

PCDD/F-Concentrations in Soil and Cows' Milk from a Hexachlorocyclohexane Contaminated Area in Rio de Janeiro - Brazil

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Introduction

During the 1950s, Brazil's emergent necessity to control the mosquitos that cause Chagas disease and Malaria led the Ministry of Health to establish the production of Hexachlorocyclohexane (HCH). The factory was located in a region of approximately 19.4 million square meters called "Cidade dos Meninos" with a population of about 3500 individuals. It operated from 1950 to 1955 when high production costs made it cheaper to import the insecticide than to produce it. Part of the production facility, HCH and its waste was abandoned there without any protection. In 1989, local newspapers had announced the illegal commerce of HCH in a free market in Rio de Janeiro which was originated from Cidade dos Meninos. From this moment on, several researches were conducted in the area of the factory and its surroundings with the main objective of evaluating the extent of a possible contamination of the local environment. According to the Environmental Agency of the State of Rio de Janeiro, around 300 tons of these residues were spread all over the place. High concentrations of this contaminant were detected in an area of about 2500 square meters around the factory.

Due to the necessity of site remediation, in 1995, the soil of the contaminated area was mixed and homogenized with lime (CaO), to degrade the HCH. After the treatment, all isomeres of HCH were still present in high concentrations; other organochlorine compounds like Chlorobenzenes and Chlorophenols were also detected and the contaminated area had become 33.000 square meters¹. PCDD/Fs as contaminants of HCH residues and the fact that the degradation products Chlorobenzene and Chlorophenols can form PCDD/Fs under alkaline conditions² led to the decision of monitoring dioxins in this site. The first step of the study consisted of a soil sample collected from the treated area and four cow's milk samples from local producers, to identify if there really exist a dioxin problem that could affect the local food chain and pose a risk to the population's health.

Methods and Materials

Soil sample was collected in the center of the treated area; ten subsamples of 200 g were taken from a 2 m circumference in a depth of 0-25 cm. After drying and homogenizing, 10 g of soil were spiked with ¹³C-PCDD/Fs and extracted with toluene during 24 h in Soxhlet extractor. In the first step of clean-up, the HCH-excess was separated by multiple, fractionated crystallization in

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hexane. Then the sample was passed through a silica-silica/sulfuric acid-silica column, a Florisil column and finally an activated carbon/silica column was used.

Samples of 500 ml of cow's milk were collected from storage containers of the daily production of dairy farms in the vicinity of the HCH site. They represented 83% of the total local milk production. Treatment and clean-up procedures were conducted as described by Malisch³.

GC/MS-detection was performed on a AutoSpec at 10 000 resolution with a DB5MS-column.

Result and Discussion

Level in soil

The PCDD/F-determination in the soil sample was performed twice. The media amount was 13,900 ng I-TEQ/kg with standard deviation of 0.9%. The normalized homologue distribution is shown in figure 1.

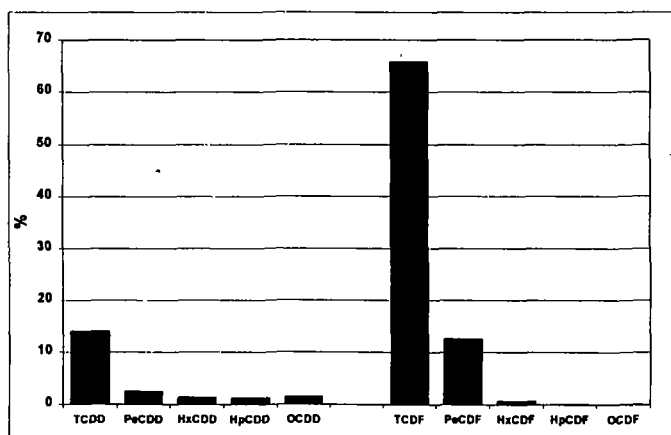


Figure 1: Normalized PCDD/F-homologue distribution in soil from Cidade dos Meninos.

Till now, such a high level of dioxins in Brazilian soil were never described in the scientific literature. The highest amount of 654 ng I-TEQ/kg was shown by Mahnke⁴ which was found nearby a siderurgy.

Comparable PCDD/F-concentrations (10,000 - 30,000 ng I-TEQ/kg) were found in the area of copper reclamation plant in Crailsheim-Maulach/Germany⁵. At this place, the contaminated soil was removed following the German guidelines for soil protection⁶. A policy guide from ATSDR has been adopted to assess the implications on the usage of residential soils near or on hazardous waste sites contaminated with dioxin or dioxin-like compounds. They propose that levels greater or equal to 1 ppb TEQs shall be assumed as a public health hazard and that human exposure shall be avoided⁷.

Levels in cow's milk

The PCDD/F-amounts in cow's milk from Cidade dos Meninos are shown in table 1. They varied from 4.1 to 6.5 pg I-TEQ/g milk fat which means a media of 4.9 pg I-TEQ/g milk fat. There is no other data about PCDD/F in cow's milk from Brazil.

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Comparing these results with the German guidelines and actions⁸ for the PCDD/F- milk contamination shows that at least one milk is in the range (> 5 pg I-TEQ/g fat) where milk is no longer marketable and also the media amount is very close to this limit. In the case of Cidade dos Meninos, milk is only consumed by the local population and no dilution with milk from other places happens.

Table 1: PCDD/F-concentrations in cow's milk from Cidade de Meninos.

Sample	Concentration in pg I-TEQ/g milk fat
Milk 1	4,5
Milk 2	4,5
Milk 3	6,5
Milk 4	4,1

Final Conclusion

Given the small sampling, the authors recommend that future research is necessary to estimate the magnitude and extent of the whole contamination. Contamination may be potentially widespread. Sampling procedure was designed on the basis of a preliminary study. Only by analysis of high number of further soil and food samples produced in the region can contribute to a real estimation of the risk.

Further environmental studies can contribute to future decisions related to treatment, recovery and usage of soil. Furthermore, a major concern about this contaminated area is whether ingestion of a food chain component produced in this region poses a threat to human health.

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