Burning of Biomass- an important source for global PCDD/F-imission?

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1. Introduction

Since the publication of the article „trace chemistries of fire" in 1980 [1], burning of organic material has been considered a possible source for polychlorinated dioxins and furans [2]. The large scale burning of tropical rainforests could therefore be an important source for world-wide contamination of the environment with PCDD/F as well as PCB [3].
In moderate climates the upper layer of forest soils containing large amounts of humic acids accumulates organic pollutants like dioxins with high Koc-values. These soils (with 15 - 53 ng I-TEQ/kg) show the same homologue and congener pattern as leaves, but higher concentrations of PCDD/F and PCB with 2 - 9 ng I-TEQ/kg [4), 5)].

Table 1: PCDD/F and PCB concentration in German soil [4), 5)].

	sample	ng I-TEQ/kg	ng I-TEQ/kg (30% l.o.i.)	*l.o.i. [%]*	total PCB [µg/kg]
Germany	leaves	2 - 9	5 - 69	*49 - 93*	**50 - 200**
(forests soils)	soil	15 - 53	11 - 44	*5 - 15*	**70**

In contrast forest soils in tropical climates do not have this characteristic upper layer, rich in humic acids, and therefore do not accumulate organic pollutants in the same way [6]. Therefore leaves in tropical forests show higher PCDD/F and PCB concentrations than the upper soil layer (table 2). This effect is made more evident after normalising the results on 30 % loss on ignition (l. o. i.), simulating the degradation of organic matter.
All leaves and soils from tropical rainforests show very low concentrations of PCDD/F, often close to the detection limit. Forest soil near burning sites is slightly more contaminated than soil from untreated forests.

Table 2: PCDD/F and PCB concentration in leaves and soil of tropical rainforests .

	sample	ng I-TEQ/ kg	ng I-TEQ/kg (30% l.o.i.)	*l.o.i. [%]*	total PCB [µg/kg]
untreated forest					
Amazon basin	leaves	0,02 - 0,03	0,05 - 0,11	*77 - 84*	**4 - 6**
	soil	0,03 - 0,05	0,03- 0,05	*14 - 23*	**0,3 - 0,7**
French Guyana	leaves	1	3,2	*78*	**151**
	soil	0,3	0,2	*17*	**6**
Ivory cost, Africa	grass	0,08 - 0,15	0,14 - 0,15	*26 - 65*	**35 - 54**
	soil	0,01 - 0,36	0,01 - 0,29	*3 - 13*	**4 - 7**

	sample	ng I-TEQ/ kg	ng I-TEQ/kg (30% l.o.i.)	*l.o.i. [%]*	total PCB [µg/kg]
forest near burning sites					
Amazon basin	leaves	0,03 - 0,19	0,12 - 0,95	*80 - 86*	**4 - 8**
	soil	0,05 - 0,4	0,04 - 0,35	*17 - 26*	**0,1 - 0,5**
French Guyana	leaves	1,4	3,5	*73*	**35**
	soil	0,7	0,6	*10*	**5**
Ivory cost, Africa	leaves	0,38 - 6,1	1,8 - 22,6	*66 - 81*	**60 - 407**
	soil	0,2 - 0,9	0,2 - 0,7	*5 - 19*	**5 - 25**

Since PCDD/F and PCB in tropical climates do not accumulate in forest soils, the collection of air-emission samples was necessary to study forest burning as PCDD/F-source. Air sampling of forest burning events is difficult because the time, precise location and development (wind direction etc.) of the fire are not known in advance. Therefore the more defined burning of sugar-cane fields in Araraquara, State of São Paulo, Brazil, was chosen for this investigation.

2. Sampling of sugar-cane burning

The State of São Paulo is the major producer of sugar-cane in Brazil. The area under cultivation in this state alone is 2,5 million hectares, which is half of the cultivation area of Brazil. Before harvesting, the sugar-cane leaves are burnt to simplify the cutting of the sugar-cane. A sugar-cane field consists of approximately 20 hectares, the burning period takes about ½ hour.
Harvesting time, where fields are burnt on a large scale is April to November. As a consequence, polluted air with high concentrations of smoke and soot can reach the city centers. Here they cause complaints in the population from sugar-cane cultivation areas (problems with soot deposition).
In October 1995 a sampling programme was established together with the CETESB (Companhia tecnologia de saneamento ambiental). Smoke trail and ambient air samples as well as particulate deposition samples and leave and soil samples of natural forests were taken. The deposition sampling sites were located within the city of Araraquara and in the surrounding area (rural sampling sites). The smoke trail samples were taken on fields 20 to 40 km from the city. An ambient air sample was taken in the city center.
The sampling of smoke trails and ambient air was done using high-volume samplers with polyurethane foams. Because of the large amounts of rainwater - up to 2000 mm/month - Deposition samples were collected in funnels equipped with polyurethane foams, in contrast to the more common „Bergerhof-sampling method" [7]. The rainwater passes the PU-filter, whereas PCDD/F and PCB are trapped in the PU-foam.

