Retrospective Monitoring of PCDDs, PCDFs, and PCBs in Pine- and Spruce-Shoots - Results from the German Environmental Specimen Bank

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Introduction

Several recent studies confirm that persistent organic pollutants from ambient air accumulate in plants. Thus, plants play an important role in the entry of such compounds into the terrestrial food chain. Time series from the beginning of the 1990s show a declining trend for PCDD/Fs in ambient air and deposition samples in Germany, particularly in wintertime, but this decrease has leveled off since approximately 1994 [1,2,3,4,5]. However there is a lack of consistent and comparable data for time series and spatial distribution in plants. Especially conifers serve as a biomonitoring system to determine ambient air concentrations and the accumulation in plants during the time of exposure. Also, only little is known about the concentrations of dioxin-like PCBs and the relationship between them and PCDD/Fs and indicator PCBs. Therefore archived samples of the German environmental specimen bank (ESB) were used for retrospective monitoring in plants.

The German ESB was established in 1985 as a permanent institution for the systematic collection, processing, characterization and storage of environmental samples from marine, fresh water and terrestrial ecosystems as well as human samples[6].

The aim of the present study was to determine the level and the time trend of PCDDs, PCDFs, dioxin-like PCBs and indicator PCBs in conifer shoots from 1985 to 2003 and to compare the findings with results of the German Dioxin Database.

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Materials and Methods

Samples. The study was conducted on one year old shoots of pine (*Pinus sylvestris*) and spruce (*Picea abies*) archived by the German ESB. The samples were collected and processed under well defined and reproducible conditions according to standard operating procedures[7] . Thus, every precaution is taken to obtain representative samples of the same quality each year. The material is stored as freshly homogenized and grinded powder in sub-samples of approx. 10 g in the vapor phase above liquid nitrogen. Spruce shoots have been collected since 1985 in Warndt, a forest in

the urban-industrialized area of the Land Saarland in the south west of Germany. Pine shoots have been collected since 1991 in Duebener Heide Mitte, a forest in an urban-industrialized area in eastern Germany.

Laboratory procedure. The whole analytical process was performed in a lab certified according to DIN EN ISO/IEC 17025 guideline. Samples were stored at –55 °C until freeze-drying was performed. After addition of all 17 2,3,7,8-substituted PCDD and PCDF as well as 12 WHO-PCB and 6 indicator PCB congeners as $^{13}C_{12}$-labelled standards, freeze-dried samples were extracted with toluene in a Soxhlet apparatus for 24 h. Clean-up, separation of PCDD/PCDFs from PCBs and fractionation of PCBs was performed in the same way as described elsewhere[8]. PCDD/PCDFs and PCBs were analyzed by high resolution capillary gas chromatography coupled with high resolution mass spectrometry (HRGC/HRMS). Gaschromatographic separation was performed on a 60 m SP-2331 and 60 m DB-XLB capillary column (PCDD/Fs) and on a 60 DB-XLB column for PCB. For congeners with a concentration below the limit of quantification (LOQ, signal to noise value of 10:1 of the mass used for quantification), these LOQ values are given as "<". Toxicity equivalent concentrations (TEQ) were calculated 1) without congeners below LOQ and 2) with half of the limit of detection (LOD, signal to noise value of 3:1 of the quantification mass).

Results and Discussion

Indicator PCBs: In spruce shoots the sum of the 6 indicator PCBs (#28, 52, 101, 138, 153, 180) decreased more than 50 % from 1985 to 1999 and increased in the last few years. In pine shoots no downward trend in indicator PCBs was ascertainable since 1991 (Fig. 1). In recent years PCB concentrations increased slightly at both locations. The profile of the congeners did not change over that time. PCB 153 dominates in all samples. Data from some years are shown in Table 1 as an example.

