DIOXINS IN SOIL TREATED WITH 2,4-D IN A MUNICIPALITY OF THE STATE OF RIO DE JANEIRO, BRAZIL

Ana Maria Cheble Bahia Braga[1], Thomas Krauss[2], Jeferson Monteiro Rosa[1]

[1]National School of Public Health, Oswaldo Cruz Foundation, Rio de Janeiro
[2]National Institute for Quality Control in Health, Oswaldo Cruz Foundation, Rio de Janeiro

Introduction

Of great concern has been the presence of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), as contaminants in 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2,4-dichlorophenoxyacetic acid (2,4-D). In fact, TCDD has been reported in 2,4,5-T formulations and in Herbicide Orange mixtures from Europe in the 60's. Humans have been exposed to PCDD/Fs in several industrial accidents, i.e., Nitro and Seveso, and through environmental contamination, i.e., Vietnam and Newark. It is well described in the literature and responsible for several actions to protect humans health and the environment[i, ii, iii, iv].

In Brazil, the herbicide 2,4,5-T was prohibited due to the presence of high dioxins concentrations as impurity in its formulations but the herbicide 2,4-D is widely used to control broad-leaf weeds in several plantations such as sugar cane, coffee, potato among others or prior to planting in order to prepare soil for plantation[v]. The National Agency for Sanitary Surveillance (ANVISA), the authority in charge of the pesticides registry, also established the concentration of 0.1 ppm as maximum limit for dioxins in 2,4-D formulations. It is also a common practice to use this herbicide associated with Glyphosate to reduce or replace manual or mechanical weeding.

In 2000, the Secretary of Health of Cantagalo, Municipality in the north part of Rio de Janeiro State was notified about a possible environmental contamination by the application of 2,4-D at a coffee farm named Santa Guilhermina. Spraying had occurred in an area close to a creek used as a source of drinking water of a school and as a water supply for a second district of this municipality. Special care was given to the possibility of PCDD/Fs contamination of the drinking water supply directly through 2,4-D aplication and indirectly through the transfer by run-off. Thus, it was requested scientific advice and analytical support to verify whether or not contamination had occurred. They had called for technical support only 8 days after the episode and considering the very low solubility of PCDD/Fs in water and their high tendency to adsorb on particles, it was decided to check if the soil had been contaminated by these activities and to use this database for further decision-making, as well. It was also looked up for original 2,4-D formulation in the area to verify the possible presence of PCDD/Fs but none was available.

Methods and Materials

Soil samples were collected at three different areas of the farm, ten days after spraying. At each sampling point, ten subsamples of 200 g were taken from a circle, 2 m in diameter and in a depth of 0-25 cm. 2,4-D was applied at area 1 and 2. No application occurred in area 3; so, the sample collected in this area was considered the control (S3). Sample 1 (S1) was taken at 10m far from the creek located in the lower treated area. Sample 2 (S2) was picked up in an upper area, 2 m far, as well.

After drying, sieving (< 2 mm) and homogenizing, 50 g of soil were spiked with ^{13}C-PCDD/Fs and extracted with toluene during 24 h in a Soxhlet extractor. The cleanup procedure consisted of series of chromatographic columns. The first cleanup column was made by silica-silica/sulfuric acid-silica, followed by a Florisil column and finally an activated carbon/silica column was used. The final extract was concentrated to 20 µl. All samples were analyzed by HRGC/HRMS using an AutoSpec Ultima (VG Analytical, Manchester) coupled to Agilent 6890N gas chromatograph. Separation was performed on a DB 5MS column (60 m, 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific) with helium as carrier gas hold at 1,5 ml/min. The mass spectrometer was operated at resolution of 10,000.

Results and Discussion

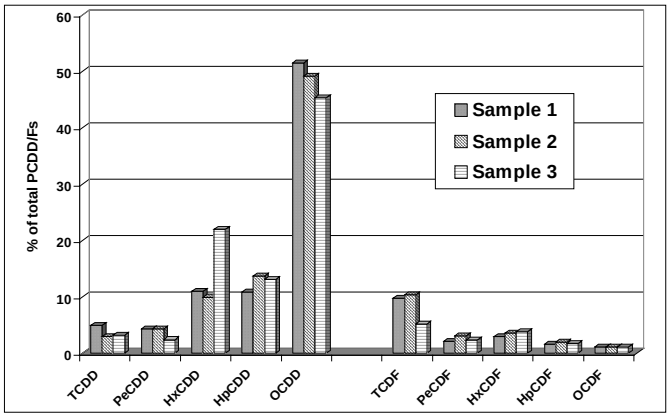
The PCDD/F concentrations in soil samples collected at the three different areas of Santa Guilhermina Farm are demonstrated in table 1. All samples showed low PCDD/Fs amounts and the highest was found in the area 3 (S3), where no 2,4-D was sprayed. Varying from 0.25 to 0.73 ng I-TEQ/kg, these values are comparable to the results from a former study performed in 1997, in the same municipality, where concentrations varied from 0.03 to 6.91 ng I-TEQ/kg. In the cited study, soil samples were collected in the surroundings of a cement kiln/co-processing waste plant, which is located in the neighbor district called Euclidelândia[vi].

