PCDD/PCDF in Soil and Pine Needle Samples in a Rural Area in the United States of America

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ABSTRACT

In summer 1994, a sampling and monitoring program was performed in a rural area in the USA to determine baseline concentrations of PCDD/PCDF in soil and in pine needles. The median soil level found in eight counties in southern Mississippi was below 1 ng I-TEQ/kg d.m. The highest level - 22.6 ng I-TEQ/kg d.m. - was found in an oxbow. The presence of PCDD and PCDF in the atmosphere of southern Mississippi was proven by analysis of pine needles, which are passive samplers for lipophilic substances. The levels detected in the pine needles were lower than those found in more populated and industrialized areas in Germany or near point-sources in the USA.

1 INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) are distributed ubiquitously. Due to the high affinity of these compounds to organic carbon and lipophilic matter, PCDD/PCDF can be found in environmental matrices such as soils and plants. The concentrations in these matrices thus can be used to describe the long-term (soil) and short-term (plants) exposure to PCDD/PCDF. Dioxin and furan levels in soil and pine needles have been extensively reported from European countries, whereas minimal data is available for the United States (Birmingham 1990, US-EPA 1987, Safe *et al.* 1992).

One purpose of this study, conducted in southern Mississippi in 1994, was to obtain an overview of PCDD/PCDF concentrations in soils from a sparsely populated region of the United States. These levels provide further information on past and recent inputs of PCDD/PCDF from various sources (*e.g.* application of pesticides, fall-out from thermal sources, flooding of rivers, *etc.*). Another purpose was to determine the present atmospheric load of PCDD/PCDF by using passive samplers such as pine needles in Mississippi.

2 MATERIALS AND METHODS

2.1 Study Design

Two matrices, soil and pine needles, were selected to determine baseline concentrations of PCDD/PCDF in southern Mississippi. The selected sampling sites were not directly impacted by human activities, *e.g.* heavy traffic or dust. Pine needles were sampled from trees with ready access to the air and, therefore, trees from dense forests were not sampled. Finally, because controlled burning is a common practice in southern Mississippi, potential sites were not excluded when traces of former fires could be seen.

2.1.1 Soil Samples

Soil samples were collected from eight counties in southern Mississippi. The samples were taken from publicly owned land (16th section land) from seven counties: Lamar, Greene, Forrest, Jackson, Jones, Perry, and Wayne. One sample was also taken from in George County. Thirty-six soil samples were collected, each was a composite of five individual samples. Two inches of top soil were taken from the first point and then four additional samples from 6 m in each of the four main directions (North, East, South, West) from the first point. Litter and interfering material were removed prior to collection.

2.1.2 Pine Needle Samples

Southern Long Leaf Pine needles (approximately 250 g) were collected from eight of the locations where soil samples were obtained. The twigs were cut with scissors at a height of approximately 3 m, after both the 1994 shoot (identified by the lighter green color of the needles) and the 1993 shoot. The needles were carefully removed and the lower, brown section was discarded. The pine needles were not rinsed with water or any other solvent in order to keep the fine particulates on the needles' surface as an indicator of atmospheric deposition. The needles were wrapped in pre-cleaned aluminum foil, placed into a plastic bag and stored at 4 °C before analysis.

2.2 Analytical

2.2.1 Soil Samples

The soil samples were air-dried in the laboratory in a glass jar for one week. The dry samples were crushed in a steel blender (Waring MC-2) and sieved; only the fraction <2 mm was analyzed.

Extraction: Aliquots of 10 to 20 g soil were extracted for 12 h with 150 mL of toluene in a Soxhlet extractor equipped with a Dean Stark collector. A ^{13}C-labelled internal standard mixture (250 pg; one compound per degree of chlorination; Cambridge Laboratories, Woburn, USA) in 50 µL of tetradecane was added to the extraction solvent. Determination of dry matter

(d.m.) content was achieved by drying a 1 to 3 g subsample at 130 °C overnight and the percent loss of ignition (LOI) was determined by heating the dry soil to 500 °C for 2 h.

