Long-term Ambient Air Measurements of PCDD/PCDF in Southern Germany (1993-1996)

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Abstract

Ambient air levels of PCDD/PCDF were determined from various sampling locations situated within an area potentially impacted by a municipal solid waste incinerator. The PCDD/PCDF concentrations from the two networks were comparable and ranged 8-206 fg I-TEQ/m³ in the surroundings of the Augsburg MSWI and 4-78 fg I-TEQ/m³ in the Burgkirchen MSWI surroundings. A clear seasonal trend was identified in both sampling campaigns with lower PCDD/PCDF concentrations in summer and higher levels in winter. PCDD/PCDF patterns and profiles were similar in all samples with Cl_8DD being the most abundant congener (and homolog); however, in terms of I-TEQ, the highest contribution was due to the presence of 2,3,47,8-Cl_5DF (23-46%) whereas Cl_8DD contributed only 1-5%. At the Augsburg site, no difference in ambient air PCDD/PCDF was found when comparing the results obtained in a sampling campaign before the MSWI went into operation and the present data obtained during operation of the MSWI.

Keywords: Polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, ambient air, monitoring, seasonal trends

1 INTRODUCTION

Combustion processes were identified as the major source of today's inputs of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF) into the environment (1). Whereas in the past, many activities were concentrated to determine the stack emissions from municipal and hazardous waste incinerators and other large facilities, there is increasing interest in monitoring the ambient air concentrations around known combustion sources. In addition, environmental legislation in Bavaria, Germany, has implemented a request to measure organic and inorganic substances in the surroundings of municipal solid waste incinerators (MSWIs), once they went into operation (2).

From Germany, there exists a large database reporting PCDD/PCDF concentrations in deposition samples or in the atmosphere (3-5). It was found, that PCDD/PCDF levels in ambient air exhibit seasonal trends and show lower concentrations in summer than in winter. In 1995, the Bavarian State Ministry of State Development and Environmental Protection reported ambient air concentrations from long-term sampling campaigns from more than samples (6). The mean concentrations from the remote locations (13 locations) were in the range 12-37 fg I-TEQ/m³ whereas the means from locations close to larger

cities or potential thermal sources (20 locations), *e.g.* municipal solid waste incinerators, steel mills, aluminum plants, *etc.*, ranged from 12-67 fg I-TEQ/m³. Here, we report the PCDD/PCDF concentrations from a three years' monitoring program in the vicinity of two MSWIs in southern Germany.

2 EXPERIMENTAL

Ambient air samplers as described earlier (7) were installed in the surroundings of two MSWIs, namely in Augsburg and Burgkirchen. Around the Augsburg MSWI, there were seven sampling devices within the area impacted by the stack emissions (A1-A7) and around the Burgkirchen MSWI there were five sampling devices installed within the potentially impacted area (B1-B5). In addition, in both networks one location was selected as background station with no major dioxin source present (A0, B0).

The sampling time was approximately six weeks per sampling period. The particle-bound PCDD/PCDF were collected on a glass fiber filter and the gaseous PCDD/PCDF were absorbed on a XAD resin. The glass fiber filters and the XAD were analyzed separately; however, we here report the concentrations of the combined fractions. Clean-up, fractionation, and detection of PCDD/PCDF followed established methods and as described earlier (7).

3 RESULTS

The results of the PCDD/PCDF measurements in fg I-TEQ/m³ from the eight locations in Augsburg are summarized in Table 1 and the results from Burgkirchen in Table 2. In addition, the mean and median concentrations of the seven or five locations within the "impact area", respectively, were calculated.

For Augsburg, the lowest concentration was 7.6 fg I-TEQ/m³ at the background station A0 found in summer'95 (= period 14, exact sampling dates: 21.6.1995-2.8.1995). However, this value is almost identical with 9 fg I-TEQ/m³ which were obtained 3-times at other locations within the impact area (A2, A3, and A7) during the same exposure time. The highest concentration with 206 fg I-TEQ/m³ was detected at A4 during Winter'94/95 (23.11.1994-4.1.1995); the maximum at the background station was 129 fg I-TEQ/m³. For the sums of PCDD and PCDF - Σ(PCDD+PCDF) - the minimum and the maximum levels differed by a factor of approximately 10: the lowest concentration was 598 and the highest was 12,690 fg/m³.

