

## Determination of PCDD/F and PCB in forest soils from Brazil

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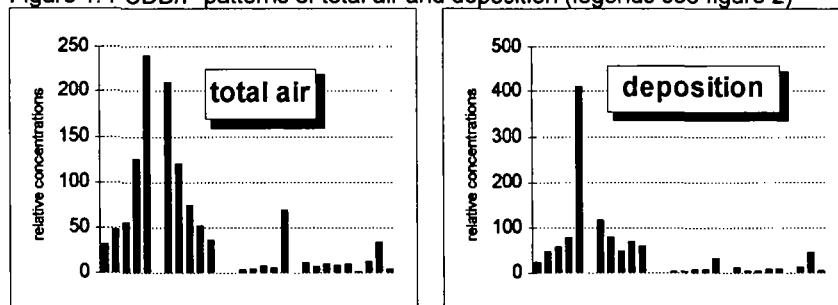
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### 1. Introduction

In Germany, agricultural soil shows PCDD/F-concentrations of about 0,2 to 7,0 ng I-TEQ/kg. However, the upper layer of forest soils with high contents of organic matter shows increased PCDD/F-concentrations between 15 and 53 ng I-TEQ/kg (median 30 ng I-TEQ/kg). Mineral soil in forests contains 5 ng I-TEQ/kg (median) [1].

The origin of the PCDD/F-load transferred to soil via air transport is known to be mainly due to processes of incineration and combustion. Leaves have the ability to strip pollutants from the particulate as well as from the gaseous phase of air. Because of the accumulation of pollutants by this process forest soils are highly contaminated. They show PCDD/F-patterns typical for total air whereas agricultural soils show PCDD/F-patterns typical for deposition [2].

Figure 1: PCDD/F-patterns of total air and deposition (legends see figure 2)



PCDD/F have an extremely high  $K_{oc}$ -value. Therefore, soils with a high content of organic matter in terms of high loss on ignition (l.o.i.) are characterized by high PCDD/F-concentrations.

The present investigation should find out whether the accumulation of dioxins in the upper layer of forest soils known for Germany also occurs in subtropical and tropical climates. In addition the effect of widespread forest burning in tropical rainforest on soil contamination with PCDD/F has been investigated.

Brazilian forest soils were chosen because it was supposed to find low PCDD/F concentrations in most soils as well as some polluted soils in the industrial areas.

Therefore samples were taken from the Amazon basin (forest burning as possible dioxin source), the surroundings of Rio de Janeiro (recreation and industrial areas) and from the industrial region of Cubatão, São Paulo (Mata Atlantica).

## 2. Results

### 2.1. Amazon basin

The Amazon basin samples were taken from 5 different areas (with 5 individual samples for each area). Three fractions were formed at every point: leaves, a fraction <2mm (detritus plus soil particles) and soil.

The PCDD/F-concentrations of all samples are extremely low (0,02 to 0,4 ng I-TEQ/kg, table 1). Only HpCDD and OCDD have been found close to the detection limit.

The PCB-concentrations are low, too (0,1 to 7,7 µg/kg as sum of all tri- to deca-PCB) and often in the order of magnitude of the blank. Leaves are slightly more polluted than soil and <2mm fraction.

Table 1: PCDD/F and PCB contents in the Amazon basin

area	material	ng I-TEQ/ kg	ng I-TEQ/kg (30%l.o.i.)	<i>l.o.i.</i> [%]	sum PCB [µg/kg]
<b>Eucalipto</b> (eucalyptus trees)	leaves (n=5)	<b>0,19</b>	0,95	86	<b>7,7</b>
	<2mm (n=3)	<b>0,04</b>	0,04	29	<b>1,2</b>
	soil (n=2)	<b>0,4</b>	0,35	17	<b>0,2</b>
<b>Capoeira</b> (wood cut)	leaves (n=5)	<b>0,07</b>	0,26	82	<b>6,5</b>
	<2mm (n=3)	<b>0,08</b>	0,15	53	<b>8,3</b>
	soil (n=3)	<b>0,05</b>	0,04	25	<b>0,1</b>
<b>Mata Natural 1</b> (natural forest)	leaves (n=5)	<b>0,03</b>	0,11	84	<b>3,9</b>
	<2mm (n=3)	<b>0,1</b>	0,11	35	<b>3,1</b>
	soil (n=2)	<b>0,05</b>	0,05	23	<b>0,7</b>
<b>Mata Natural 2</b> (natural forest)	leaves (n=5)	<b>0,02</b>	0,05	77	<b>5,5</b>
	<2mm (n=3)	<b>0,02</b>	0,02	30	<b>1,2</b>
	soil (n=2)	<b>0,03</b>	0,03	14	<b>0,3</b>
<b>Mata Degradada</b> (new grown forest)	leaves (n=5)	<b>0,03</b>	0,12	80	<b>4,1</b>
	<2mm (n=3)	<b>0,05</b>	0,06	43	<b>0,4</b>
	soil (n=2)	<b>0,1</b>	0,09	26	<b>0,5</b>

