3,8	2,9	1,7	2,3	7,6	8,8	<1	4,6	<1	4,1	11	
p,p'-DDT	239	138	144	177	116	118	109	131	123	125	100	102	116	355	140	97	124	97	134	355	61

*) Abbreviations see Table 1; HEPO, cis-heptachlor epoxide; n, number of samples; MIN, minimum; MAX, maximum; MEANs calculated using half the detection limits and weighted on the basis of 497 samples; n.a., not analyzed; REF, reference samples from Western Germany (means) [16]

Table 4: PCB, OC, PCDD and PCDF Concentration in Human Milk Samples from Ilsenburg

	MIN	MEAN n=10	MAX		MIN	MEAN n=9	MAX
PCB 28	<1	<1	<1	2378-TCDF	<0,5	0,3	0,8
PCB 52	<1	<1	<1	2378-TCDD	3,1	5,8	7,8
PCB 101	<1	<1	<1	12378-PeCDF	<0,5	0,9	2,2
PCB 138	49	93	132	23478-PeCDF	33	54	84
PCB 153	72	120	184	12378-PeCDD	12	21	26
PCB 180	23	44	67	123478-HxCDF	24	34	46
PCB 105	<1	5	9	123678-HxCDF	24	35	53
PCB 118	7	15	21	234678-HxCDF	11	20	38
PCB 156	10	18	30	Total HxCDFs	60	89	137
PCB 187	6	10	18	123478-HxCDD	8,4	17	27
				123678-HxCDD	22	40	64
a-HCH	<1	<1	<1	123789-HxCDD	5,9	10	15
ß-HCH	7	62	133	Total HxCDDs	39	67	101
Lindane	<1	3	12	1234678-HpCDF	3,6	11	22
HCB	264	426	618	1234678-HpCDD	17	28	43
HEPO	<1	8	17	OCDF	<1	<1	<1
Dieldrin	<1	4	11	OCDD	65	195	475
p,p'-DDE	810	1340	2440				
p,p'-DDD	<1	2	9	I-TEq	36	59	86
p,p'-DDT	70	124	203				

Concentrations for PCBs and OCs in ng/g fat; for PCDDs/Fs in pg/g fat; HEPO, cis-Heptachlor epoxide; n, number of samples; MIN, minimum; MAX, maximum; Means and I-TEq calculated using half the detection limits

REFERENCES

1) Fürst, P. (1993). Organohalogen Compounds, 13, 1-8.
2) Frommberger, R. (1990). Chemosphere, 20, 333-342.
3) Fürst, P., Meemken, H.-A., and W. Goebel (1986). Chemosphere, 15, 1977-1980.
4) Fürst, P., Meemken, H.-A., Krüger, Chr. and W. Goebel (1987). Chemosphere, 16, 1983-1988.
5) Fürst, P., Fürst, Chr., Meemken, H.-A. and W. Groebel (1989). Z Lebensm Unters Forsch, 189, 338-345.
6) Ende, M. (1988). Lebensmittelchem.Gerichtl.Chem., 42, 42-43.
7) Heinzow, B. (1991). internist. prax., 31, 547-554.
8) Horwitz, W. (Ed.) (1980). Official Methods of Analysis of the Association of Official Analytical Chemists, 13th Ed., Washington, 470.
9) Smith, L.M., Stalling, D.L. and J.L. Johnson (1984). Anal. Chem., 56, 1830-1842.
10) Beck, H., Eckart, K., Mathar, W. and R. Wittkowski (1989). Chemosphere, 18, 1063-1066.
11) Beck, H., Eckart, K., Mathar, W. and R. Wittkowski (1988). Biomed. & Environm. Mass Spectrom., 16, 161-165.
12) Specht, W. and M. Tillkes (1980). Fresenius Z. Anal. Chem., 301, 300-307.
13) Beck, H.and W. Mathar (1985). Bundesgesundheitsblatt, 28, 1-12.
14) Beck, H., Droß, A., Ende, M., Fürst, Chr., Fürst, P., Hille, A., Mathar, W. and K. Wilmers (1991). Bundesgesundheitsblatt, 34, 564-568.
15) Beck, H., Droß, A. and W. Mathar (1994). EHP, 102 (Suppl. 1), 173-185.
16) Beck, H., Heinrich-Hirsch, B. and B. Vieth (1994). Paper in preparation.