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PCDD/PCDF in the Atmosphere of Southern Mississippi, USA

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Abstract

In winter 1995/96 and summer 1996, we measured PCDD/PCDF levels in the air from a rural area of the southeastern United States. Baseline concentrations of PCDD/PCDF in air were determined by three sampling methods. First, we collected direct atmospheric samples using high-volume samplers. Second, we collected atmospheric deposition using Bergerhoff samplers. Third, we measured PCDD/PCDF levels in pine needles. Generally, the mean concentration of PCDD/PCDF in winter was approximately 3 times higher than in summer using the high-volume samplers. Individual concentrations ranged from 1.1 to 18 fg I-TEQ/m³. The deposition from the Bergerhoff method resulted in very low PCDD/PCDF concentrations (0.42-3.1 pg I-TEQ/m²·d). Finally, the present study confirmed our earlier results of low PCDD/PCDF levels in pine needles.

Key Words: Polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, ambient air, high-volume samplers, deposition, pine needles, seasonal variation, southeast USA

1 INTRODUCTION

Many current combustion processes are significant sources of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) in the environment. Once emitted into the air, PCDD/PCDF can be transported long distances *via* the atmosphere and, thus, can be detected in remote areas with no known major point sources. Data for PCDD/PCDF in ambient air are available from western Europe (*e.g.* Germany and the United Kingdom) (1-5) and USA (6, 7).

In 1994, we measured atmospheric PCDD/PCDF concentrations in southern Mississippi, USA, by analyzing pine needles from eight locations (8). The results indicated that the concentrations of PCDD/PCDF in this area were relatively low compared to other areas (1-7). This was not surprising given the primarily rural nature of this state. In our present study, we sought to confirm our earlier results by expanding our collection methods to include high-volume samplers and Bergerhoff samplers and by repeating our analysis of pine needles.

2 MATERIALS AND METHODS

We used three sampling methods to measure PCDD/PCDF concentrations in the atmosphere of southern Mississippi. The results from each method are discussed later in this paper. The high-volume air samplers and the Bergerhoff samplers were set up at the same time and for the same duration on private properties in Lamar County and in George County. The pine needles were collected from trees adjacent to these samplers.

2.1 Ambient Air Samples

Air sampling was performed with high-volume samplers as developed and used by the Norwegian Institute for Air Research (NILU), Kjeller, Norway (9). Each sampling period - December 1995/January 1996 (winter exposure) and June/July 1996 (summer exposure) - consisted of four one-week exposures. The sampler consisted of a glass fiber filter to collect particulates, and a polyurethane foam (PUF) plug to absorb the finest particulates and any gaseous PCDD/PCDF. The air flow was controlled with a pump; the flow rate was set at 7.1 m^3/h (118 L/min). The top of the sampling unit was approximately 2 m from the ground and was protected with an iron cap to keep out precipitation. Before exposure, the filters were spiked with $^{13}C_{12}$-labeled PCDD/PCDF. Extraction, clean-up, fractionation, identification, and quantification of PCDD/PCDF was performed according to standard procedures and as described by Fiedler *et al.* (8).

2.2 Deposition Samples

The Bergerhoff method is a standard procedure of the German VDI (Association of German Engineers) to collect dry and wet deposition (10). Fifteen pre-cleaned amber glass jars were placed in a grid consisting of three lines with five jars each (approximately 1 m between adjacent poles). The jars were approximately 1.8 m above the ground and exposed for 27-29 days. The total sampling area was 0.0933 m^2 per location. After exposure, the glass jars were removed from the poles and, all water, if any, from the jars was combined in one pre-cleaned brown glass bottle. To remove all PCDD/PCDF collected in the samplers, each jar was first rinsed with distilled water (150 mL) and acetone (150 mL); all rinsates were combined into one glass jar. Then, the jars were wiped with pre-cleaned glass fiber filter papers until the filters did not contain any visible color. All filter papers were placed in one pre-cleaned amber glass jar. PCDD/PCDF concentrations were determined by analyzing the combined water phases and filters according to standard procedures (11-14).

2.3 Pine Needle Samples

Southern Long Leaf Pine needles (approximately 250 g) were collected from the two locations where the high-volume samplers and the Bergerhoffs were set up. The collections were in January 1996 and July 1996, the same sampling times for the other methods. We identified by visual inspection exposure periods from the January 1996 pine needles of 9 months (growth starting in April 1995) and 21 months (growth starting in April 1994). Similarly, we identified exposure periods of 15 months (growth starting in April 1995) and 3 months (growth starting in April 1996) for the July 1996 collection. Table 3 includes these exposure periods. The sampling and analytical procedures were described by Fiedler *et al.* (8).

3 RESULTS

The PCDD/PCDF concentrations for the ambient air samples are given in Table 1 for the sum of the homologues (ΣPCDD/PCDF) and for the I-TEQ. In addition, we calculated the dioxin/furan ratio (ΣPCDD/ΣPCDF). The ΣPCDD/PCDF and the I-TEQ were higher in winter than in summer by a factor of approximately 3. The mean concentration was 10.9 fg I-TEQ/m³ (range: 5.6-17 fg I-TEQ/m³) for the winter exposure and 3.7 fg I-TEQ/m³ (range: 2.3-6.1 fg I-TEQ/m³) for the summer exposure. The results for the two sampling locations were comparable. There were more PCDD present than PCDF in all samples except the Lamar Co., 1st week winter exposure (Table 1).

