PCDD/F Concentrations in the Surroundings of a Cement Kiln/Co-Processing Waste Plant in Rio de Janeiro, Brazil

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Introduction

The detection of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in dust and stack gas samples indicated that cement kilns which burn hazardous waste are a source of these pollutants to the environment [1]. According to the US Environmental Protection Agency it was estimated to be the second most important known source of PCDD/F's in 1995 in the United States. The emission amount was calculated to be 850 g I-TEQ, which is 19,7% of the total PCDD/F emissions (4308 g I-TEQ) [2].

Cantagalo is a municipality in the State of Rio de Janeiro, Brazil, where various cement kilns with co-processing of industrial hazardous waste are located. During 1997, it was of great concern to the local health system as to how these plants could contribute to the quality of life by modifying the environmental standards and interfering with human's health. The dioxins generated during this process were considered, at the time, one of the significant possibilities. The main purpose of this study was the evaluation of PCDD/F content in this region and the possibility of considering this cement kiln as the principal source. Soil samples from the vicinity of one of these plants and also cement kiln dust (CKD) from the electrostatic precipitator and cement were collected and analysed.

Material and Methods

Soil samples were collected from the upper 2 cm layer at various sites. Cement and CKD samples were collected inside the plant. Soil samples were air dried and homogenized. After spiking with ^{13}C- labelled PCDD/F as internal standard, ca. 100 g of soil were extracted with toluene in a Soxhlet-apparatus (24 h). 20 g of Cement and CKD were extracted as described by Blaha [3] for fly ash. Clean-up was conducted by treating the extracts with H_2SO_4 and liquid cromatography on Silicagel and Alumina B Super I. All samples were analyzed by HRGC/HRMS on a DB 5ms column.

Results and Discussion

The PCDD/F's amounts in soil samples varied from 0,03 to 6,91 ng I-TEQ/kg (table 1).

The concentrations in all samples are in the same range as those found by Mahnke in soils from recreation areas located in the State of Rio de Janeiro. These levels varied from 0.03 ng I-TEQ/kg in Saquarema to 1,8 ng I-TEQ/kg in Itaipuaçu (table 2). However, the amount in sample #2 is 6,91 ng I-TEQ/kg which is in the range of concentrations found in soils nearby defined emission sources (table 2). However, this is in the lower end of this range (4 – 654 ng I-TEQ/kg).

Table 1: PCDD/F concentrations in soils of Cantagalo, State of Rio de Janeiro, Brazil.

Sample #	Amount (ng I-TEQ/kg)	Sample #	Amount (ng I-TEQ/kg)
1*	1,87	6*	1,12
2*	6,91	7	0,14
3	0,22	8	0,35
4	0,10	9*	0,79
5	0,03	10	0,20

* residential area

Table 2: Dioxins in soils from the State of Rio de Janeiro, Brasil [4].

Location	Amount (ng I-TEQ/kg)
Niterói, Hospital Waste Incinerator	23 – 73
São Gonçalo, Siderurgy	15 – 36
Santa Cruz, Siderurgy	27 – 654
Nova Iguaçu, Copper Recycling	4 – 70
Itaipuaçu, Recreation Area	0,6 – 1,8
Serra de Mauá, Recreation Area	0,4
Saquarema, Recreation Area	0,03

Mahnke also showed that the PCDD/F concentrations in deposition samples from Cantagalo are low in comparison with other locations in the vicinity of different emission sources (table 3).

Table 3: PCDD/F´s in deposition samples from the State of Rio de Janeiro [4].

Location	Amount (pg I-TEQ/m^2d)	
	Nov. 95	*Dez. 95*
Cantagalo, Cement Kiln 1	2,0	0,6
Cantagalo, Cement Kiln 2*	2,1	1,1
Cantagalo, Cement Kiln 3	2,5	0,8
Belford Roxo, Chemical Industry, Incinerator	54	51
Santa Cruz, Siderurgy	265	149
Volta Redonda, Siderurgy	32	1,8
Barra Mansa, Siderurgy	39	4,2

* plant sampled

These low PCDD/F levels could indicate that only background levels are present in this area, but we can also demonstrate that there must be an influence from the cement kiln emissions by comparing the normalised homlogue distributions from the soil samples with those from the cement and CDK samples (amounts shown in table 4)