***Table 1*: PCDD/F concentrations in soil at Santa Guilhermina Farm.**

Sample	Amount (ng I-TEQ/kg)
S1	**0.25**
S2	**0.40**
S3	**0.73**

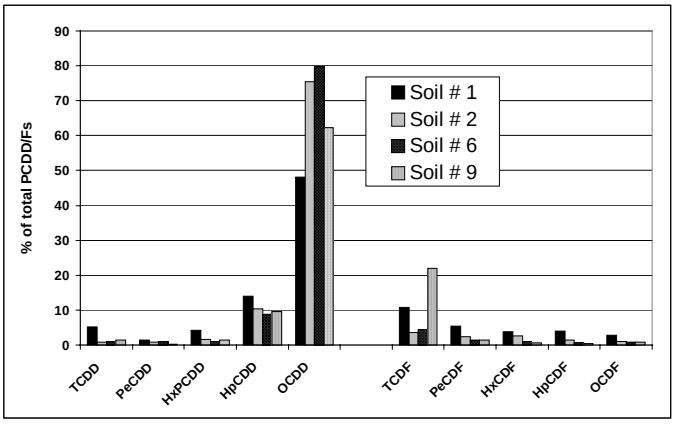
The distribution pattern of the homologue groups of Sample 3 was slightly different in comparison to the other two areas (figure 1). Higher amount of hexachlorodibenzo-p-dioxins and lower amount of tetrachlorodibenzofurans was observed as the main difference.

***Figure 1*: PCDD/F distribution patterns in soil at Santa Guilhermina Farm.**



The distribution patterns appeared to be very similiar to the patterns identified in soils from the residental area nearby the cement kiln in Euclidelândia (figure 2), showing in both situations octachlorodibenzo-p-dioxin as the main component, with decreasing amounts from hepta through tetrachlorodibenzo-p-dioxins and tetra through octachlorodibenzofurans. It also indicates similar contamination pathways.

***Figure 2*: PCDD/F distribution patterns in soils from the residental in Euclidelândia.**



adapted from Krauss et al., 1999

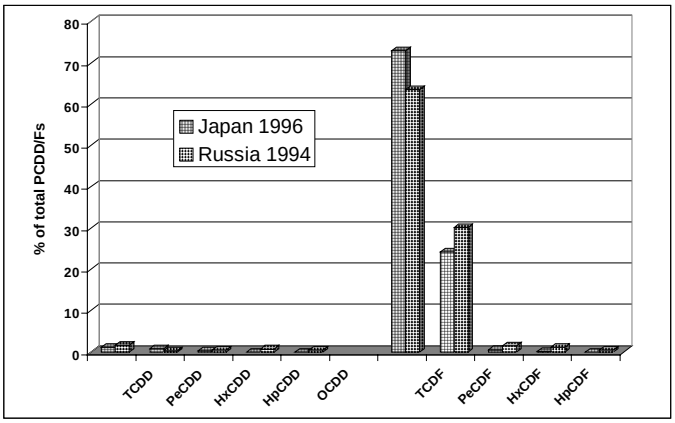
In Germany, PCDD/Fs in agricultural soil can vary from 0,2 to 7,0 ng I-TEQ/kg. Brazilian data related to soil contamination by PCDD/Fs is very scarse. Industrial, recreation, waste incineration areas and Amazon basin soil were sampled and analysed in 1995[vii].

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

Location	Amount (ng I-TEQ/kg)
Waste Incineration Areas	22 – 72
Industrial Areas	15 – 654
Amazon Basin	0,05 – 0,4
Recreation Area	0,4 – 1,8

In order to find out if there is any link between the analyzed samples and the PCDD/Fs distribution pattern in some agrochemicals formulations including 2,4-D, two studies were evaluated. The first study was conducted in Japan and had shown a broad spectra of PCDD/Fs and dioxin-like PCBs in some agrochemicals formulations including 2,4-D[viii] and the second study took place in Russia[iv]. Besides the significant difference in total PCDD/F concentrations with 160 ng I-TEQ/g in the Russian sample and the 16 pg I-TEQ/ g in the Japanese one, both had shown almost the same PCDD/F distribution pattern with high levels of tetra and pentachlorodibenzofurans and insignificant amounts of the others homologues (figure 3). Under the presumption that 2,4-D used at Santa Guilhermina Farm had a similar PCDD/F content, no influence of PCDD/Fs originated from 2,4-D was observed.

***Figure 3*: PCDD/F distribution patterns in 2,4-D samples from Japan and Russia.**



adapted from Schecter et al., 1994 and Masunaga et al., 2001.

Conclusion

The Secretary of Health was informed that the PCDD/Fs found in the three areas represented no risk to the local population due to the very low concentrations which were also in the same range obtained in soil samples from the same region influenced by different emission sources. Based on the available data, it was concluded that possible additional PCDD/F burden via 2,4-D spraying was too low to be recognized. Significant PCDD/F exposure through drinking water was also excluded since water solubility is very low and the tendency to adsorb on

particles high. Attention was called to the fact that no pesticide apllication close to water bodies should be made.

Acknowledgments

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