3. Results

AIR

The ambient air in the city of Araraquara shows PCDD/F-concentrations between those for rural and urban areas in Germany [8]. The city of São Paulo has slightly higher PCDD/F-concentrations than urban regions in Germany. Smoke trail samples show higher concentrations than ambient air, but not as high as emission samples (for real emission samples of solid waste incineration, e. g. , the emission limit is 0,1 ng I-TEQ/m³, which is a factor of 1000 or more).

PCB-concentrations are higher for all smoke trail samples than for ambient air in different regions of the State of São Paulo, which is also true for the PAH. The ambient air sample from Araraquara city center is comparable to German urban areas.

Table 3: PCDD/F, PCB and PAH concentration in air samples

air-samples	PCDD/F [fg I-TEQ/m³]	total PCB [ng/m³]	PAH (16 EPA) [ng/m³]
Araraquara ambient air	46	9	11
Araraquara smoke trail	42 - 267	23 - 274	400 - 1800
City of São Paulo	86 - 187	5 - 6	38 - 136
Industrial region Cubatão	38 - 48	17 - 23	33 - 167
Germany rural region [8)]	14 - 27		
Germany urban region [8)]	53 - 99	0,2 - 12	

DEPOSITION

Deposition samples in Araraquara show PCDD/F-concentrations in the same range as German rural areas (table 4). PCDD/F-concentrations of São Paulo city are comparable with German urban areas. Araraquara deposition samples show normal background levels in PCDD/F and PCB. There is no effect visible resulting from sugar-cane burning (though ash-pieces could be seen on the PU-foams in the funnels). Only for PAH the maximum concentration is higher than São Paulo city.

Table 4: PCDD/F, PCB and PAH concentration in deposition

deposition-samples	PCDD/F [pg I-TEQ /m²d]	total PCB [µg/m²d]	PAH (16 EPA) [µg/m²d]
Araraquara (October 95)	1 - 17	2,5 - 17	1 - 40
City of São Paulo (October 95)	34 - 87	5 - 23	12 - 27
Industrial region Cubatão (October - December 95)	8 - 72	3 - 11	1 - 76
Germany rural region [8)]	3 - 10		
Germany urban region [8)]	34 - 41	0,1 - 12	

FOREST SOILS

In natural forests around sugar-cane fields, where accumulation of PCDD/F emitted from sugar-cane burning should take place, the same phenomenon occurs as in tropical rainforests. Leaves from those areas show comparable concentrations to German leaves (compare table 1 and 5). The upper soil layer, however, shows lower PCDD/F, PCB and PAH-concentrations, there is no accumulation like in German forest soil.

Table 5: PCDD/F, PCB and PAH concentration in natural forests around Araraquara

forest-samples	PCDD/F [ng I-TEQ/kg]	total PCB [µg/kg]	PAH (16 EPA) [µg/kg]
leaves	1 - 4	25	230 - 1500
soil	0,1 - 1	3 - 10	76 - 1800

3. Analytical remarks

The analytical procedure followed German standard methods [9]. The HRGC/HRMS analyses (for PCDD/F) were performed using a Carlo Erba HRGC 5160 Mega Series and a Finnigan 8230 MS. The smoke trail samples were analysed using a VG autospec. For PCB analyses, a HP Chemstation 5890 GC/MS system was used. The PAH analyses were done with HPLC (Merck-Hitachi) using a Perkin-Elmer Fluorescence Detector LS30.
PCDD/F-concentrations are given in international toxicity equivalents (NATO/CCMS), total PCB means sum of all tri- to decachlorobiphenyls and the PAH-concentration is the sum of the 16 EPA PAH's without acenaphthene (not detectable with fluorescence detector).

4. Summary

To evaluate the effects of burning sugar-cane fields before harvesting around the city of Araraquara, smoke trail samples have been taken using high volume samplers. There is an increase in PCDD/F-concentrations to approximately 300 fg I-TEQ/m³ in the smoke trail compared to 50 fg I-TEQ/m³ in ambient air. Nevertheless, in deposition and soil samples of the region there is no evidence for increased amounts of PCDD/F, PCB or PAH. Like in other tropical forest soils, there is no accumulation of PCDD/F or PCB in the upper layer of soils from natural forests around Araraquara. Further investigations will show whether deposition and ambient air PCDD/F-concentrations go down in winter (November till May) when there is no harvesting. Since the smoke trail air is already diluted at the time the sample is taken, the concentrations of PCDD/F, PCB and PAH obtained indicate their formation.

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6. References

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