PCDD/F CONTAMINATION IN CITRUS PULP PELLETS FROM BRASIL: STATUS OF THE MONITORING PROGRAM

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Introduction

In late 1997, in the State of Baden-Württemberg, Germany, unusually high levels of PCDD/F's were detected in milk fats. After an exhaustive investigation the source of the contamination was traced to Citrus Pulp Pellets (CPP) that are used as part of the feed for dairy cows (Malisch, 1997). Shipment receipts clearly pointed to Brasil as the origin of the contaminated CPP. Consequently, the use of Brazilian CPP was halted and the Ministry for Baden-Württemberg had secured support from the feeds industry to stop the consumption of CPP from Brazil in mixed feed products and to remove compound feed containing PCDD/F's. In the following months, the use of CPP from Brazil in all European Community countries was halted. In 1997 approximately 1,400,000 tonnes of CPP had been shipped through the Brazilian port of Santos, representing a considerable source of revenue for the Citrus growers in Brasil.

Towards the end of March 1998, the Ministry of Agriculture for Brazil was made aware of the preliminary findings in Germany of the link between PCDD/F's in cows milk and CPP feed. A concerted effort was established to discover the source of the contamination, which pointed to a lime converter who provided lime milk as a raw material for the CPP production (Carvalhaes,1999).

Figure 1 shows the normalised distribution pattern of the seventeen 2,3,7,8- congeners for the lime sample together with that of the contaminated CPP. It is apparent that the distributions are almost identical showing the distinctive pattern of high (>70%) OCDF content and low PCDD content

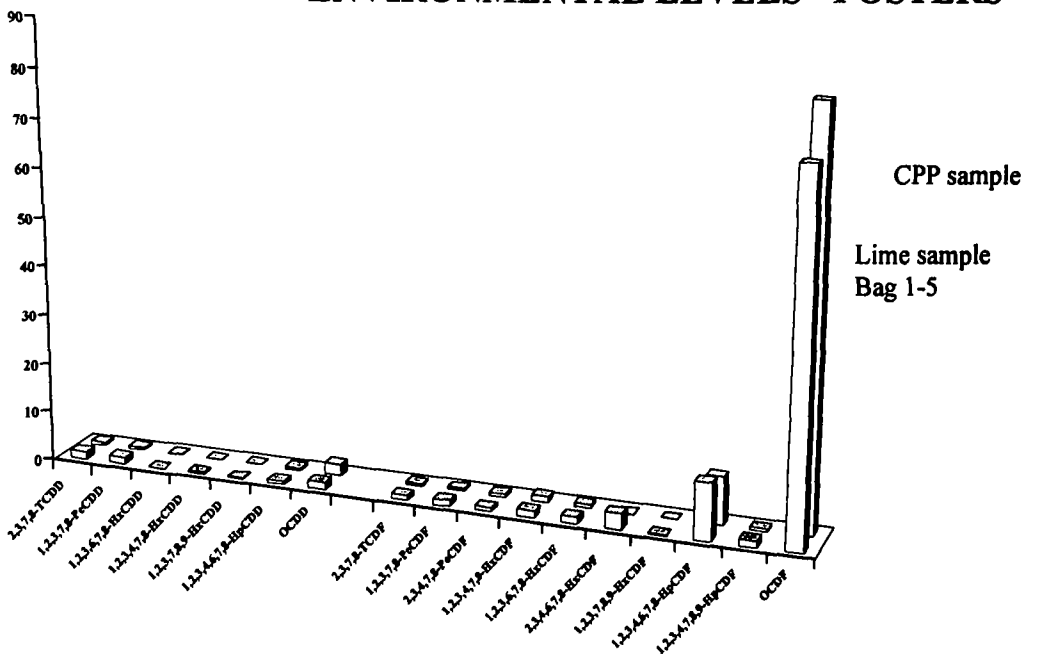

Figure 1

After the identification of the source, a specific legislation was published in Brazil to control the levels of dioxins and furans in CPP and lime. Thus, an upperbound value of 500 pg/kg was stablished as a tolerance level for any lime that should be used in animal feed. The same level was applied for citrus pulp pellets. This paper shows the result of this program during the year of 1999.