For Burgkirchen, the lowest concentration was found with 4.4 fg I-TEQ/m³ at B4 during period 6 in Summer'94 (20.7.1994-31.8.1994). This value and an additional one (5.3 fg I-TEQ/m³ during period 14 = Summer'95 at B1) were lower than the lowest concentration detected at the background station B0 (6.5 fg I-TEQ/m³). The highest concentration was 78 fg I-TEQ/m³ at B2 during period 20 (Winter'95/96).

The minimum and maximum concentrations as well as the ratio of ΣPCDD to ΣPCDF are summarized in Table 3. As can be seen, in most samples there were more PCDD than PCDF present. However, if the concentrations were low, the ratio was inverse independently if the normalization is to I-TEQ or to Σ(PCDD+PCDF). Based on I-TEQ, the PCDD/PCDF concentrations were lower in the Burgkirchen area than in the Augsburg area. In addition, the ranges between minimum and maximum levels were smaller in Burgkirchen (see Table 3) However, once the concentrations are presented in a graphical form (see Figure 1), there is no difference between the PCDD/PCDF concentrations from the two locations.

Table 1: Augsburg: PCDD/PCDF concentrations in ambient air samples (Concentrations in fg I-TEQ/m³)

	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
	Sum'94	Fall'94		Winter'94/95		Spring'95		Summer'95		Fall'95		Winter'95/96			Spring'95	
A1	50	48	73	61	33	34	15	11	14	43	82	106	78	55	26	15
A2	48	55	68	62	37	28	21	9.4	16	36	92	100	71	48	20	10
A3	57	67	60	64	35	40	18	9.3	18	53	91	91	95	42	20	14
A4		130	206	82	66	48	26	31	27	68	151	140	116	72	30	27
A5	66	87	68	65	41	26	15	10	21	64	102	97	98	57	32	16
A6		83	68	74	43	25	16	11	18	72	111	96	105	82	22	18
A7	39	46	62	57	34	17	10	9.3	20	40	73	81	90	44	16	10
Mean	52	74	86	67	41	31	17	13	19	54	100	101	93	57	24	16
Median	50	67	68	64	37	28	16	10	18	53	92	97	95	55	22	15
A0		37	48	36	20	17	16	7.6	15	33	128	129	75	49	19	9.4

Table 2: Burgkirchen: PCDD/PCDF concentrations in ambient air samples (Concentrations in fg I-TEQ/m³).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	20	21	22
	Winter'93/94		Spring'94		Summer'94			Fall'94		Winter'94/95		Spring'95		Summer'95		W'95/96	Spring'96	
B1	46	47	30	13	10	8.8	21	44	62	72	41	16	10	5.3	9.0	36	14	7.9
B2	40	42	19	10	10	7.5	25	44	58	68	26	14	11	7.4	10	78	18	10
B3	37	38	20	14	12	13	24	46	52	39	31	24	11	15	19	53	21	12
B4	39	47	19	13	11	4.4	31	48	64	63	23	19	7.1	6.5	10	46	18	8.8
B5		51	25	12	10	7.7	26	49	70	74	36	19	12	10	12	52	22	11
Mean	40	45	23	12	11	8.3	25	46	61	63	32	19	10	8.8	12	53	18	10
Median	39	47	20	13	10	7.7	25	46	62	68	31	19	11	7.4	10	52	18	10
B0										49	19	14	7.7	6.5	7.9	42	17	6.6

In other words: the minimum and maximum values of the median values form Augsburg and from Burgkirchen are almost identical and were obtained at the same sampling period. Unfortunately, there were no parallel measurements available for Burgkirchen when we found the high concentrations in Augsburg (periods 16-19 = Fall/Winter'95/96).

