PCDD/F ANALYSIS IN BRAZIL; CASE STUDIES, PART 2, A NEW CASE OF LIME CONTAMINATION IN BRAZIL

Gabriela Kernick Carvalhaes; Paul Brooks; Carla Gama Marques; Thomas Krauss

PETROBRAS CENPES CEGEQ
Cidade Universitaria Q7 Cep 21949-900 Rio de Janeiro Brazil

Introduction

During the last year our laboratory has been involved in at least two major projects of public concern involving the determination of PCDD/F's. One has involved the continuous monitoring program of several types of food taken from the Brazilian ports for the Ministry of Agriculture and the other has involved analysis of lime, soil samples and residues from various manufacturers and waste sites in the State of Minas Gerais for the Public Ministry (Minas Gerais) and the GreenPeace Organisation.

We would like to present preliminary results from the a new case of contamination in this presentation and to discuss future monitoring studies that may be undertaken on behalf of the Government of Brazil.

In 1998, lime was identified as the source of contamination of Citrus pulp pellets, (Carvalhaes,1999). In this case, it was very clear that a specific lime converter used contaminated lime milk as raw material. The case presented in this paper is also related to lime, but the source is still under investigation. It is very important to say that this case has no contribution to the previous Brazilian contamination, and for the moment, only the formation of PCDD/F during this specific lime production is verified.

The state of Minas Gerais has lots of different lime producers, including the ones registered and monitored for PCDD/F content. A separated group of manufactures use as fuel for calcium carbonate burning several materials, including wood, rubber from tires, carbon pellets, plastics and residues from the production of cars and carpets. It was identified that the process of burning this mixture has an intense dioxin formation, and so soil, ashes and the residual lime were analysed.

Materials and Methods

The sampling was made with the coordination of the Public Ministry and FEAM, the environmental agency in Minas Gerais.

As the process takes place in open air, where all materials are burned together with calcium carbonate, samples from the lime resultant, as well as soil, dust and ashes located around the furnace were taken.

Standard isotope dilution techniques were used for all samples. Thus, solid samples (typically 10 – 30 g) were spiked with ^{13}C labelled internal standards (1ng) and extracted with dichloromethane under soxhlet conditions (minimum 16 hours). Samples were subjected to column chromatography (silica/sulphuric acid and florisil).

Following addition of recovery standard, the samples were analysed by selected ion monitoring GC-MS at 10000 resolution (10% valley definition) using a Micromass Ultima mass spectrometer. The GC column used was a DB-5MS (60m).

Results and Discussion

The US EPA/i-TEQ total toxic equivalent amounts for each of the samples are given below. Note that the results are reported in pg/kg.

SAMPLES	Amount i-TEQ
DUST IN THE FLOOR	72
CARBON PELLETS WITH COFFEE PEEL	1200
LIME, FINAL PRODUCT	0
SOIL FROM 150 M	1400
BURNER ASHES	1300000
BURNER RESIDUES	23000
SOIL, BESIDE THE BURNER	62000
SOIL FROM 100M	5000
SOIL, BESIDE THE BURNER	20000
LIME, FINAL PRODUCT	3200

Other studies were made regarding the investigation of the immediate consequences of this source. For that, oil, milk and soil samples from surrounding areas were analyzed.

Figures 1 and 2 show the pattern observed for a contaminated lime sample and for the burner ashes, respectively. The patterns are similar, but not quite the same, as expected, once several different materials are burned.