Clean-up: After evaporation of the solvent, clean-up was carried out using a three disposable column set (A = glass column, I.D. = 3.8 cm, L = 20 cm, packed with 0.5 cm of sodium sulfate, 4 cm of silica and 3 cm of potassium hydroxide silica; B = a double column, one packed with 0.5 cm of acid washed copper, 0.5 cm of sodium sulfate, 2.5 cm of silica and 2.5 cm of sulfuric acid silica and a second alumina column packed with 0.5 cm of sodium sulfate and 4 cm of basic alumina; C = Carbopack C (18 %) on celite column). The samples were eluted using 35 mL of toluene into a 40 mL vial. 30 µL of *n*-tetradecane and 250 pg of recovery standard mixture was added to the eluate.

PCDD/PCDF Analysis: Final separation and detection of PCDD/PCDF were performed using a high resolution gas chromatograph equipped with first a 60 m SP-2330 fused silica column for the 2,3,7,8-substituted congeners or second a non-polar 60 m DB-5 fused silica column for the homologues, which are interfaced to a VG 70-250S double focusing mass spectrometer operating at a resolution of 8,000-10,000. The instrument was operated in a selected ion monitoring (SIM) mode. A blank sample was analyzed for every batch of 4-6 samples.

2.2.2 Pine Needle Samples

The analysis of PCDD/PCDF in pine needles was performed using a modification of the method developed by Reischl *et al.* (1987 and 1989).

Sample Preparation: Pine needles (80-150 g) were cut into 1 cm long pieces and extracted with dichloromethane in an ultrasonic bath for 10 min. This procedure was repeated twice with fresh dichloromethane. The combined extracts were filtered over glass wool. The internal standard mixture was added and the mixture concentrated with a rotary evaporator. The extracted needles were dried at 105 °C for 24 h for determination of the dry-weight; additionally, the amount of extracted waxy material was determined.

Clean-up: The extracts were cleaned-up *via* a mixed column (33 % NaOH-silica/ 44 % H_2SO_4-silica (1:4) and 33 % NaOH-silica/22 % H_2SO_4-silica) followed by two additional columns (B and C) as described for soil and deposition samples.

PCDD/PCDF Analysis: The pine needle analysis was conducted in the same manner as described above for the soil samples.

3 RESULTS

The results for the soil samples are reported in Table 1. PCDD/PCDF levels ranged from 0.16 to 22.9 ng I-TEQ/kg with a mean value of 3.0 ng I-TEQ/kg and a median value of 0.76 ng I-TEQ/kg. In most samples Cl_8DD was the predominant congener and contributor to the I-TEQ. The example shown in Figure 1 is representative of the majority of the soil samples (I-TEQ is 1.42 ng/kg).

The highest concentration (22.9 ng I-TEQ/kg) was found in a sample taken from an oxbow adjacent to the Leaf River. This site has been flooded in the past and the homologue distribution is similar to sediment samples collected from the Leaf River drainage system (see Figure 2) (Rappe *et al.* 1995). No correlation was observed between the organic carbon content of the soils and the levels of PCDD/PCDF. However, as shown in Figure 3 (I-TEQ is 7.15 ng/kg), there were major contributions from the lower chlorinated PCDF (for more detail, see Rappe *et al.* 1995b). 2,3,7,8-Cl_4DD at a detection limit of 0.02-0.05 ng/kg sample could be detected in 17 of the 36 soil samples. However, 2,3,7,8-Cl_4DD was never a major contributor to the I-TEQ (more than 20 %) (see Figures 1, 2, and 3).

Table 1: PCDD/PCDF concentrations in soil samples (ng I-TEQ/kg d.m.)

County	I-TEQ	County	I-TEQ	County	I-TEQ
George	0.16	Jones	20.30	Perry	0.52
Jackson	0.63	Jones	1.31	Perry	0.17
Jackson	0.38	Jones	14.30	Wayne	0.17
Jackson	0.31	Jones	2.81	Wayne	7.15
Jackson	0.32	Lamar	0.63	Wayne	3.41
Jackson	0.27	Lamar	0.55	Wayne	0.08
Forrest	10.90	Lamar	1.42	Wayne	1.66
Forrest	1.12	Lamar	0.36	Greene	0.20
Forrest	1.05	Lamar	0.15	Greene	1.03
Forrest	0.93	Perry	8.09	Greene	5.26
Forrest	0.25	Perry	2.75	Greene	0.18
Jones	0.90	Perry	22.90	Greene	0.37
Mean	**3.14**	**Min**	**0.08**		
Median	**0.77**	**Max**	**22.90**		