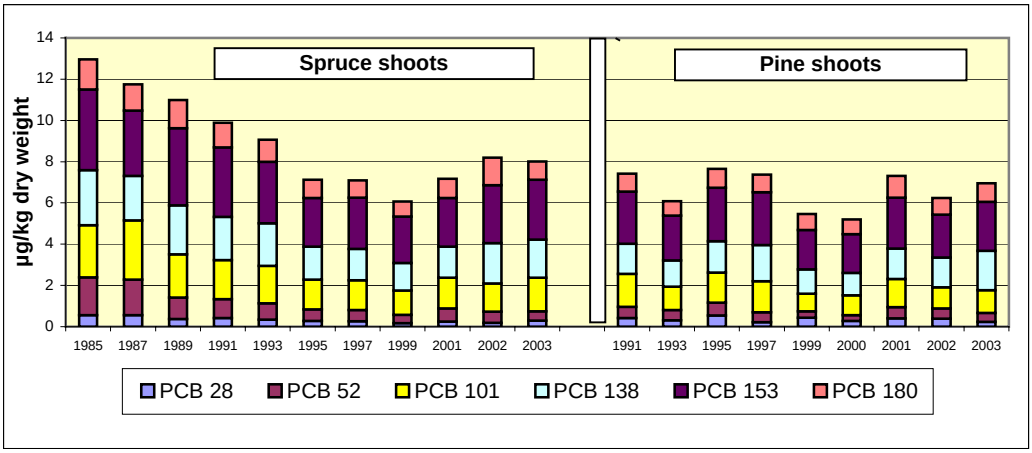

Fig. 1: Sum of 6 indicator PCBs and congener profiles in conifer shoots, time series from 1985 to 2003 (spruce) and 1991 to 2003 (pine).

PCDD/Fs and dioxin-like PCBs in spruce shoots: As shown in Fig. 2 concentrations of PCDD/Fs and the 12 WHO-PCBs decreased about 75 % from 1985 to 1999. The highest values date from 1985 with a total amount of 5.6 ng WHO-TEQ/kg dry weight, PCDD/Fs of 3.7 ng WHO-TEQ/kg and dioxin-like PCBs of 1.9 ng WHO-TEQ/kg. Since 1999 no clear trend in concentrations of PCDD/Fs and PCBs was observed. Dioxin-like PCBs contribute in all samples less than 40 % to the total TEQ (range 24 – 39 %). The contribution of PCB 126 to the PCB-TEQ is in the range of 44 to 81 %.

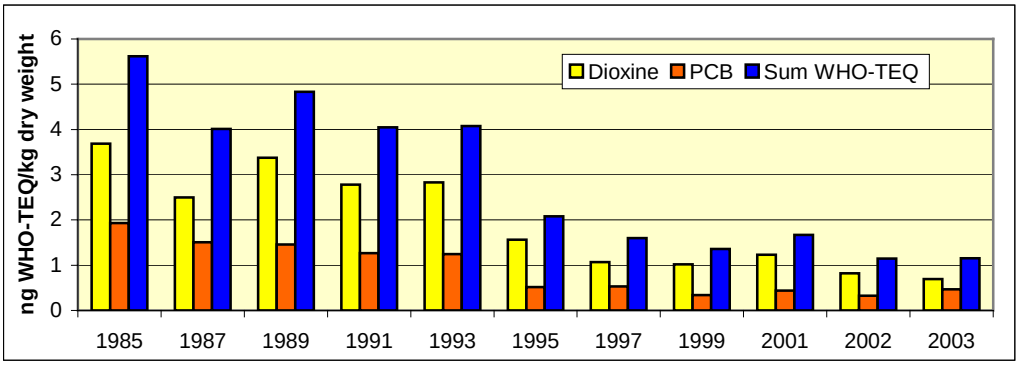

Fig. 2: Concentrations of PCDD/F and WHO-PCBs in spruce shoots at the location Warndt, time series from 1985 to 2003

PCDD/Fs and dioxin-like PCBs in pine shoots: As shown in Fig. 3 in pine shoots PCDD/Fs decreased from 1991 to 1995 by about 40 %, then leveled off, and increased in 2003. Dioxin-like PCBs decreased only about 30 % over this period. The contribution of dioxin-like PCBs to the total TEQ is low, ranging from 11 to 22 %. The contribution of PCB 126 to the PCB-TEQ is in the range of 20 to 47 % and is thus also quite small compared to spruce shoots.

