Status of organochlorine contamination in lime and related products five years after Brazilian dioxin crisis

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[1]Analytical Solutions

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[1]. 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.

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 [2]. Since then, not only the feed and lime have been intensively monitored, but also the company that holds the lime area has performed a wide characterization work followed by continuous PCDD/F monitoring. Five years after the accident, no PCDD/F were detected in all samples.

Materials and Methods

Samples were taken by companies previously registred by the Ministry of Agriculture. The number of samples was determined according to the production of each company. For CCP companies, one sample of 250 g is collected every 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 100 g is taken, generating also a composite sample. For animal feed, both production and exportation have been analyzed. As the lime reservoir is located close to a water dike, groundwater has been also checked for PCDD/F content.

Standard isotope dilution techniques were used for all samples. Thus, solid sample (typically 10 – 30 g) were spiked with ^{13}C labelled internal standards (0.5ng) and extracted with dichloromethane under soxhlet conditions (minimum 16 hours) while water samples were extracted in dichloromethane using liquid liquid extraction. Samples were subjected to column chromatography (sílica/sulphuric acid and florisil) in order to remove interferences. Following addition of recovery standard, the samples were analysed by selected ion monitoring GC-MS at 1000 resolution (10% valley definition) using a Micromass Ultima mass spectrometer. The GC column used was a DB-5MS (60m).

Results and Discussion

Since that time, over 1000 samples were analyzed as a part of the monitoring program of Brazilian Ministry of Agriculture. No sample showed upperbound levels higher than 500 pg WHO-TEQ/kg, in accordance with European Directive EC 201/2002 and Brazilian legislation. The results were directly send to the producers, and latety 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) showing data from production and analyses.

The lime reservoir was characterized according to a joint project with the environmental agencies and the Public Ministry, and performed with all quality criteria by the company that holds the lime. During over 6 months several alternatives were studied to destroy the reservoir, but considering the reservoir size, a complete isolation was done separating the lime from the soil and thus avoiding future leakages. Also no lime was taken again from the site and wells were built to add to the ones already controlled by the company´s environmental monitoring programme.

Frequent batches of around 70 samples are taken during these five years, where not only PCDD/Fs are analysed, but also other organochlorine compounds have been constantly monitored. During these five years, also in those samples no significant contamination has been detected in this monitoring programme.

Thus, it can be considered that the concerted effort with private industries, Brazilian environmental agencies and the Ministry of Agriculture has resulted in reliable monitoring of the Brazilian products exported to Europe and also the isolation and continuous monitoring of PCDD/F in the surroundings of the lime reservoir.

References

1. R. Malisch, *Organohalogen Compounds*, 38, **1998**

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