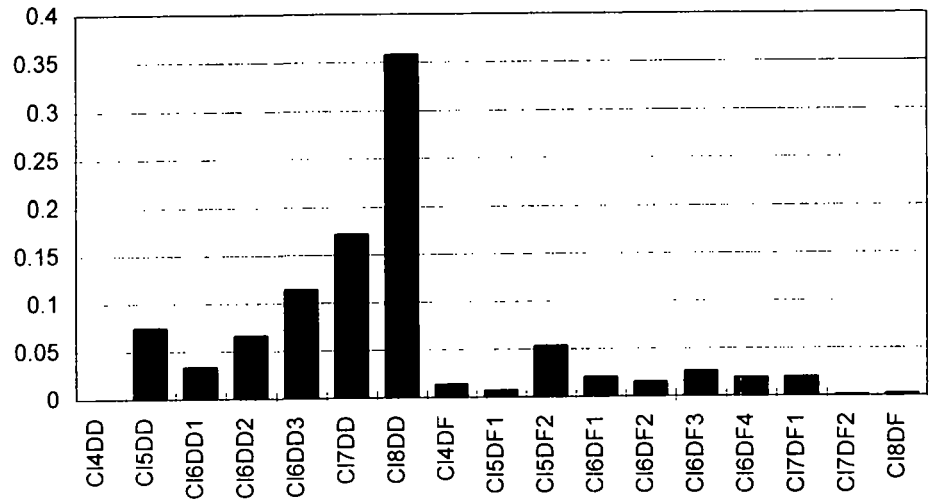

Figure 1: Contribution to I-TEQ; sample representative for majority of samples

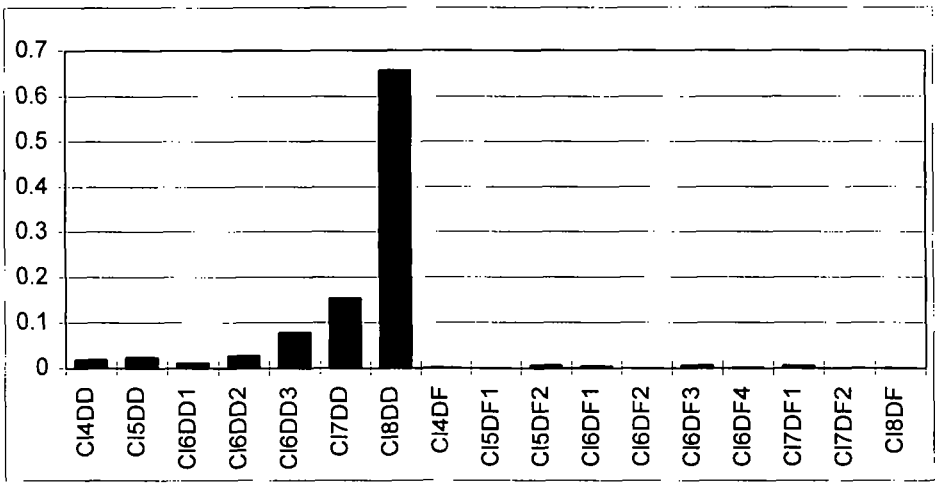

Figure 2: Contribution to I-TEQ; Cl_8DD dominating in soil from oxbow

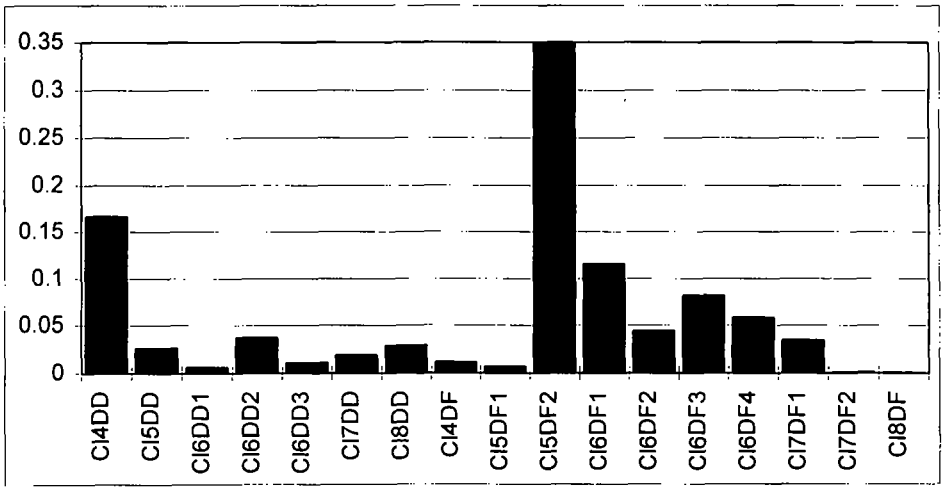

Figure 3: Contribution to I-TEQ; PCDF dominating

The results for the pine needles are reported in Table 2. PCDD/PCDF levels ranged from 0.11 to 0.23 pg I-TEQ/kg d.m. for the 1994 shoot and 0.07 to 0.51 pg I-TEQ/kg d.m. for the 1993 needles. The highest concentrations were found in the samples from Forrest County and the lowest were from Perry County. These results are in agreement with the regional situation considering the sampling sites in Forrest and Lamar Counties were only a few miles from the city of Hattiesburg with potential dioxin sources, such as hospital waste incinerators and automobile emissions. Thus, the impact from this more populated urban area was evident in the higher PCDD/PCDF levels in pine needles.

Table 2: PCDD/PCDF concentrations in pine needle samples (pg I-TEQ/g d.m.; the I-TEQ includes ½ detection limit in cases of non-detectable concentrations)

	I-TEQ (1994)	I-TEQ (1993)
George	0.15	0.31
Lamar	0.21	0.39
Greene	0.15	0.14
Forrest	0.23	0.51
Perry	0.11	0.07
Wayne	0.14	0.17
Jackson *	0.18	
Jones *	0.17	

* No differentiation between 1994 and 1993 needles was apparent.

4 DISCUSSION

A PCDD/PCDF database of 1,594 soil samples from Germany was published in 1992 (BLAG 1992). The soil levels from rural areas ranged between 1 and 5 ng I-TEQ/kg. Also, relatively high concentrations - up to 46 ng I-TEQ/kg - were detected in the organic top-layers of forest soils. A maximum level of 140 ng I-TEQ/kg d.m. was found in litter. In urban areas, typically the PCDD/PCDF levels in soil were between 10 and 30 ng I-TEQ/kg d.m., whereas in industrial areas the concentrations were up to 100 ng I-TEQ/kg d.m. PCDD/PCDF soil levels of 30,000 ng I-TEQ/kg were detected near point-sources, such as copper smelting plants, or in chemical waste disposal sites. Other, more recent data from Bavaria (Germany), showed that 89 % of 120 soil samples from arable land had concentrations below 1 ng I-TEQ/kg (Joneck *et al.* 1992). The highest level was found to be 25 ng I-TEQ/kg.

