Long term monitoring of PCDD,PCDF and PCB in bulk deposition samples.

Hiester,E. , Böhm,R. , Eynck,P. , Gerlach,A. , Mülder,W. ,Ristow,H.
Landesanstalt für Immissionsschutz des Landes Nordrhein- Westfalen (LIS),
Wallneyer Straße 6, 45133 Essen 1 , FRG

Atmospheric transport and subsequent deposition via precipitation is assumed to be the mechanism responsible for the spreading of a lot of inorganic and organic substances in the environment.Therefore investigations of deposition samples are able to indicate the pollution of the environment with organic compounds like polychlorinated dibenzo-p-dioxins (PCDD),polychlorinated dibenzofurans (PCDF) and polychlorinated biphenyls (PCB).Recent studies showed a good correlation between the PCDD/F concentrations in deposition samples and the intake of dioxins and furans by food.
In 1992 the LIS (Landesanstalt für Immissionsschutz des Landes Nordrhein- Westfalen), collected deposition samples in seven urban locations and in one remote rural location,remote from urban and inustral areas . Each deposition sample was collected over a four weeks period. The samples of two consecutive months were combined for analysis. The sample collection was performed according to the German VDI guideline 2119,sheet 2 with the Bergerhoff collector[1]. The deposition samples were cleaned up using an extraction procedure [2] .PCB were separated from PCDD/F by chromatography with basic aluminia .The final step of the analysis was done by HRGC/MSD or by HRGC/HRMS [3]
The annual averages of the PCDD/F,determined for individual congeners and homologues, are summarized in table 1.The PCDD/F concentration in deposition samples at urban locations ranged from 10 to 83 pg TE / m^2*d .The patterns of the congeners are characterized by low TCDD levels and increasing levels of penta- ,hexa- ,hepta-and octa-CDD.
The PCDF patterns show a maximum at the PeCDF decreasing to the OCDF . Even at the rural location of the Eifel ,remote from any industrial sources, the annual average of PCDD/F in deposition samples was 12 pg TE/m^2*d . The seasonal variation of the PCDD/F deposition showed a minimum during the sampling periods in summer , which can be attributed mainly to climatic influences.
The annual averages of PCB in deposition samples of urban locations ranged from 32 to 257 ng/m^2*d [table 2] . At the rural location of the Eifel an annual average of 23 ng/m^2*d was determined.
The pattern of the isomers showed a maximum level for penta- and hexachlorobiphenyls.
The annual averages of the coplanar PCB IUPAC NO. 77 , 126 and 169 were <1 ng/m^2*d. Depending on the season the concentration of the coplanar isomers varied between the following values :

TRANS

PCB No.	ng/m²*d
77	0,04 -1,5
126	0,01-0,14
169	0,002-0,012

The evaluation of concentrations of coplanar PCB with toxicity equivalent factors, proposed by several authors[4,5] , makes the PCB comparable to PCDD/F with respect to their effects on man.During a winter period with higher levels of PCDD/F the contribution of the coplanar PCB to a total toxicity equivalent came up to approximately 10 to 60 % of the PCDD/F values.In a summer period with low levels of PCDD/F the contribution of the coplanar PCB exceeded the toxicity equivalent of the PCDD/F [table 3].

Table 3: Comparison of TE-values of PCDD/F[a] and TE-values of coplanar PCB[b] in deposition samples [pg TE /m²*d]

sampling location	sampling period			
	01-02.92		07-08.92	
	PCB[b]	PCDD/F[a]	PCB[b]	PCDD/F[a]
Düsseldorf	22	200	- -	- -
Duisburg	20	36	20	8,3
Dortmund	19	49	14	6,8
Gelsenkirchen	6,9	30	7,3	4,8
Köln	9,7	15	3,8	4,1
Essen	3,7	32	7,9	6,0
Borken	2,3	14	3,9	4,0
Eifel	3,0	15	1,2	1,3

b= total coplanar PCB-77,-126,-169; TE-factors acc. to [4]
a= TE-value NATO/CCMS 1988

1. German Standard Method VDI 2119 ,sheet 2; Measurement of dustfall , Bergerhoff Instrument
2. Kirschmer,P., Mülder,W., Eynck ,P., Chemosphere 24 ; 575-580 , (1992)
3. German Standard Method VDI 3498 , sheet 1 ; Measurement of polychlorinated dibenzo-p-dioxins and dibenzofurans - LIB filtering method-
4. Safe,S., et al , Toxicology 21, 51 ff ,(1990)
5. Tarhanen,I., et al, Chemosphere 18 , 1067-1077 (1989)

Table 1 : Annual averages of PCDD/F in depositon samples [pg / m² * d] a)
sampling period : 11/91 - 10/92 ; n = 12