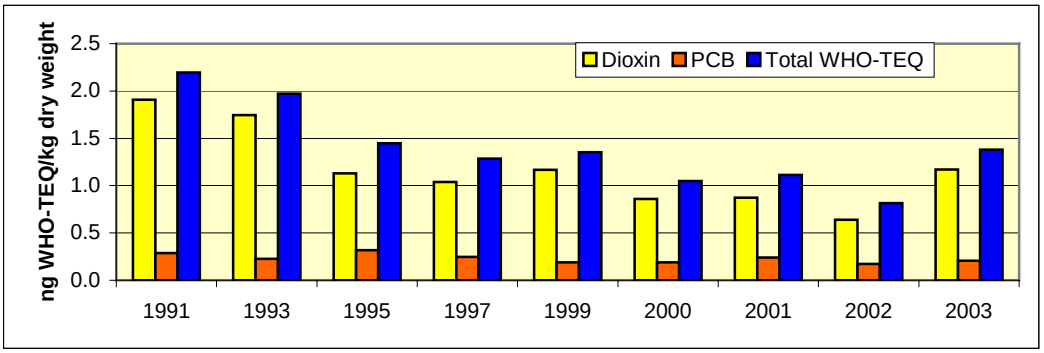

Fig. 3: Concentrations of PCDD/Fs and WHO-PCBs in pine shoots at the location Duebener Heide, time series from 1991 to 2003

Homologue profiles of PCDD and PCDF: The homologue profiles from spruce shoots vary only a bit with the years. Pine shoots have similar homologue profiles of furans but differ a little more within the dioxin homologue groups. TCDF-homologues are dominant with more than 30 percent of the total amount. Similar distribution is found in grass [4]. In contrast the dominant homologue group in ambient air and deposition samples is OCDD as the example of a background station in Hessen shows [4].

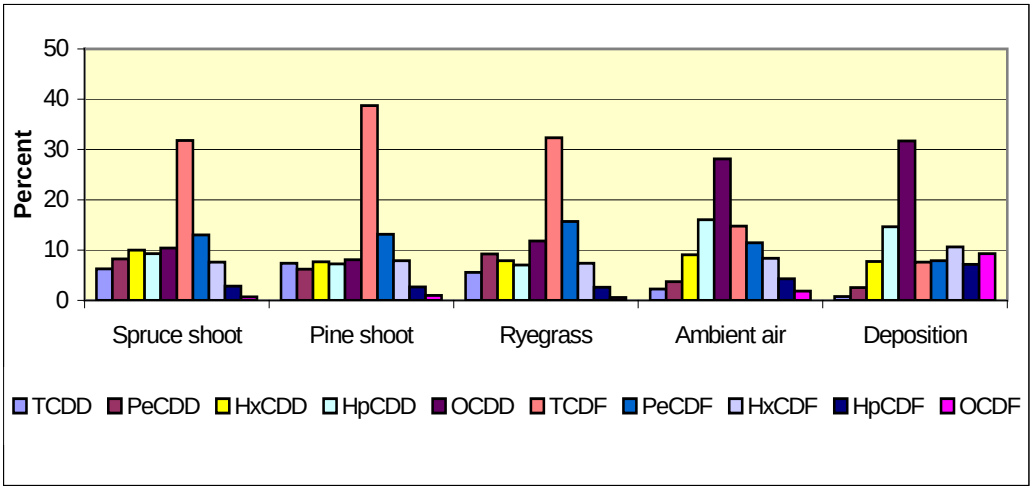

Fig. 4: Homologue profiles of PCDDs and PCDFs in spruce shoots (means 1981-2003) and pine shoots (means 1991-2003) compared with homologue profiles in ryegrass (means 1996/97, n=42) and in ambient air and deposition at a background station (means 1990-1998) (Source: 4th Report on Dioxins [4])

