Concentrations of PCDD/PCDF in Atmospheric Samples in Germany

Heidelore Fiedler [1*], Horst Rottler [1], Ludwig Peichl [2], Gerlinde Knetsch [3], and Armin Basler [4]

[1] University of Bayreuth, Ecological Chemistry and Geochemistry, D-95440 Bayreuth, Germany
[2] Bavarian State Office for Environmental Protection, Bgm.-Ulrich-Straße 160, D-86179 Augsburg, Germany
[3] Federal Environment Agency, Postfach 33 00 22, D-14191 Berlin, Germany
[4] Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, Postfach 12 06, D-53048 Bonn, Germany

1 ABSTRACT

The Dioxin Database maintained by the German Federal Environment Agency is the central collection point for documentation of PCDD, PCDF and PCB concentrations analyzed in the concentration in the various environmental compartments, in feedstuffs, foods/residues, products, vegetation, wildlife and humans. Atmospheric concentrations are amongst the best documented in the database. An evaluation of the 10 years of atmospheric measurements show overall decreasing trends and seasonal variations. Data indicate that in general in the New Laender of Germany the concentrations tend to be higher than in the Old Laender. Biomonitoring data from the Frankfurt Rhein-Main Airport showed that air traffic does not result in elevated PCDD/PCDF concentrations; however, a local source of PCB existed close to the terminal in the early 1990s.

2 INTRODUCTION

Since the early 1980s and with more emphasis since the late 1980s, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) have been the subject of intensive monitoring programs in Germany. Research and routine monitoring projects have produced an abundance of measured data which since around 1989 have been generated with similar analytical methods utilizing high-resolution gas chromatography and mass spectrometry with sufficient resolution resolution to identify and quantify the 17 "toxic" PCDD/PCDF congeners, the 2,3,7,8-substituted. Quite stringent quality measures have been applied and thus, in general the data are of a high quality and comparable between individual programs. The measured concentrations of PCDD, PCDF and polychlorinated biphenyls (PCB) from various governmental and state agency funded programs in Germany are being reported and managed in the Dioxin Database maintained by the Federal Environment Agency (UBA; for environmental matrices including emissions) and by the Federal Institute for Consumer Safety and Veterinary Medicine (bgvv; for food and concentrations in humans). The Dioxin Database is a living tool which allows amongst other purposes to study the effects of dioxin-reducing measures, to derive of limit values on a scientific basis, to generate state of the environment reports, and to establish trends.

---

* Present address: UNEP Chemicals, 11-13 chemin des Anémones, CH-1219 Châtelaine (GE), Switzerland

For trend analysis, all matrices are suitable that rapidly respond on changes in the immediate environment. Amongst these are those matrices that are influenced by atmospheric concentrations such as ambient air, particulate deposition and vegetation as biomonitors. Here we summarize these data for the reporting period 1989 to 1998.

3 MATERIALS AND METHODS

All data are taken from the Dioxin Database at the UBA and the Microsoft ACCESS version of the database has been used for filtering the datasets for the matrices of interest. Most data have been reported on a congener-specific basis and the I-TEQ has been calculated from the concentrations of the individual congeners. For some data, the data source so far has not reported more than the I-TEQ for the sample, although congener-specific data are at the site of the analyzing laboratory or agency, respectively. Evaluation of the data was done with standard programs such as Microsoft EXCEL or Simca 7.0 (Umetri).

4 RESULTS

By May 2000, the database contains measured data from a total of 1,687 ambient air and deposition samples from eight federal states. Results from these samples have been aggregated by season and year for each of the States. The period covered is from fall 1989 until winter 1998.

The 589 deposition data are shown in Table 1, left site and as an example for the seasonal trends, Figure 2 displays the means from 398 deposition samples in Hesse per season. Each mean represents 6-15 individual samples (fall 1989, 89-3, is a single sample). This very coarse evaluation shows a decreasing trend from 1989 to 1998 and annual highs during the cold seasons, namely in winter (designated by –1) and in fall (designated by –4). For Hesse, the seasonal means are in a relatively small range between 3.5 and 38 pg I-TEQ/(m^2 d). Most data exist for ambient air samples where results from 1,098 measurements in five States are documented. The overview of all samples is displayed in Table 1, right site and for Hesse, the seasonal means are displayed in Figure 2. As for the deposition samples, seasonally higher concentrations are found during the cold season. On average each mean represents 20-30 samples. The seasonal means range from 12 fg I-TEQ/m^3 (summer 1997, spring 1998) to 234 fg I-TEQ/m^3 (fall 1989; mean of 15 samples).

Although data between Laender cannot be compared directly, it can be concluded that concentra-tions are higher and ranges are larger in the New Laender (Brandenburg, Saxony, Thuringia) than in the Old Laender (Bavaria, Hesse, Hamburg, Northrhine Westphalia, Rheinland-Palatinate).