sampling location :	Düssel-dorf	Duis-burg	Dort-mund	Gelsen-kirchen	Köln	Essen	Borken	Eifel	Blank
total TCDD	645	36	59	34	25	26	20	24	n.d.
total PeCDD	479	59	65	52	36	51	32	23	n.d.
total HxCDD	332	120	135	109	96	121	81	85	n.d.
total HpCDD	298	149	170	164	111	163	157	181	7,6
OCDD	695	316	363	353	214	339	512	486	28
total TCDD to OCDD	2128	679	782	712	451	687	790	791	31
2,3,7,8-TCDD	19	1,1	1,5	1,1	0,76	1,0	0,46	0,62	< 3,9
1,2,3,7,8-PeCDD	23	5,1	5,0	4,0	2,2	4,3	2,1	1,8	< 2,3
1,2,3,4,7,8-HxCDD	11	4,7	5,7	4,3	2,6	4,4	2,9	2,4	< 2,2
1,2,3,6,7,8-HxCDD	17	8,6	10	8,1	5,9	8,8	6,6	7,3	< 2,2
1,2,3,7,8,9-HxCDD	41	12	15	10	11	15	8,4	8,3	< 2,2
1,2,3,4,6,7,8-HpCDD	157	79	89	84	60	85	86	100	3,4
total TCDF	1057	223	262	114	53	105	48	98	n.d.
total PeCDF	764	252	304	144	68	148	65	58	n.d.
total HxCDF	281	144	209	129	53	129	61	77	n.d.
total HpCDF	206	76	127	74	42	77	62	74	1,7
OCDF	188	40	48	37	28	42	48	54	4,6
total TCDF to OCDF	2496	721	949	498	223	500	285	361	3,1
2,3,7,8-TCDF	45	17	15	11	4,7	8,9	3,8	5,5	< 2,3
1,2,3,7,8/1,2,3,4,8-PeCDF b)	59	22	24	12	4,1	12	5,0	4,9	< 1,7
2,3,4,7,8-PeCDF	49	18	24	14	4,9	13	5,4	6,0	< 1,7
1,2,3,4,7,8/1,2,3,4,7,9-HxCDF b)	35	18	25	14	4,9	14	5,7	7,1	< 1,5
1,2,3,6,7,8-HxCDF	30	15	22	14	4,7	14	5,9	7,2	< 1,5
1,2,3,7,8,9-HxCDF	11	2,3	3,3	2,0	1,0	2,2	1,6	2,3	< 1,0
2,3,4,6,7,8-HxCDF	29	14	24	12	5,8	13	6,7	7,9	< 1,0
1,2,3,4,6,7,8-HpCDF	100	56	94	50	27	54	38	47	0,8
1,2,3,4,7,8,9-HpCDF	6,8	2,9	9,2	3,0	2,3	3,3	2,1	3,8	< 1,3
total TCDD/F to OCDD/F	4624	1401	1732	1211	674	1187	1075	1152	33
TE value (BGA 1984)	90	24	30	18	10	18	10	12	0,1
TE value (NATO / CCMS 1988)	83	25	32	20	10	20	10	12	0,1

a) - For the calculation of averages, concentrations below the detection limit (D.L.) are included with ½ D.L
For totals and toxicity equivalents (TE) undetected congeners and homologues are not included.
b) - congeners not separable on SP 2380
n.d. - not detected

Table 2 : Annual averages of PCB in depositon samples [ng / m² * d] a)
sampling period : 11/91 - 10/92 ; n = 12

sampling location :	Düssel-dorf	Duis-burg	Dort-mund	Gelsen-kirchen	Köln	Essen	Borken	Eifel	Blank
total Monochlorbiphenyls	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
total Dichlorbiphenyls	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
total Trichlorbiphenyls	16	13	11	10	5,4	3,9	2,5	3,0	4,1
total Tetrachlorbiphenyls	31	14	11	11	7,0	4,1	2,8	4,5	1,5
total Pentachlorbiphenyls	91	24	16	11	10	7,0	4,6	7,1	2,6
total Hexachlorbiphenyls	72	34	19	14	18	10	7,2	7,1	3,3
total Heptachlorbiphenyls	45	23	21	11	16	7,6	5,1	2,8	2,0
total Octachlorbiphenyls	4,0	2,1	1,8	1,1	1,4	0,7	0,5	0,2	0,1
total Nonachlorbiphenyls	n.d.	0,1	0,1	n.d.	0,1	n.d.	n.d.	n.d.	n.d.
Decachlorbiphenyl	< 2,8	< 0,5	< 4,5	< 1,3	< 8,0	< 0,6	< 0,7	< 0,4	< 2,6
total Tri- to Decachlorbiphenyl	257	106	79	55	53	32	23	23	12
2,4,4'-Trichlorbiphenyl	3,4	2,8	2,2	2,3	1,7	1,3	0,7	0,6	1,4
2,2',5,5'-Tetrachlorbiphenyl	11	2,8	2,0	2,5	1,8	1,3	0,8	1,2	0,5
3,3',4,4'-Tetrachlorbiphenyl	< 1,1	< 0,6	0,6	< 0,5	< 0,5	< 0,3	< 0,1	< 0,4	< 0,3
2,2',4,5,5'-Pentachlorbiphenyl	35	7,9	4,5	3,8	4,8	2,8	1,7	3,1	1,3
2,3,3',4,4'-Pentachlorbiphenyl	11	3,6	3,9	1,7	1,3	1,0	0,7	0,5	0,5
3,3',4,4',5-Pentachlorbiphenyl	< 1,1	< 0,3	< 0,4	< 0,5	< 0,6	< 0,3	< 0,1	< 0,2	< 0,4
2,2',4,4',5,5'-Hexachlorbiphenyl	24	10	5,2	4,5	5,9	3,4	2,2	2,3	1,1
2,2',3,4,4',5'-Hexachlorbiphenyl	30	13	8,6	5,8	7,1	4,2	2,9	2,1	1,3
3,3',4,4',5,5'-Hexachlorbiphenyl	< 0,5	< 0,2	< 0,2	< 0,2	< 0,3	< 0,2	< 0,1	< 0,1	< 0,2
2,2',3,4,4',5,5'-Heptachlorbiphenyl	13	6,5	4,8	3,2	4,5	2,2	1,5	0,7	0,6

a) - For the calculation of averages, concentrations below the detection limit (D.L.) are included with ½ D.L
n.a. - not analysed
n.d. - not detected