PCDD/F in ambient air and deposition in Baden-Württemberg, Germany

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1. Abstract

To obtain more information about PCDD/F transport in Baden-Württemberg (Germany), particulate deposition and ambient air were measured monthly at 16 different sampling sites. The local environment of these sampling points can be subdivided in five typical regions.

Region 1: rural area
Region 2: rural area with special exposition (Black Forest)
Region 3: suburban area
Region 4: urban area
Region 5: multi type impact area

In region 1 deposition samples were taken only every 2-3 months.
Dioxin concentration in particulate deposition ranged from 5 to 30 pg I-TEQ /m² x d, while the ambient air concentration ranged from 14 to 77 fg I-TEQ /m³.
Dioxin concentrations in particulate deposition ranged from 83 to 420 ng I-TEQ/m² x d.
The rural area in specific exponation (Black Forest) reflects the influence of weather and long range transport. In fall 1992 a high dioxin (especially OCCD) concentration in deposition material could be detected at this site. Dioxin concentration in suspended particles ranged from 1167 to 2139 fg I-TEQ /m³. Rural areas (region 1,2) and urban areas (region 3-5) show PCDD/F pollution at different levels.

2. Experimental

Deposition samples were collected in Bergerhof beakers, according to German standard procedures (1). The glass beakers were wrapped in aluminum foil to minimize photodecomposition. To protect the glasses from breaking caused by freezing , a teflon tube of 20 cm length was inserted. To obtain enough deposition material 6 to 10 beakers were pooled together depending on location and sampling time. The samples were filtered with pre-extracted filters and the beakers were cleaned with pre-extracted cotton wool. Filter and cotton wool were air dried, then Na_2SO_4 and ^{13}C standards were added. The water phase was extracted 3 times with toluene, dried with Na_2SO_4 and then used as a solvent for extraction.The clean up of the extracts was done by column chromatography on silicagel and alumina B super I .
Ambient air samples were collected with an air pump unit (Kleinfiltergerät GS050 according to VDI 2463) connected to a cartridge, combining an air sampling head, a glass fiber filter and a PU foam. The air sampling conditions only allowed particles < 10µm to pass the sampling head, and then precipitate on the filter. The cartridges were replaced after two weeks. The total amount of sampled air was about 1000 m³ for one month. The PU foam and the filter of two cartridges from one month were spiked with ^{13}C standards

and extracted with toluene. Sample clean up was done as described above.
The samples were analysed by HRGC-HRMS. (DB-Dioxin column (30m x 0.25mm x 0.25µm) on a Finnigan 8230).
Deposition particulate was measured according to German standard procedure (1). Dust suspended on the filter was measured in an air conditioned room by weighing the filter before and after sampling .

3. Results and discussion

3.1. Deposition

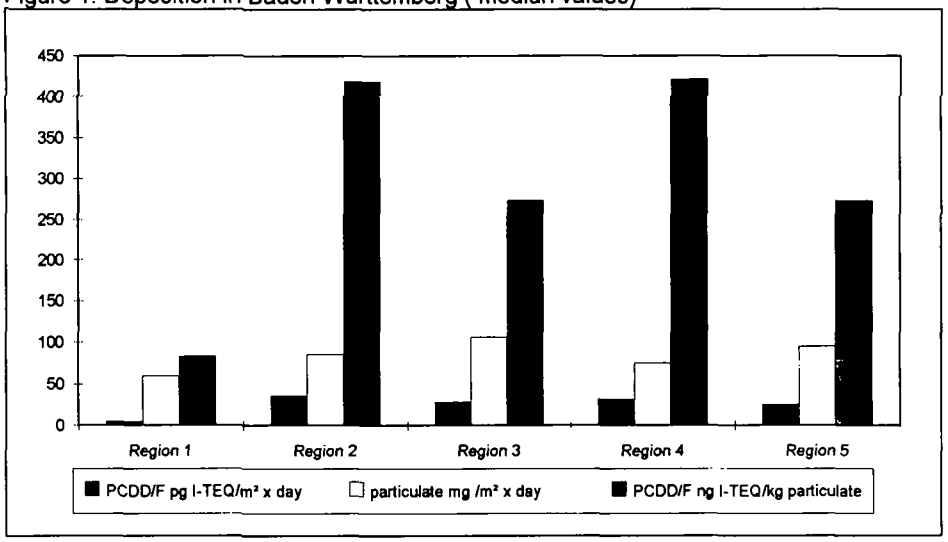
Table 1 and figure 1 show PCDD/F deposition on a daily basis, as well as the amount of particulate deposition and the concentration of PCDD/F in particulate for regions 1-5.

