

DETERMINATION OF PCDD/Fs IN COW'S MILK FROM BRAZIL

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Introduction

Most phenolic compounds used in agricultural chemicals are chlorinated phenols, commonly used in wood preservation (e.g.: PCP) or as industrial biocides, as opposed to use on food crops or animals. Large quantities of phenols are also the starting material for the production of the phenoxic acetic herbicides (2,4-D, 2,4,5-T, MCPA). Although forbidden in several countries around the world, and at least one state of the Brazilian Federation, this kind of compounds are still ubiquitous in our market.

The phenoxic herbicides and/or other phenol products for wood preservation had different degrees of toxicity, but there are concrete suspicions that its formulations may contain considerable amounts of highly toxic condensation products like 2,3,7,8-tetrachlorodibenzo-p-dioxins, by far the most toxic one, sometimes called the "Seveso" dioxin, after a massive contamination that occurred in 1976 in Italy¹.

There are a large number of chlorinated dibenzo-p-dioxins and the closed associated chlorinated dibenzofurans that can be largely distributed and are more likely to occur in foods than the tetrachlorinated isomer and it is necessary to determine their significance and what will be done about them. Although several governmental and NGO's efforts have been done around the world in order to reduce the presence of dioxins and furans in food items, the current level of dioxins and furans in cow's milk from Brazil is unknown.

In the end of the 1990 decade, a huge amount of dioxins and furans was detected in exported parcels of citrus pulp originated from Brazil with very severe and negative effects upon the milk market in Germany². This isolated incident is just one of several other cases around the world of notorious contamination that are often denominated by the press as a "food crisis". Keeping this in mind, the Radioisotopes Laboratory of the Biophysics Institute of the Rio de Janeiro Federal University (LREPF/IBCCF/UFRJ) started, in the end of the 2000 decade, a project to investigate the presence of different polyhalogenated compounds in several foodstuffs, which included this question.

Herewith, we present the results of the first determinations we've made, aiming to start the operation of some new equipments that are based on computerized automatic schemes (Pressurized Liquid Extraction - PLE - and Power PREP from FMS inc.), whose acquisition in Brazil was pioneer. Besides that, we started cooperation with one of the few commercial laboratories in our country that are capable of doing such kind of non trivial analysis.

Material and methods

We worked with freeze-dried and liquid samples of crude milk as well. All glassware were used after 12 h of decontamination in oven furnace (400 °C). The solvents used, all for pesticide residue analysis or nanograde equivalent, were purchased from TediaBrazil and/or Merck Co.

Conventional soxhlet extraction (a) procedures as well as PLE/Power prep methods (b) were utilized.

- a) In brief, toluene extraction running overnight was followed by open chromatographic clean-up columns using acidic silica gel and alumina and concentration of the pollutants to nonane (3).
- b) The use of FMS/Power-prep is based on the previous mixture of the sample with Hydromatrix (or CELITE 566). The extraction step is followed by clean-up on acidic silica, followed by partition chromatography on alumina, silica and carbon cartridges.

All extracts had their concentration of 17 PCDD/Fs determined by High Resolution Gas Chromatography/High Resolution Mass spectrometry (Magnetic Sector Thermo Dual Focused system -DFS) using isotopic dilution methods.

Results and discussion

The range of TEQ (WHO-2005) was 0.23 to 0,54 pg, with the pentachlorinated Dioxins and Furans being the most important contributors, followed by the hexa's and tetra's congeners.

Figure 1 presents the first results obtained up to now.

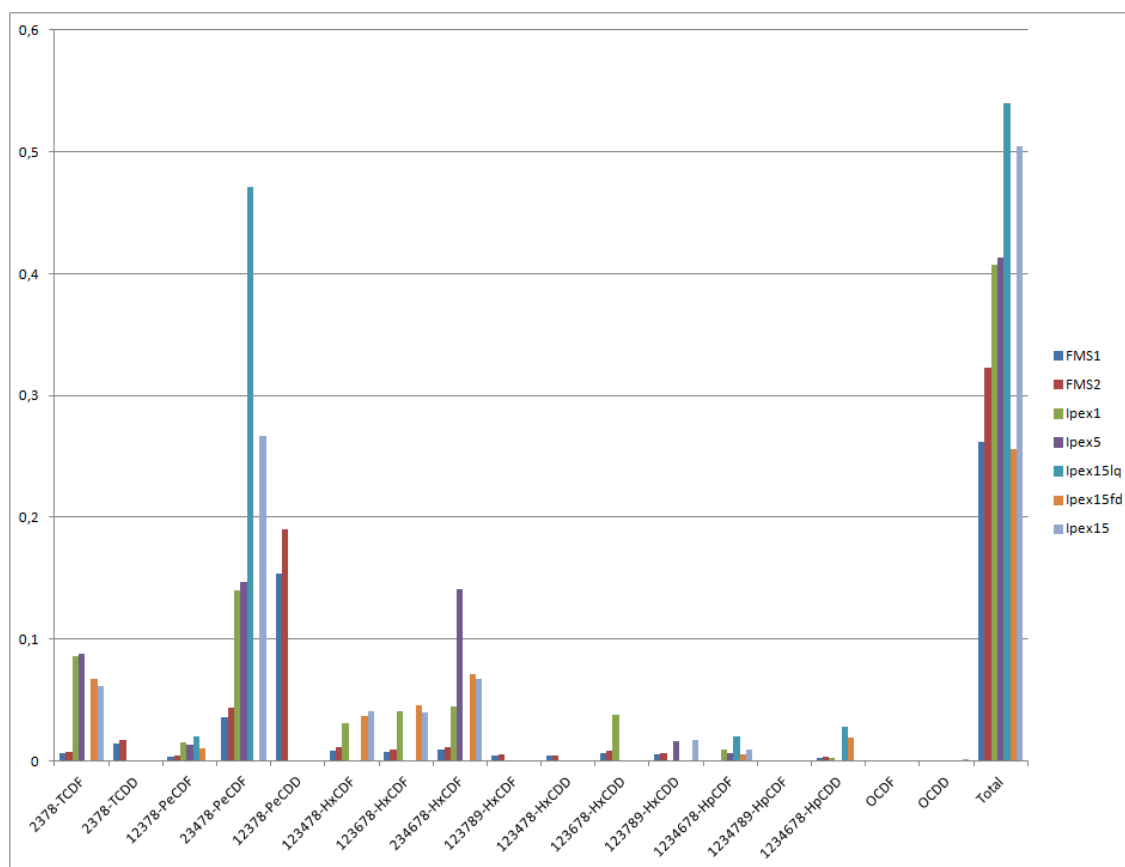


Figure 1- PCDD/Fs in crude cow milk from Brazil

Conclusion

The analysis of pictogram per gram levels of the chlorinated dioxins and furans is difficult and expensive, and this tends to limit the amount of environmental and food monitoring can be done. However, it appears that the use of an innovative automatic apparatus will have a key role in this stage, in order to establish the significance and the sources of such contaminants in a changing era of global food market were countries like Brazil will have an always increasing importance.

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