	Spruce shoots in µg/kg dry weight				Pine shoots in µg/kg dry w		
Year	**1985**	**1991**	**2001**	**2003**	**1991**	**2001**	**2003**
di-ortho PCB							
PCB 28	0.55	0.42	0.25	0.29	0.43	0.40	0.23
PCB 52	1.83	0.92	0.64	0.46	0.54	0.54	0.43
PCB 101	2.53	1.89	1.48	1.63	1.59	1.37	1.10
PCB 138	2.67	2.10	1.51	1.83	1.47	1.47	1.91
PCB 153	3.90	3.36	2.35	2.90	2.52	2.47	2.38
PCB 180	1.46	1.20	0.94	0.89	0.88	1.06	0.91
Sum 6 indicator PCB	**13.0**	**9.89**	**7.17**	**8.00**	**7.42**	**7.32**	**6.96**
mono-ortho PCB							
PCB123	0.112	0.082	0.017	0.045	0.032	< 0.008	0.021
PCB118	1.87	1.00	0.552	0.722	0.616	0.673	0.726
PCB114	0.027	0.008	< 0.005	0.007	0.006	< 0.009	< 0.012
PCB105	0.801	0.363	0.166	0.183	0.110	0.059	0.120
PCB167	0.119	0.110	0.071	0.078	0.082	0.040	0.042
PCB156	0.262	0.247	0.178	0.162	0.182	0.123	0.102
PCB157	0.037	0.025	0.013	0.016	0.019	< 0.006	0.007
PCB189	0.025	0.015	0.012	0.014	0.015	< 0.018	0.020
Sum mono-ortho-PCB	**3.25**	**1.85**	**1.01**	**1.23**	**1.06**	**0.853**	**1.03**
non-ortho PCB							
PCB81	0.0034	0.0020	< 0.0008	0.0008	< 0.0008	< 0.0004	< 0.0004
PCB77	0.134	0.0690	0.0294	0.0286	0.0244	0.0083	0.0111
PCB126	0.0147	0.0096	0.0026	0.0027	0.0010	0.0010	0.0006
PCB169	< 0.0004	0.0009	< 0.0006	0.0003	< 0.0004	< 0.0003	< 0.0002
Sum non-ortho-PCB	**0.152**	**0.082**	**0.032**	**0.032**	**0.025**	**0.009**	**0.012**
PCB-WHO-TEQ [ng/kg dry weight]	**1.93**	**1.27**	**0.44**	**0.47**	**0.29**	**0.24**	**0.21**
% PCB126 of PCB-TEQ	**76**	**76**	**60**	**58**	**36**	**43**	**29**
PCDD/F-WHO-TEQ [ng/kg dry weight]	**4.05**	**2.93**	**1.30**	**0.74**	**1.90**	**0.87**	**1.17**
Total WHO-TEQ [ng/kg dry weight]	**5.98**	**4.19**	**1.73**	**1.21**	**2.19**	**1.11**	**1,38**
PCB-TEQ in % Total -TEQ	**32**	**30**	**25**	**39**	**13**	**22**	**15**

Table 1: Concentration of 6 Indicator PCBs, dioxin-like PCBs and PCDD/Fs (WHO-TEQ) from spruce shoots, time series 1985 -2003 and pine shoots from 1991 – 2003 (from 1985, 1991, 2001, 2003); Congeners below limits of quantification (LOQ) are indicated as "<…", sum and TEQ are without congeners below LOQ

PCDD/Fs levels in ambient air and deposition show a seasonal trend with concentrations increasing in winter, while PCBs reveal an opposite seasonal variation in ambient air[5]. In conifer samples only the cumulative exposure during the growth period of 1 year was determined. Comparing these values with the annual averages in ambient air and deposition samples, the downward trend of PCDD/Fs leveled off in the mid-1990s for all three sample types.

As shown in this study conifer shoots are an excellent biomonitoring system for persistent organic pollutants like dioxins and PCBs, to determine the airborne accumulation of PCDD/Fs and PCBs in plants and time trends of annual average concentrations in the atmosphere, if the sampling procedure and the analytical method are harmonized as given in the German environmental specimen bank.

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