Table 1: PCDD/PCDF in deposition and ambient air samples

State	Deposition (pg I-TEQ/m²·d)				Ambient Air (fg I-TEQ/m³)			
	n	Min	Max	Mean	n	Min	Max	Mean
Bavaria					199	3	343	29
Brandenburg	3	26	47	38				
Bremen	30	8.6	23	13				
Hesse	398	2	183	9.2	812	0	812	58
Hamburg	54	2.1	109	9.7				
Northrhine Westphalia	14	9	38	21				
Rheinland Palatinate	24	4.5	24	11				
Saxony					21	307	3648	900
Thuringia	66	6.4	465	44	66	15	230	78

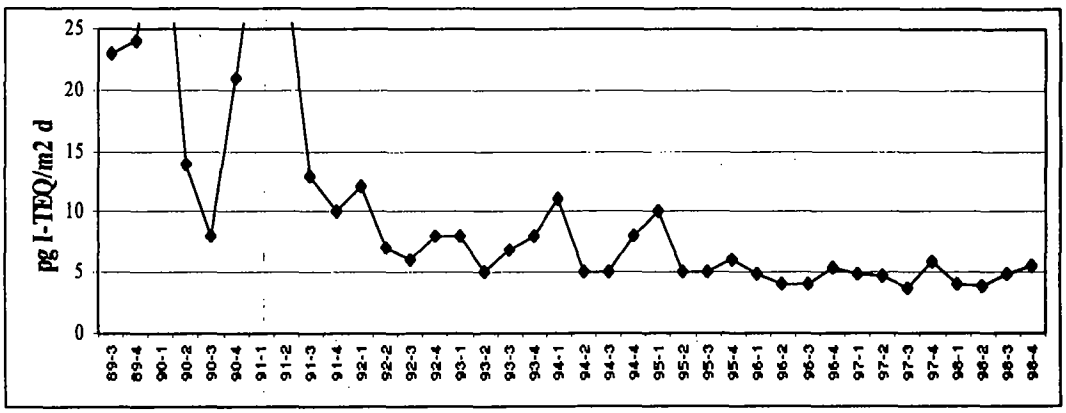

Figure 1: Seasonal trends in deposition data from Hesse (with 2 digits for the year and seasons as follows: 1=winter, 2=spring, 3=summer, 4=fall)

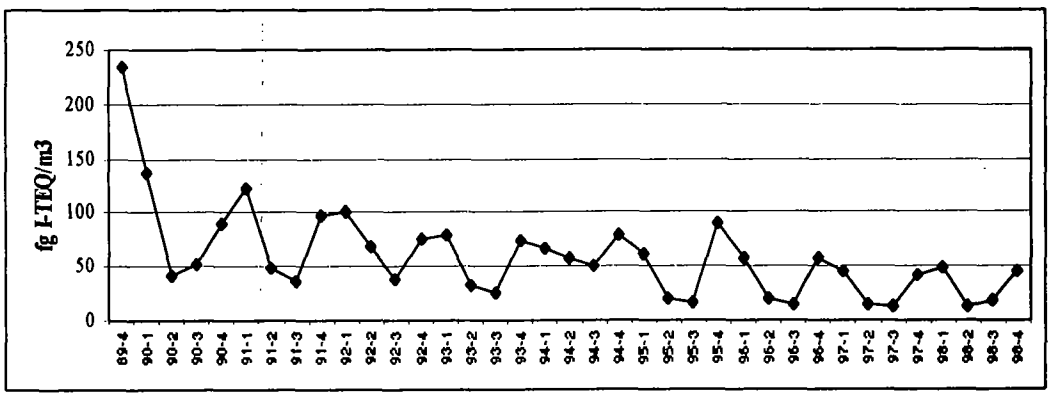

Figure 2: Seasonal trends in ambient air samples from Hesse (with 2 digits for the year and seasons as follows 1=winter, 2=spring, 3=summer, 4=fall)

The database also contains 163 results from spruce needle monitoring performed in the State of Bavaria between 1992 and 1998. Samples have been taken in the fall and in the spring of the following year. This means that the needles collected in spring had a month longer exposure time compared to the needles collected in fall. Table 3 shows the minimum, maximum and median concentrations of for the various seasons. The concentrations range from 0.12 ng I-TEQ/kg d.m. to 3.45 ng I-TEQQ/kg d.m. with a mean concentration of 0.67 ng I-TEQ/kg d.m. for all samples. It can be seen that the concentrations in spring are always higher than in the preceding fall.

Table 2: PCDD/PCDF concentrations in spruce needles from Bavaria (ng I-TEQ/kg d.m.)

	Fall 92	Spring 93	Fall 93	Spring 94	Fall 95	Spring 96	Fall 97	Spring 98
N	26	26	15	15	20	20	21	20
Min	0.18	0.27	0.14	0.18	0.14	0.52	0.12	0.24
Max	1.2	3.45	1.1	1.33	1.53	1.91	0.52	0.65
Median	0.53	1.12	0.5	0.74	0.56	1.01	0.31	0.46

An extensive biomonitoring program has been performed in Hesse in the year 1992/93. Spruce trees and kale have been exposed in standardized soil at 24 monitoring stations and a special program was performed at Frankfurt Rhein-Main airport. At four of these stations, the local soil has been used to grow the plants. PCDD/PCDF concentrations on these soil were between 1.4 and 23.9 ng I-TEQ/kg d.m. For each matrix, two "clean" exposures have been included in the program for comparison: an open-top chamber and a background station with no known dioxin source nearby. The results are shown in Tables 4 and 5.