Table 3: Summary of PCDD/PCDF ambient air concentrations in Augsburg (n=125) and Burgkirchen (n=98)

	ΣPCDD (fg/m³)	ΣPCDF (fg/m³)	Σ(PCDD+PCDF) (fg/m³)	I-TEQ (fg/m³)	ΣPCDD/ΣPCDF Ratio
Augsburg					
Mean	2090	1597	3687	52	1.44
Median	1977	1388	3291	44	1.30
Minimum	329	270	599	7.6	0.60
Maximum	8753	6372	12690	206	3.96
Burgkirchen					
Mean	1227	759	1986	27	1.55
Median	824	554	1393	19	1.43
Minimum	95	207	337	4.4	0.39
Maximum	5315	2148	7213	78	2.80

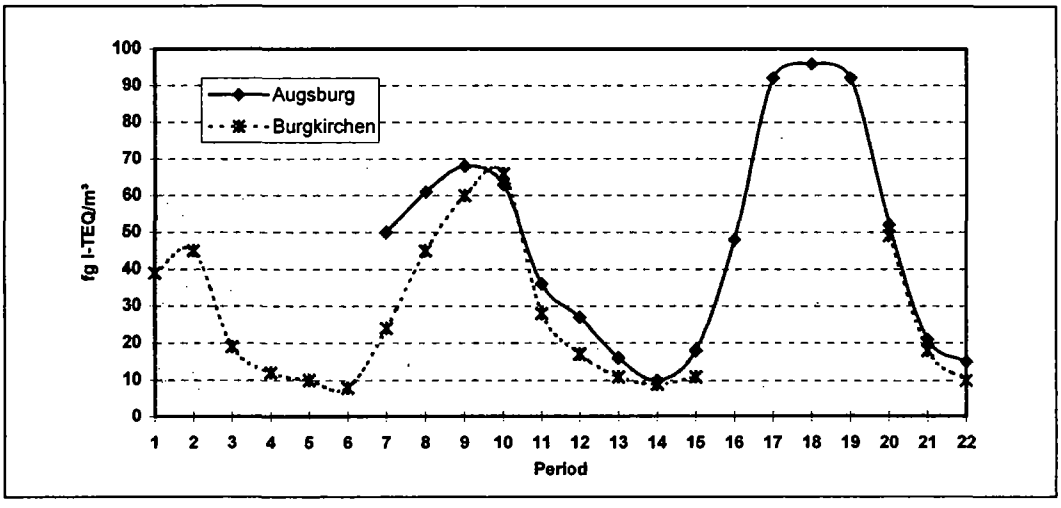

Figure 1: Graphical sketch of the median concentrations of PCDD/PCDF (concentrations in fg I-TEQ/m³) from the two sampling networks

The PCDD/PCDF profiles and patterns were quite similar for all samples. Figure 2 shows the homolog distribution of the samples with the highest and the lowest PCDD/PCDF concentrations. As can be seen from Figure 2, Cl_8DD is the most abundant homolog in all samples (up to 44% of the Σ(PCDD+PCDF)); second is Cl_4DF. However, the highest contribution to the I-TEQ is due to the presence of 2,3,4,7,8-Cl_5DF (23-46%; see Figure 3) whereas Cl_8DD contributes only between 0.7 and 5.4%.