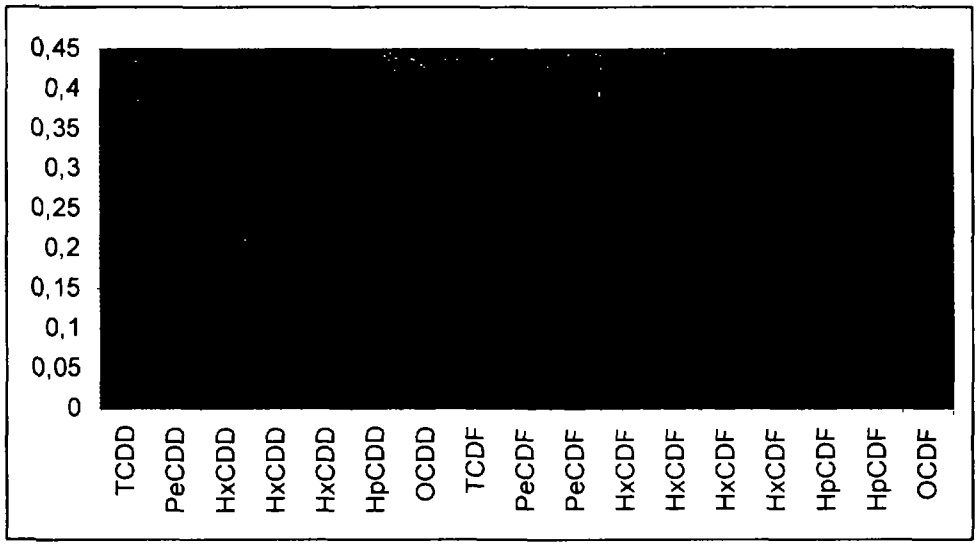

Figure 1 – PCDD/F pattern for contaminated lime, 3200 pg/kg I-TEQ

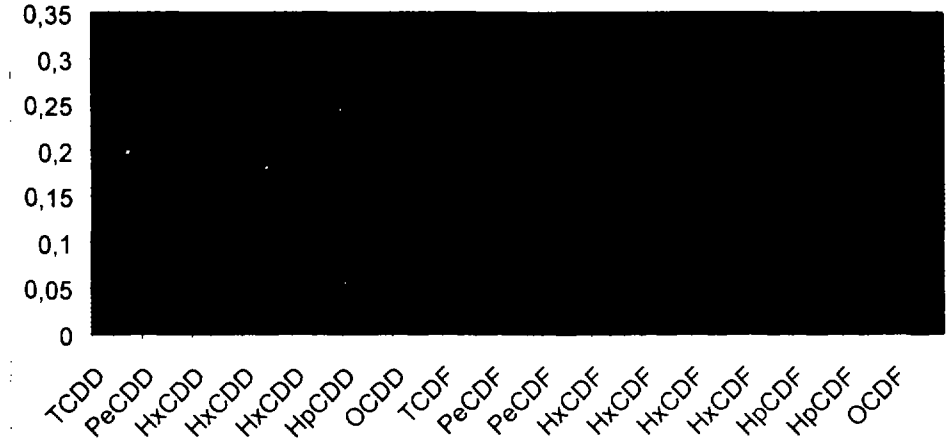

Figure 2 – PCDD/F pattern for burner ashes, 1300000 pg/kg I-TEQ

Table 2 shows a preliminary comparison between the levels found in this case with other examples. The samples shown in italic are reference results found in the literature.

Table 2 – Levels of PCDD/F

Description	I-TEQ (ppt)
Virgin lime	0
Ashes from burner	0
Virgin lime	0
Virgin lime	0
Virgin lime	0
Ashes from burner	0.021
Residues	0.063
Floor dust	0.072
Carbon pellets used as fuel	1.2
Road dust	1.4
Cement kiln dust from kilns burning hazardous waste (average excluding 1 very high result)	*2.9*
Virgin lime	3.2
Soil 100m from burner	5
Uncontaminated soil in USA (average)	*8*
Uncontaminated soil in Europe (average)	*9*
Soil near burner	20
Residues near burner	23
Cement kiln dust from kilns burning hazardous waste (average including 1 very high result)	*35*
Soil dioxin concentration above which land cannot be used for grazing (Germany)	*40*
Soil near burner	62
Ash/soil from PVC/cable open burn sites (average)	*1300*
Ashes from burner	1300
Ash/soil from PVC/cable open burn sites (maximum)	*6600*
Ash from open burning at landfill in Malta	*48000*

Conclusions

A new case of PCDD/F contamination inBrazil is shown. For the moment, only the formation of dioxins and furans was detected, the consequences of this contamination are still under investigation. It is very important to notice that this case has nothing to do with the CPP contamination, and has no chance to interfere in the quality of lime and CPP produced today in Brazil, once there are registered lime and CPP producers who are submitted to a very intense dioxin monitoring program.

References

G.K. Carvalhaes *et al.* Lime as the Source PCDD/F contamination in citrus pulp pellets from Brazil, *OrganoHalogen compounds 41 , p.137 , 1999*