Table 1

Numbers of sample sites	3	1	3	3	4
	Region 1	**Region 2**	**Region 3**	**Region 4**	**Region 5**
PCDD/F					
(pg I-TEQ/m² x day)					
average	7	298	42	47	43
median	5	36	29	32	26
minimum	1	4	6	8	6
maximum	26	2666	143	160	220
Particulate deposition					
(mg/m² x day)					
average	63	93	110	74	106
median	60	86	106	76	95
minimum	20	40	28	22	33
maximum	200	210	170	170	300
PCDD/F in particulate deposition					
(ng I-TEQ/kg)					
average	111	320	382	635	406
median	83	419	274	421	274
minimum	20	55	100	80	50
maximum	1000	66340	1600	3500	2100

In rural areas dioxin deposition is around 5-7 pg I-TEQ/ m² x d. These values seem to be typical (2). Regions 3-5 are influenced by urban impact like traffic, industry and households. None of these sites were close to a point source. Differences between these regions in dioxin deposition are small and range around 30 pg I-TEQ/ m² x d. PCDD/F deposition at all urban sites is close to 30 pg I-TEQ/m² x d. The amount of particulate deposition at the same sites approaches 100 mg/m² x d, which is almost twice as much as in rural areas with 50-60 mg/ m² x d.

Figure 1: Deposition in Baden Württemberg (median values)



Dioxin concentrations in deposition particulate ranged from 100-150 ng I-TEQ/kg in rural areas and from 300-400 ng I-TEQ/kg in urban areas. Particulate deposition (>10 µm) has a lifetime in the atmosphere of some days, depending on particle size and climate. Short range transport and precipitation are therefore the dominating processes. Nevertheless long range transport can be an important path for the contamination of rural areas. One example for this transport phenomenon can be reported for the Black Forest (Hornisgrinde mountain, region 2). The industrial center of Straßburg /Kehl is about 50 km to the west. Though Hornisgrinde mountain is regarded to be a rural recreation area, high PCDD/F concentrations have been found. 30 pg I-TEQ/m² x d have been found as a background value but an extreme value in September 1992 of 2666 pg I-TEQ/ m² x d has been detected too, basing mainly on a high OCDD value.

3.2. Dioxins in ambient air

Table 2 and figure 2 show PCDD/F concentrations in total air, concentration of suspended particulate <10µm in air and PCDD/F concentration in suspended particulates.
In rural areas air dioxin concentrations were found to be 15-20 fg I-TEQ/m³. In urban areas dioxin concentrations were 70-80 fg I-TEQ/ m³. In suburbans and multi impact areas the level is 50% lower (50 fg/m³). Suspended particulate concentration in air is approximately the same for region 3-5 with 35-40 µg/m³. In rural areas the particulate concentration is only 20 µg/m³.
PCDD/F concentrations in total air are decreasing from city center to suburban areas and the surroundings. In rural areas PCDD/F and particulate concentration are about 1/2 to1/3 lower than in urban and suburban areas. Dioxin concentration in suspended particulate is near 1220 ng I-TEQ/kg for rural areas and 1800-2000 ng I-TEQ/kg for urban areas. In rural areas more particulate and particles from plants like pollen are „diluting" actual PCDD/F concentrations in suspended particulate.