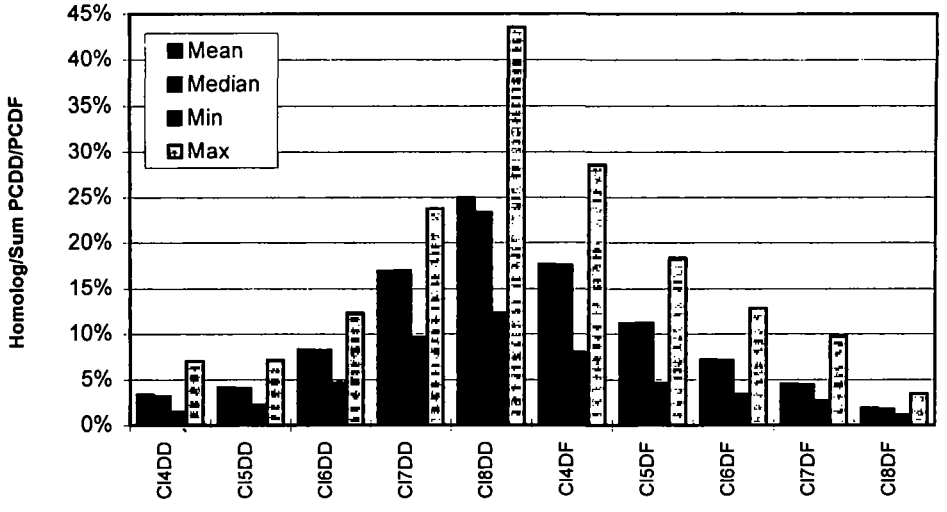

Figure 2: Augsburg: Percentage contribution of homologs to Σ(PCDD+PCDF)

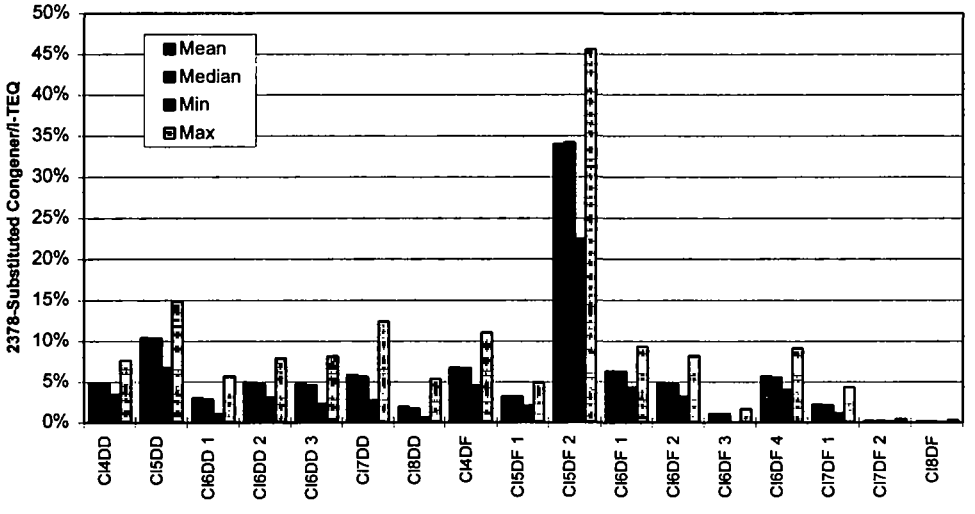

Figure 3: Augsburg: Percentage contribution of 2,3,7,8-substituted congeners to I-TEQ

4 DISCUSSION

Evaluation of 223 ambient air samples obtained from two sampling areas in Bavaria during 2½ years expressed a strong seasonal trend for PCDD/PCDF concentrations. In both sampling networks, higher concentrations were found during the winter months - periods 10+11 and 18-19 - than during the summer months (periods 5-7 and 14+15). During fall, the concentrations generally increase and decrease during spring. At Augsburg with a population of more than 200,000 as well as at Burgkirchen, which is a smaller city, we did not find any difference in the concentrations obtained from sampling locations

situated within the area impacted by the stack emissions from the local incinerator and the background stations with no known dioxin source present.

In an earlier study (8), we reported mean ambient air concentrations from the same sampling locations in the Augsburg network from 14 fg I-TEQ/m³ in June/July 1992 to 120 fg I-TEQ/m³ in December/January 1992/93. The mean concentration from the six sampling locations and over twelve months was 49 fg I-TEQ/m³ (Σ(PCDD+PCDF) was 3,700 fg/m³). These values were obtained during a one year monitoring study before the MSWI went into operation. From these data and our present results obtained when the Augsburg MSWI was operating, we could not identify any difference in ambient air PCDD/PCDF concentrations, in PCDD/PCDF patterns or in spatial distribution.

The mean and median concentrations we found are in agreement with the concentrations reported for the sampling campaign by the Bavarian Ministry for the Environment during 1992/93. Combining these data and our data, the ambient air concentrations in Bavaria have not changed during the last five years and stay on a low level.

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