Table 1: PCDD/PCDF in ambient air samples. ½ the LOQ (limit of quantification) for non-quantifiable congeners was used to calculate the I-TEQ.

Location - Week	ΣPCDD/PCDF (fg/m³)		I-TEQ (fg/m³)		ΣPCDD/ΣPCDF Ratio	
	Winter	Summer	Winter	Summer	Winter	Summer
Lamar Co. - 1	1756	568	17	6.1	0.97	3.42
Lamar Co. - 2	845	559	12	5.1	2.30	3.41
Lamar Co. - 3	1226	287	13	2.6	3.85	4.02
Lamar Co. - 4	555	*	6.0	*	3.94	*
George Co. - 1	521	214	5.6	2.6	1.47	1.61
George Co. - 2	1911	*	13	*	7.08	*
George Co. - 3	1616	184	15	2.3	5.31	1.68
George Co. - 4	567	*	7.0	*	2.59	*
Mean	**1126**	**362**	**10.9**	**3.7**		

* No sample available due to breakage of sampler or pump.

The PCDD/PCDF results for the deposition samples are summarized in Table 2. The mean concentration normalized to pg I-TEQ/(m²·d) for the winter exposure was approximately 4 times higher than the summer exposure in both counties. Similarly, the sum of the homologues was three times higher in the winter exposure than the summer exposure for Lamar County. This difference, however, was not observed for the sum of the homologues in George County, where the summer exposure was actually greater than the winter exposure (153 pg/(m²·d) *vs.* 115 pg/(m²·d)) (Table 2).

The results for the pine needles are shown in Table 3. The ΣPCDD/PCDF concentrations ranged from 10 to 54 pg/g d.m. and I-TEQ ranged from 0.16 to 0.79 pg/g d.m. As can be seen from Table 3, there is a trend towards higher concentrations with increasing exposure times. However, there was not a linear correlation between time and PCDD/PCDF concentration.

Table 2: PCDD/PCDF in deposition samples (Bergerhoff method). ½ the LOQ for non-quantifiable congeners was used to calculate the I-TEQ.

Location	ΣPCDD/PCDF pg/(m²·d)		I-TEQ pg/(m²·d)		ΣPCDD/ΣPCDF Ratio	
	Winter	Summer	Winter	Summer	Winter	Summer
Lamar Co.	188	63.5	3.1	0.42	4.6	8.9
George Co.	115	153	2.0	0.73	3.8	6.1
Mean	**152**	**108**	**2.6**	**0.58**		

Table 3: PCDD/PCDF in pine needle samples. ½ the LOQ for non-quantifiable congeners was used to calculate the I-TEQ.

Location	Shoot	Exposure Time (Months)	ΣPCDD/PCDF (ng/kg)	I-TEQ (ng/kg)	ΣPCDD/ΣPCDF Ratio
Lamar Co.	1995	9	20	0.29	2.0
George Co.	1995	9	19	0.23	2.5
Mean		**9**	**20**	**0.26**	
Lamar Co.	1994	21	37	0.56	2.1
George Co.	1994	21	27	0.40	1.6
Mean		**21**	**32**	**0.48**	
Lamar Co.	1995	15	49	0.55	2.6
George Co.	1995	15	54	0.79	2.0
Mean		**15**	**51**	**0.67**	
Lamar Co.	1996	3	20	0.30	1.9
George Co.	1996	3	10	0.16	2.4
Mean		**3**	**15**	**0.23**	

4 DISCUSSION

In this study, we confirmed the ubiquitous presence of PCDD/PCDF in ambient air from this rural area in the southeastern United States. To our knowledge, this is the first study to use three separate methods at the same time to determine PCDD/PCDF in ambient air at the same locations. All three methods can be used to detect PCDD/PCDF; however, more work must be done before meaningful correlations between methods can be made. Our data also confirm the findings from Europe that there is seasonal variation in PCDD/PCDF concentrations, with higher levels in winter than in summer. Depending on the method applied (high-volume sampler *vs.* deposition sample) and the normalization of data (ΣPCDD/PCDF *vs.* I-TEQ), winter concentrations are greater than summer concentrations by a factor of 1.5 to 4.5.

The PCDD/PCDF levels we measured in southern Mississippi using the high-volume samplers (2.3-17 fg I-TEQ/m³) are lower than ambient air concentrations (15-20 fg I-TEQ/m³) reported from remote areas in Germany (1, 2). Likewise, the deposition from southern Mississippi (0.42-3.1 pg I-TEQ/(m²·d)) is lower than in rural areas in Germany (5-7 pg I-TEQ/(m²·d), Ref. 2).

Smith *et al.* reported 1,200 fg ΣPCDD/PCDF/m³ in a rural site and 2,000 fg ΣPCDD/PCDF/m³ near an urban site in the northeast USA (6). The 1993 average deposition was determined to 532 pg ΣPCDD/PCDF/(m²·d), but no I-TEQ was reported. These levels are two and four times higher, respectively, than our Mississippi results for the air concentrations and the deposition (see Table 1 and Table 2).

The pine needle concentrations (0.16-0.79 ng I-TEQ/k.g. d.m.) are consistent with our earlier results where we measured between 0.07 and 0.51 ng I-TEQ/kg d.m. (8).

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