### 2.2. Rio de Janeiro

#### -Industrial areas

The samples were taken as close as possible to forests or small woods.

The PCDD/F-concentrations are listed in table 2. In São Gonçalo and Sta. Cruz (Cosigua) a PCP-pattern is found, which can be recognized by the dominance of 1,2,4,6,8,9-HxCDF and 1,2,3,4,6,8,9-HpCDF in the corresponding isomer distributions.

In case of the Sta. Cruz plant PCDD/F accumulate in the upper soil layer (654 ng I-TEQ/kg). This layer is by far more contaminated than leaves (77 ng I-TEQ/kg). After normalization on 30% loss on ignition the difference is considerably lower.

In Niterói (close to the hospital waste incineration) a deposition pattern and not the expected combustion pattern is found. With increasing distance to the plant the PCDD/F-concentrations return to normal background levels.

Table 2: PCDD/F contents in Rio de Janeiro - industrial regions

area, material		ng I-TEQ/kg	ng I-TEQ/kg (30% L.o.I)	I.o.I [%]
Niterói, hospital waste incineration	soil (from plant)	23	17	4
	soil (street nearby)	73	56	9
	soil (reference)	3	3	9
São Gonçalo, metal industry	soil (nearby)	38	27	8
	soil (outer wall)	15	13	18
Santa Cruz (COSIGUA), iron industry	sludge	21	16	11
	soil	27	21	10
	leaves	77	323	83
	soil beyond leaves	654	834	45

#### -Recreation areas

Samples were taken from forest soils (Mata Atlantica) close to Rio de Janeiro from the upper layer (leaves) and the upper soil layer (mineral soil).

Table 3: PCDD/F and PCB contents in Rio de Janeiro - recreation areas

area, material		ng I-TEQ/kg	ng I-TEQ/kg (30% I.o.I.)	I.o.I [%]	sum PCB [µg/kg]
Itaipuaçu	leaves	2,6	3,6	49	21,1
	1. soil layer	0,6	0,5	12	34,5
	2. soil layer	1,8	1,5	17	9,9
Serra de Mauá	leaves	0,6	0,6	33	9,5
	soil	0,4	0,3	13	58,2
Saquarema	leaves	0,4	1,2	77	3,02
	soil (sand)	0,03	0,02	2	0,26

In Saquarema leaves show a PCDD/F-pattern of total air which is also typical for moderate climates. The soil layer consists of sandy material with low content of organic matter (2% I.o.I.). The dioxin concentration is close to the detection limit. In contrast to leaves, soil shows a deposition pattern.

Leaves and soil from the Serra de Mauá both have PCDD/F-patterns typical for total air. While there is not much difference in PCDD/F-concentrations (0,4 and 0,6 ng I-TEQ/kg), PCB-concentrations show a significant increase from leaves to soil (9,5 to 58,2 µg/kg as sum of tri- to deca-PCB).

The PCDD/F-concentration in Itaipuaçu is lowest in the first soil layer (deposition pattern) whereas the higher contaminated leaves and second soil layer have PCDD/F-patterns of

total air. The PCB-concentration - like in Serra de Mauá - has its maximum in the first soil layer.

### 2.3. Cubatão (Mata Atlantica)

The industrial region of Cubatão, southeastern of São Paulo is known to be highly polluted. The main industries of this region are:

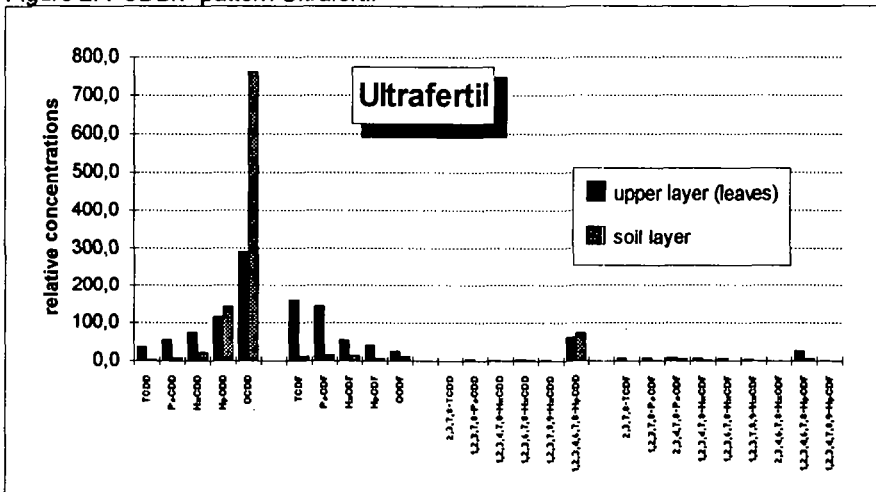
- 11 chemistry/petrochemistry plants
- 7 fertilizer plants
- 1 plant for nonmetallic minerals
- 1 paper plant
- 1 cement factory

Forests close to the plants of Ultrafertil (fertilizer production), Eletropaulo and Carbocloro (chlorochemistry plant) were chosen for sampling of leaves and soil (5 samples for each sampling point).

Table 4: PCDD/F and PCB contents in Cubatão

location, material		ng I-TEQ/kg	ng I-TEQ/kg (30%l. o. i.)	l. o. i. [%]	sum PCB [µg/kg]
Ultrafertil	leaves	10	23	69	20,8
	soil	11	9	12	13,8
Eletropaulo	leaves	12	54	84	22,3
	soil	54	53	23	26,9
Carbocloro	leaves	49	254	86	57,7
	soil	341	283	16	232,3

Figure 2: PCDD/F pattern Ultrafertil



The PCDD/F-concentration of leaves and soil near Ultrafertil lie close together (10 and 11 ng I-TEQ/kg) though their PCDD/F-pattern differs significantly. Leaves show a PCDD/F-pattern of total air, soil a deposition pattern (see figure 2).

Near Eletropaulo and Carbochloro PCP patterns are found. Here PCDD/F accumulate in soil, which is significantly higher contaminated than leaves. When the PCDD/F-concentrations are normalized to 30 % loss on ignition, simulating the loss of organic matter by natural degradation, PCDD/F-concentrations of leaves and soil are nearly the same.

Soil near Carbochloro is highly polluted with PCB, too.

### 3. Analytical remarks

The analytical procedure follows German standard methods [3]. The HRGC/HRMS analyses were performed using a Carlo Erba HRGC 5160 Mega Series and a Finnigan 8230 MS.

### 4. Summary

In the Amazon basin the PCDD/F- and PCB-concentrations of soil are very low (PCDD/F: 0,02 to 0,4 ng I-TEQ/kg, PCB: 0,1 to 7,7 µg/kg), the measured values being close to the detection limits.

Possible explanations for the low PCDD/F-concentrations could be:

1. There are no dioxins in the Amazonas basin and they are not formed by forest burning (which takes place on a large scale). The reported values would then reflect only analytical errors caused by contamination during clean-up etc.
2. Dioxins cannot be adsorbed by soil due to a lack of humic acids. The transformation of organic matter to humic acids in tropical climate is quenched [4].

In industrial regions around Rio de Janeiro and São Paulo highly contaminated soils with typical PCP patterns were found.

In recreation areas total air patterns are found for leaves and for soil (Itaipuaçu, Serra de Mauá). This corresponds to results from Germany.

In other Brazilian forest soils leaves still show the PCDD/F-pattern of total air, but soil shows a deposition pattern. This phenomenon can in part be attributed to the lack of humic acids. Heavy tropic rainfalls will then wash out especially those PCDD/F with lower  $K_{oc}$  (mainly tetra- and penta CDD and CDF).

Further investigations on tropical forest soils, total air and deposition are carried out at the moment.

### 5. Literature

- [1] H. Hagenmaier, P. Krauß, Th. Wallenhorst: „Einträge von Dioxinen in den Boden“ (pathways of dioxins into soil), DECHEMA, 1995 in press.
- [2] P. Krauß, Th. Krauß, H. Hagenmaier, Organohalogen Compounds, **18**, 39-54, 1994
- [3] „Klärschlammverordnung“, Bundesgesetzblatt Teil I (15.02.1992).
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