CHLORINATED COMPONENTS IN LIME USED IN PRODUCTION OF CONTAMINATED CITRUS PULP PELLETS FROM BRASIL

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Introduction

It has been established that the source of PCDD/F's contamination in Citrus Pulp Pellets (CPP) from Brasil was lime that is added to neutralise the pulp and to facilitate drying (Carvalhaes *et al.* 1999). However, the source of the PCDD/F contamination of the lime is in question. In order to further our understanding of the contamination we examined both a contaminated lime and CPP sample for the distribution of polychlorinated biphenyls (PCB's) and chlorinated benzenes (tri-hexa). Furthermore, the lime sample was examined in more detail for the presence of other polychlorinated compounds.

Material and Methods

Solid samples (typically 10 – 30 g) were spiked with deuterated polynuclear aromatic hydrocarbon internal standards (1µg) and extracted with dichloromethane under soxhlet conditions (minimum 16 hours). No clean up of the extracts was performed.

The samples were analysed by selected ion monitoring GC-MS at 5000 resolution (10% valley definition) using a Micromass Ultima mass spectrometer for PCB and chlorobenzenes. The GC column used was a DB-5 (30m). Prior to sample analysis, authentic standard calibration solutions were analysed to obtain relative response factors in the normal manner. The lime sample extract was examined using full scanning from m/z 550-50 at 1 second/decade and using the same GC conditions.

Results and Discussion

Table 1 shows the absolute concentrations of individual PCB congeners and total homologous series and also tri to hexachlorobenzenes for a typical contaminated CPP product and for the lime sample (Bag 1-5 supplied by a Citrus Company) contaminated with PCDD/F's (Carvalhaes *et al.* 1999). It can be seen that absolute levels of the PCB's and chlorobenzenes is high in the lime sample (ca. 3000000 and 200000 ng/kg respectively) and also in the CPP sample (ca. 2000 and 2000 ng/kg respectively).

Figure 1 shows the normalised distributions for the total tri – hepta PCB's for the lime and the CPP samples. Clearly the distributions are extremely similar as are the plots if the normalised individual congeners are taken.

	Lime BAG 1-5 ng/kg	CPP ng/kg		Lime BAG 1-5 ng/kg	CPP ng/kg
Trichloro, BZ #28	95000	76	Trichlorobenzene	0	0
Tetrachloro, BZ #52	35000	19	Tetrachlorobenzene	440	40
Tetrachloro, BZ #77	3200	8.4	Pentachlorobenzene	1200	70
Pentachloro, BZ #101	92000	23	Hexachlorobenzene	200000	2100
Pentachloro, BZ #118	230000	170			
Pentachloro, BZ #105	51000	73			
Pentachloro, BZ #126	1000	0			
Hexachloro, BZ #153	220000	100			
Hexachloro, BZ #138	150000	100			
Hexachloro, BZ #156	41000	45			
Hexachloro, BZ #169	0	0			
Heptachloro, BZ #180	140000	68			
Total Trichloro	10000	2.8			
Total Tetrachloro	400000	400			
Total Pentachloro	110000	120			
Total Hexachloro	59000	31			
Total Heptachloro	65000	37			

Table 1

A normalised plot for the chlorobenzenes for the lime and CPP samples are also very similar. Thus, this is added confirmation that the lime is the primary source of the contamination of the CPP product, as suggested by the PCDD/F distributions shown by Carvalhaes *et al*. 1999.

Figure 2 shows the Total Ion Current (TIC) trace for the analysis of the lime sample. Marked on the trace are identities of the major components identified. These components are primarily:

- Hexachlorobenzene
- PCB’s
- Hydroxy PCB’s
- Polychloro diphenylethers

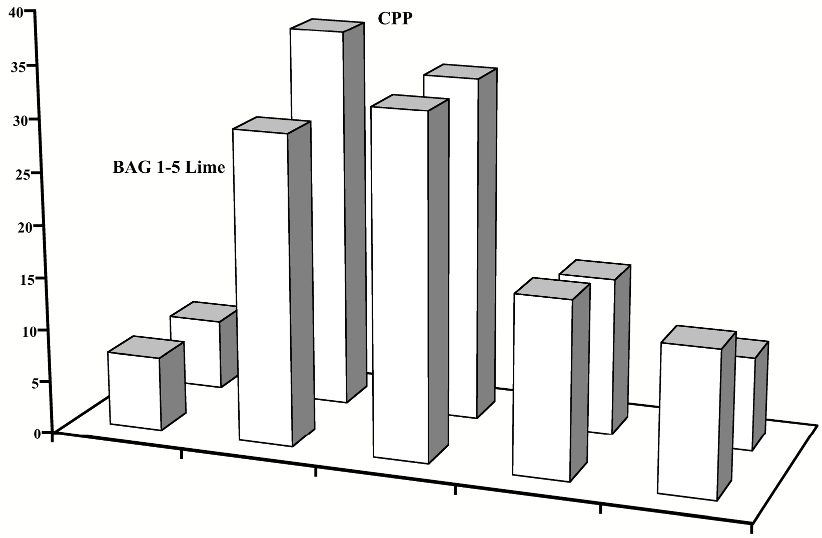

Figure 1

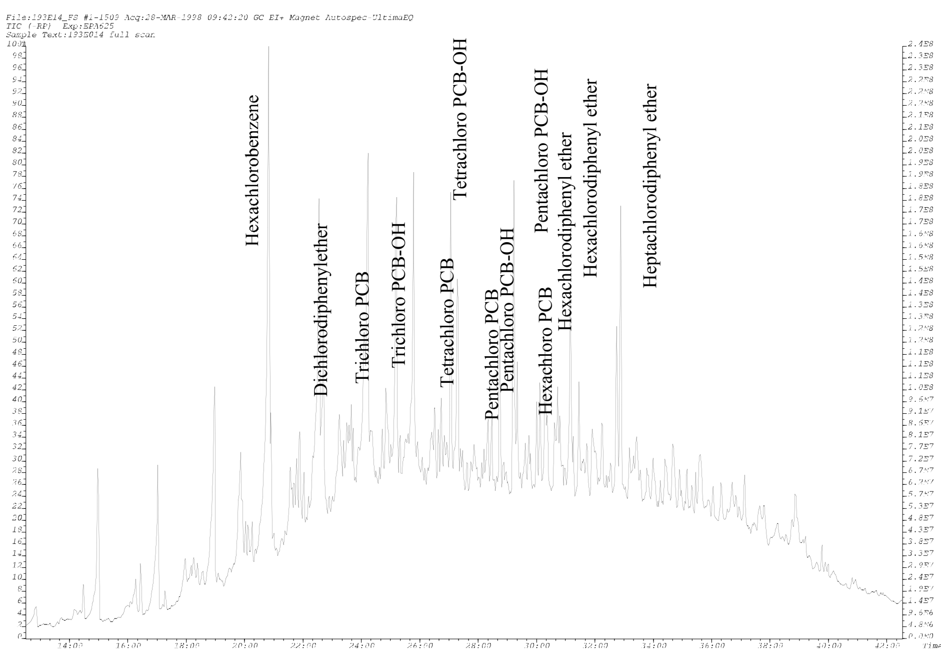

Figure 2

The hydroxy PCB's are present in high relative abundance at concentrations similar to the PCB's themselves. The polychloro diphenyl ethers are present in lesser but significant amounts. It is well established that hydroxy PCB's and polychloro diphenylethers can readily form PCDD's and PCDF's (Kurz, 1994) and thus, it is our belief that these components, are potential precursors of the PCDD/F contamination in the lime samples and consequently the CPP product.

Conclusions

Lime that is used in the production of CPP product is highly contaminated with PCB's and chlorobenzenes. The normalised distributions of these components is almost identical for the lime and CPP product.

The PCDD/F contamination in the lime and CPP product (Carvalhaes *et al.* 1999) is almost certainly related to the presence of hydroxy PCB's and polychlorinated diphenylethers in high abundance in the lime sample and hence the CPP product.

Acknowledgements

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References

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