LIME AS THE SOURCE OF PCDD/F CONTAMINATION IN CITRUS PULP PELLETS FROM BRASIL

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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.

Citrus Pulp Pellets are a by-product from the production of Citrus drink concentrates. The pulp, after the juice has been squeezed from the fruit, is neutralised, dried and made into pellets. CPP is mixed with other components such as maize, molasses and rape, to produce a Compound Feed. These compound feeds may contain approximately 25% CPP

In the European Community, as a whole, there is about 92000 tonnes of CPP (worth approximately $US 10 million) stockpiled and unusable. The cost for disposing of this CPP is estimated at approximately $US 2 million.

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. A large variety of samples from the CPP processing plants were collected and significantly high levels of PCDD/F's were detected in certain CPP products.

We report here the primary source of the contamination of the CPP.

Material and Methods

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

In cooperation with the Citrus Industry, many samples of CPP, juice, wet peel, essential oil extracts and other ingredients produced or added to the CPP were analysed. Table 1 shows the absolute values for the seventeen 2,3,7,8- PCDD/F congeners for a typical contaminated CPP product.

	CPP ng/kg	Wet Peel ng/kg	Dry Peel ng/kg	Wet Peel * ng/kg	Dry Peel* ng/kg	Lime Bag 1-5 ng/kg
TCDD	26	(0.03)	(0.03)	(0.03)	(0.03)	1200
12378PeCDD	24	(0.03)	(0.03)	(0.03)	(0.03)	1100
123478 HxCDD	4.4	(0.03)	(0.03)	(0.03)	(0.03)	140
123678 HxCDD	1.3	(0.03)	(0.03)	(0.03)	(0.03)	240
123789 HxCDD	3.8	(0.03)	(0.03)	(0.03)	(0.03)	170
1234678 HpCDD	16	(0.03)	(0.03)	(0.03)	(0.03)	600
OCDD	92	(0.03)	(0.03)	(0.03)	(0.03)	1200
TCDF	19	(0.03)	(0.03)	(0.03)	(0.03)	750
12378 PeCDF	19	(0.03)	(0.03)	(0.03)	(0.03)	920
23478 PeCDF	22	(0.03)	(0.03)	(0.03)	(0.03)	630
123478 HxCDF	53	(0.03)	(0.03)	(0.03)	(0.03)	1200
123678 HxCDF	28	(0.03)	(0.03)	(0.03)	(0.03)	1100
234678 HxCDF	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)	2700
123789 HxCDF	(0.03)	(0.03)	(0.03)	(0.03)	(0.03)	63
1234678 HpCDF	410	(0.03)	(0.03)	(0.03)	(0.03)	9600
1234789 HpCDF	21	(0.03)	(0.03)	(0.03)	(0.03)	1100
OCDF	3500	(0.03)	(0.03)	(0.03)	(0.03)	61000
Total (upper bound)	4239.5	(0.5)	(0.5)	(0.5)	(0.5)	83713.0
Total I-TEQ (upper bound)	69	(0.09)	(0.09)	(0.09)	(0.09)	2923
Note * after addition of certain additives						

Table 1

The levels given in parentheses represent the “upperbound level’ or detection limit. All PCDD/F data include these upperbound levels.

The typical CPP product contained significant amounts of PCDD/F (a total of 4240 ng/kg or 69 ng/kg I-TEQ). Figure 1 shows the normalised distribution of the seventeen congeners in the CPP sample shown in table 1. The normalised distribution pattern of the 2,3,7,8- PCDD/F congeners is highly unusual (fig. 1), characterised by extremely high relative amounts of OCDF and low levels of PCDD's. Such a pattern has not been described previously and may be used to define the source of the contamination.

No PCDD/F's were detected in the wet peel or dry peel, with or without certain additives (at an upperbound level of 0.5 ng/kg or 0.09 ng/kg I-TEQ). This suggests that the peel itself was not contaminated and that the drying process of the peel alone was not involved in the generation of PCDD/F's. Thus, the source of the contamination must have been external to the peel involving another additive used during the production process.

Table 1 shows the absolute distribution of PCDD/F's in a sample of lime (Bag 1-5, supplied by a Citrus Company), used as a neutralising and drying agent, in the CPP production. Extremely high levels of PCDD/F's were observed in this component of the process (ca. 84000 ng/kg or 2923 ng/kg I-TEQ).

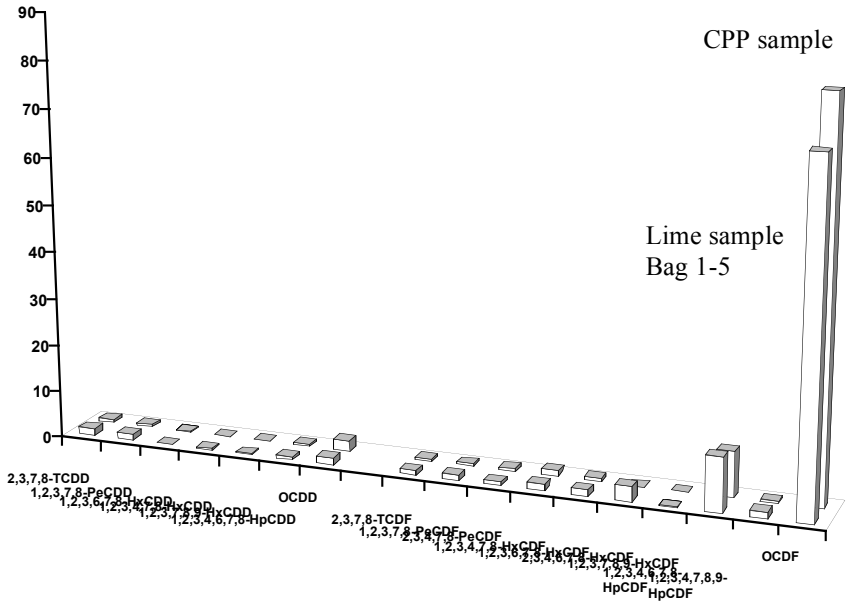

Figure 1

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.

Lime is added to the wet peel at a level of 2% which corresponds to about 7-8% of the dry CPP. Lime is supplied to the Citrus companies from a variety of sources. It was found that Lime supplied by only one company contained these levels of PCDD/F's. Lime from all other suppliers was free of contamination.

As soon as the use of the lime from this supplier was stopped and an alternative used, the levels of PCDD/F's in the CPP product was below the target tolerance level of 0.5 ng/kg I-TEQ (European Directive 98/60/EC).

Conclusions

It has been shown that lime was the source of the PCDD/F contamination of CPP product that was distributed to the European Community in 1997. After terminating the use of this batch, the PCDD/F content of CPP product was below the European Community tolerance level of 0.5 ng/kg I-TEQ. Continuous monitoring of the PCDD/F content of CPP product is now performed, at the production and shipping stages and only product with a PCDD/F content of less than 0.5 ng/kg I-TEQ will be acceptable for use as animal feed for both internal (Brasil) and external consumption.

The initial cause of the contamination the lime supply is under active investigation and will be reported separately.

Acknowledgements

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References

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