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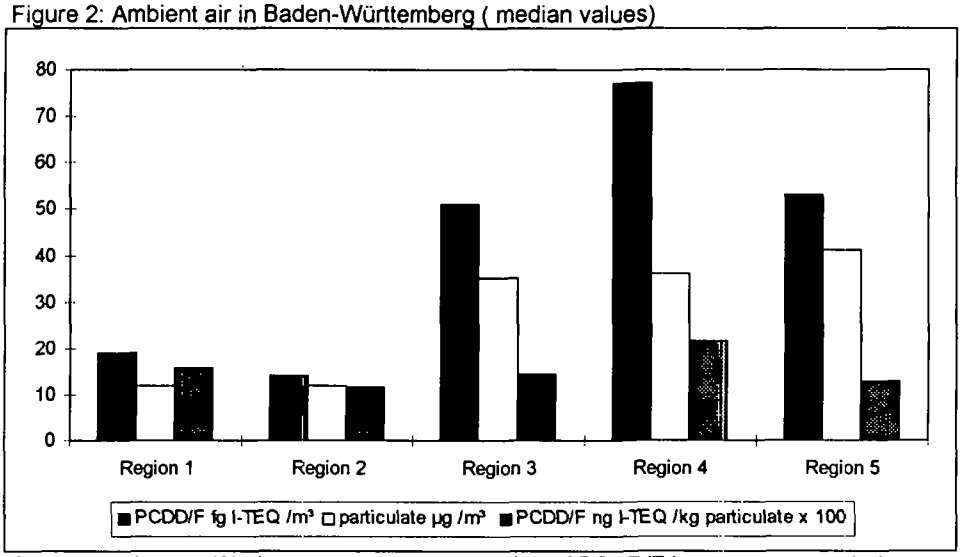
Table 2

Numbers of sample sites	2	1	3	3	4
	Region 1	**Region 2**	**Region 3**	**Region 4**	**Region 5**
PCDD/F in total air					
(fg I-TEQ /m³)					
average	21	18	56	83	62
median	19	14	51	77	53
minimum	8	5	9	21	14
maximum	54	49	98	217	130
Suspended particulate <10µm					
(µg/m³)					
average	16	16	36	39	42
median	12	12	35	36	41
minimum	40	10	18	25	23
maximum	370	27	71	119	72
PCDD/F in suspended particulate					
(ng I-TEQ/kg)					
average	1313	1125	1556	2128	1476
median	1583	1167	1457	2139	1293
minimum	470	370	530	600	500
maximum	235	6370	3480	5440	4000

Figure 2: Ambient air in Baden-Württemberg (median values)



Other experiments (3) show an average distribution of PCDD/F between suspended particulate and gaseous phase of about 50:50 based on I-TEQ values depending mainly on temperature.

Suspended particulate (<10µm) in the air with 600-1000 ng I-TEQ/kg is 2 to 6 times more contaminated than particulate deposition with concentrations of 100-500 ng I-TEQ/kg.

At Hornisgrinde mountain (region 2) there is a correlation between PCDD/F concentration in deposition, soil and plants (grass) (4).However a correlation between PCDD/F concentration in deposition and ambient air (not necessarily including deposition material) is hardly recognizable.

4. References:

1. VDI Richtlinien 2119 Blatt 2.
2. Fiedler, H. „Sources of PCDD/PCDF and impact on the environment", Organohalogen Compounds, 20, 229 (1994).
3. Hagemaier H., Krauß P., Wallenhorst Th., „ Eintäge von Dioxinen in den Boden" DECHEMA, 1995 in press.
4. Krauß P., Wallenhorst Th., Mahnke K., Deyhle M., Wilke M., „ Case study at Hornisgrinde mountain- an example for long range transport", in preparation.