Material and Methods

Samples were taken by companies previously registered by the Ministry of Agriculture. The number of samples was determined according to the production of each company. For CPP companies, one sample of 250 g was collected each two hours, resulting in a composite sample of 15 days or 30 days, depending on the production capacity. For lime producers, a daily sample of 100g is taken, generating a composite sample of thirty or sixty days , also depending on the production capacity. Samples of citrus pulp pellets that were destinated for exportation were also analysed. Those were colleted in the port of Santos, Brasil, as a composite sample for each 7,000,000 kg.

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

Over 500 samples were analysed as a part of the monitoring program of Brazilian Ministry of Agriculture. No sample showed upperbound levels higher than 500 pg/kg I-TEQ. The results were directly sent to the producers, and lately presented to the representants of the Ministry of Agriculture in each city. Besides that, a monthly report is sent to the Federal Ministry of Agriculture in Brazil by all the companies involved (CPP producers, Lime producers and laboratory).

Table 1 shows an example of the summary report sent from CEGEQ to the Ministry of Agriculture in a monthly basis. This report is shown as a summay of the laboratory activities and is a complement of the analysis report sent to the producers. The names of the producers were not mentioned here for confidentiality purposes.

Besides the monitoring program applied by the Ministry of Agriculture, citrus and lime companies; efforts from governamental institutions were also made aiming a final destination of the lime milk. As a consequence of that effort, an agreement between the owner of the lime, CETESB (the environmental agency of the state of Sao Paulo) and the Public Ministry was officialized in the end of 1999. This agreement has as primary objective finding a solution for the destination or destruction of the lime milk.

LIME

COMPANY	SHIP	PRODUCTION	DATE	CODE CEGEQ	DIOXIN CONTENT I-TEQ (UPPERBOUND)
LIME 1		X	11-Feb-00	784E	<250 pg/kg
LIME 2		X	11-Feb-00	781E	<250 pg/kg
LIME 3		X	02-Feb-00	769E	<250 pg/kg
LIME 4		X	11-Feb-00	785E	<250 pg/kg

COMPANY	SHIP	PRODUCTION	DATE	CODE CEGEQ	DIOXIN CONTENT I-TEQ (UPPERBOUND)
CPP					
CPP 1		X	28-Feb-00	799E	<250 pg/kg
CPP 2		X	24-Feb-00	794E	<250 pg/kg
CPP 3		X	03-Feb-00	776E	<250 pg/kg
CPP 4		X	01-Feb-00	765E	<250 pg/kg
CPP 5		X	02-Feb-00	773E	<250 pg/kg
CPP 6		X	22-Feb-00	788E	<250 pg/kg
CPP 7		X	28-Feb-00	802E	<250 pg/kg
CPP 8		X	11-Feb-00	778E	<250 pg/kg
CPP 9	X		02-Feb-00	771E	<250 pg/kg
CPP 10	X		02-Feb-00	774E	<250 pg/kg
CPP 11	X		03-Feb-00	777E	<250 pg/kg
CPP 12	X		11-Feb-00	787E	<250 pg/kg

Conclusions

It has been shown that the continuous monitoring of the PCDD/F content of citrus pulp pellets for both internal (Brazil) and external consumption was performed with success. The program, the first dioxin monitoring program in Brazil, is now used as a model for other environmental issues in Brazil.

No Citrus pulp pellets was produced and comercialized (both internally and internationally) with dioxin content of over 500 pg/kg I-TEQ upperbound.

The site were the lime milk is stored is under an intensive investigation, concerning the determination of the real dioxin and furan leves, as well as other chlorinated compounds, like PCB's and other organochlorine compounds.

Acknowledgements

We gratefully acknowledge the cooperation provided by the Ministry of Agriculture (Brazil).

References

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