Birmingham (1990) previously summarized PCDD/PCDF levels in 30 soil samples from urban areas in Canada (Ontario) and the United States (Midwest) with mean concentration of 0.4±0.6 ng I-TEQ/kg. The EPA 1987 National Dioxin Survey (EPA 1987) reported that for 100 contaminated sites, soil levels of 2,3,7,8-Cl_4DD were < 1 µg/kg at only 11 sites and concentrations > 2,000 µg/kg were found at some locations. Due to differences in study design it is difficult to compare the results of the present study with previous soil data from the United States and Canada. Nonetheless, the results summarized in Table 1 demonstrate that PCDD/PCDF soil levels in most locations in southern Mississippi were < 1 ng I-TEQ/kg. The higher concentrations were observed in impacted areas and these data are consistent with results previously reported for soil.

The outer waxy surface of pine needles absorbs atmospheric lipophilic pollutants (Reischl *et al.* 1987, 1989) and serves as an excellent biomonitoring system for these compounds. Recent studies from Bavaria and Hessen in Germany reported that mean PCDD/PCDF levels in pine needle extracts ranged from 0.53 to 1.64 pg I-TEQ/g d.m. (Köhler *et al.* 1994, Fiedler *et al.* 1995). Safe *et al.* (1992) reported higher levels of PCDD/PCDF in pine needles in the vicinity of a wood-preserving waste site (7.7 and 5.4 pg I-TEQ/g d.m.) and lower levels off-site (1.3 and 2.7 pg I-TEQ/g d.m.). The results summarized in Table 2 for sampling locations in southern Mississippi show that PCDD/PCDF levels in the surface layer of pine needles varied from 0.07 to 0.51 pg I-TEQ/g d.m. These data suggest that atmospheric concentrations of PCDD/PCDF in Mississippi are relatively low and this reflects the primarily rural nature of this state.

5 ACKNOWLEDGEMENT

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