There are two different PCDD/F distributions in the soils. Figure 1 shows the distributions in the samples collected from the residential area. These patterns are very similar to those of the deposition samples (figure 5) which were collected by Mahnke at same location as soil sample #1. They are dominated by octachlordibenzo-p-dioxin (OCDD). Figure 2 shows the distributions of the soil samples taken outside of the residential area. They are dominated by tetradibenzofurans (TCDF) and are very similar to the pattern found in the CKD (figure 3), with only the OCDD being lower compared with the soils. The cement extract shows OCDD and TCDF as major compounds (figure 4). We assume that the PCDD/F's found in soils are principally from the result of the deposition of CKD which was not held back by the electrostatic precipitator and from cement which was windblown during production. In the residential area there could also be an influence from the uncontrolled open air incineration of domestic waste, which is an usual way of eliminating residues in Brazil.

Table 4: PCDD/F´s in Cement and CKD samples.

Sample	Amount (ng I-TEQ/kg)
Cement (05/02/98)	0,35
CKD 1 (05/02/98)	7,7
CKD 2 (06/05/98	8,3

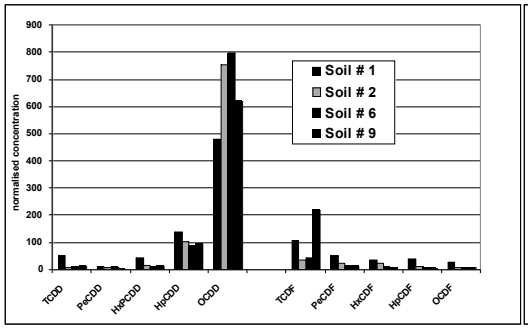

Figure 1

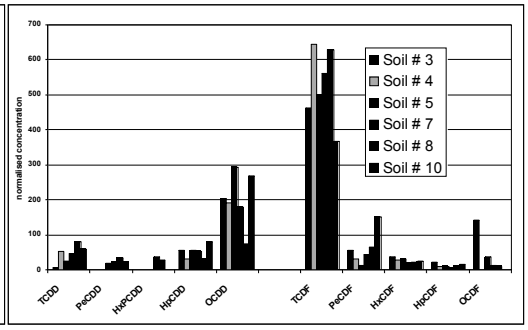

Figure 2

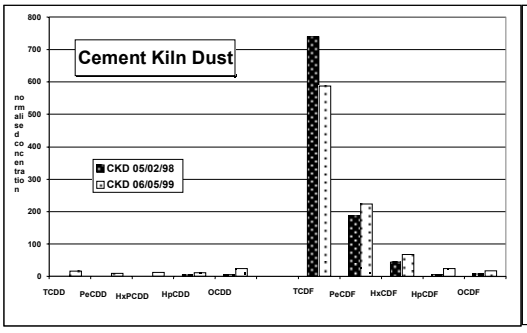

Figure 3

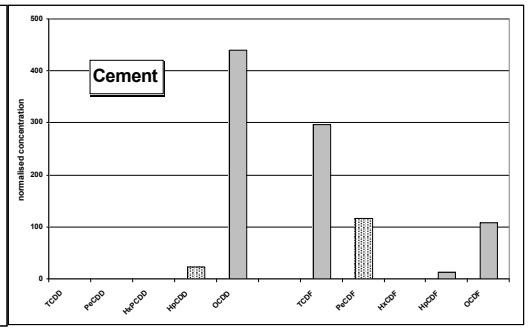

Figure 4

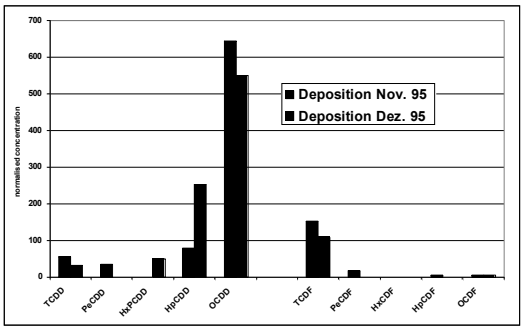

Figure 5 [4]

Conclusion

The cement kiln can be defined as an emission source for PCDD/F's, due to the similar PCDD/F distributions found in nearby soils, CKD and cement. However, the emissions must be low or generally deposited further away as we found low amounts in soils near the plant. The actual emission levels can only be evaluated by measuring PCDD/F's in the stack gas.

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