The concentrations in spruce needles and kale in Hesse are comparable with concentrations typically found in industrially impacted areas in Germany in the early 1990s. The program at the Frankfurt airport did not give higher concentrations of PCDD/PCDF but found extremely high concentrations of PCB in one sample at a station close tot he terminal. This result is an indicator that PCB containing equipment was still in use at the end of 1992.

Table 3: PCDD/PCDF concentrations in spruce needles and kale in Hesse (ng I-TEQ/kg d.m.)

Station	Min	Max	Mean	Median	Background Station	Open-Top Chamber
Stations 1-24 (standardized soil) (n=24)						
Spruce	1.02	2.5	1.72	1.71	2.14	1.25
Kale	0.59	1.51	0.91	0.91	2.44	0.89
Stations 2a ,9a, 15a, 17a using local soil (n=4)						
Spruce	1.45	2.67	2.09	1.83		
Kale	0.67	0.96	0.85	0.88		

Table 4: PCDD/PCDF concentrations in kale at Frankfurt Rhein-Main airport (n=10)
* without maximum concentration at sampling station FAG 7

	Minimum	Maximum	Mean	Median
PCDD/PCDF (ng I-TEQ/kg)	0.64	1.47	0.95	0.92
PCB (#52, 101, 105, 138, 153,180) (µg/kg)	3.04	43.99	4.57*	4.61*
PCB (3-10 Cl) (µg/kg)	8.07	120.28	11.90*	11.99*

From Bremen, there are results from a biomonitoring program with kale from the year 1992/93. The concentrations ranged from 0.61 ng I-TEQ/kg d.m. to 2.64 ng I-TEQ/kg d.m. with a mean of 1.69 ng I-TEQ/kg d.m. and a median of 1.55 ng I-TEQG/kg.

5 DISCUSSION

The levels of PCDD/PCDF in the atmosphere can be monitored either directly by sampling the gaseous and the particle phase with high volume samplers or by measuring the bulk deposition or indirectly through biomonitors like spruce needles and kale. In Germany, sampling and analysis for all matrices has been standardized and together wit quality control programs in place, the data contained in the Dioxin Database are comparable. However, it should be noted that PCDD/PCDF concentrations measured in *e.g.* spruce needles (per congener in ng/kg) cannot be compared to results obtained *e.g.* for ambient air (per congener in fg/m³).

Monitoring of PCDD/PCDF in the atmosphere has been performed since the late 1980s; for some regions, there exists an abundance of data. If studies allow, time trends have been established which confirmed downwards trends for recent years. Further, seasonal trends with higher concentrations in winter and lower concentrations in summer have been confirmed for PCDD/PCDF. There are much less data for PCB and no trend analysis could be performed. From the Hesse biomonitoring program, the relatively high concentrations of PCDD/PCDF at the background station is due to the fact that the station is located in a mountaneous area where high windspeeds result in increased levels.

6 ACKNOWLEDGMENT

We acknowledge receipt of State-specific data from the following institutions Landesamt Brandenburg, Bremer Entsorgungsbetriebe, Umweltbehörde Hamburg, Landesumweltamt Nordrhein-Westfalen, Ministerium für Forsten Rheinland-Pfalz, and Sächsisches Landesamt für Umwelt und Geologie

7 REFERENCES

EU DG Environment (1999): Compilation of EU Dioxin Exposure and Health Data. Report produced for European Commission DG Environment and UK Department of the Environment Transport and the Regions (DETR), October 1999

Fiedler H., D. Buckley-Golder, P. Coleman, K. King, and A. Petersen (1999): Compilation of EU Dioxin Exposure and Health Data: Environmental Levels. Organohalogen Compd. **43**, 151-154

Fricke W-, T. Zimmermann, M. Frank, M. Bender, G. Gasch, K. Hanewald, W. Ott, L. Grünhage, H.-J. Jäger, H. Fiedler, G. Gaßner, O. Hutzinger, C. Lau, and E. Weidner (1996): Ökosystemares Biomonitoring-Programm in der Region Biebesheim 1992-1994. Schriftenreihe der Hessischen Landesanstalt für Umwelt, Umweltplanung, Arbeits- und Umweltschutz, Heft **193**, November 1996

Knetsch G., A. Basler, and M. Büchen (2000): The German Dioxin-Database – Application in Trend Monitoring of Polychlorinated Dibenzp-*p*-dioxins and Furans in the Environment. Submission to DIOXIN'2000

ORGANOHALOGEN COMPOUNDS
Vol. 45 (2000)