FINDINGS OF PCDDs/PCDFs IN SELECTED OLEORESINS

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Introduction

In 2013 some notification of elevated polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) concentration have been reported for special feed additives and feed premixtures on basis of oleoresins by the EU Rapid Alert System for Food and Feed (RASFF) ranging between 2,0 and 40,0 pg $TEQ_{WHO\ 2005}$/g sample.

Paprika oleoresin and Marigold Oleoresin are used in the food and feed production.

Paprika oleoresin is an oil soluble extract from the fruits of *Capsicum annum* or *Capsicum frutescens* (Indian red chilies), and is primarily used as a coloring and/or flavoring agent in food products. It is composed of *capsaicin*, the main flavoring compound giving pungency in higher concentrations, and *capsanthin* and *capsorubin*, the main coloring compounds (among other carotenoids). Foods colored with paprika oleoresin include cheese, orange juice, spice mixtures, sauces, sweets and emulsified processed meats. In poultry feed, it can be used to deepen the color of egg yolks and skin pigmentation.

Marigold oleoresin is a natural yellow color which is extracted from marigold flower (*Tagetes erecta*). Its main composition is *lutein*. It has bright color and superior coloring strength. The product is widely used in food, pharmaceutical, cosmetic, feed industries etc.

Materials and methods

Samples: Samples of oleoresins and similar products from Paprika and Marigold have been analyzed in our laboratory since a few years. The samples were produced in various countries of Asia, America, a few came from Europe. In total we analyzed 163 samples made of paprika/pepper and 193 samples of marigold. One of the authors visited production areas in Asia in 2013. Resulting from this we could collect information on the various steps of production. The main steps in the production processes are:

- Harvesting
- Fermentation (Marigold only)
- Drying (by sun or oven)
- Extraction of dried products by solvent(s)
- Filtering
- Evaporation/concentration

The following average concentration factors of such production processes could be determined: 10 metric tons of fresh *Tagetes erecta*-flowers resp. 12 metric tons of fresh *Capsicum*-fruits are required to produce one metric ton of the corresponding oleoresin.

Figure 1:
Sun drying of paprika

Figure 2:
End of fermentation of Marigold flowers

Experimental: With the exception of three samples, the analyses have been performed at the Eurofins GfA Lab Service GmbH at the Dioxin competence centre in Hamburg. After lyophilisation and homogenisation (if necessary, depending on the specific matrix), sample aliquots have been used for the different analytical processes. These consisted of an extraction, column-chromatography and by state-of-the-art determination methods using HRGC/HRMS.
Generally, isotope dilution quantification has been employed with a broad variety of ^{13}C-labelled standards added to the sample before extraction. For PCDD/Fs and dl-PCBs (not reported here), the methods are based on the EC legislation requirements for reference analyses[1], using HRMS at mass resolution r ≥ 10.000.
Further details for the methods have been described elsewhere[2,3,4,5].
The analytical quality has been maintained by monitoring the recovery rates by calculation against appropriate ^{13}C-labelled standards added before GC injection. Recovery rates were well within an acceptable range or 50-130%. Alongside with the samples, routine QA/QC-measures have been taken, e.g. batch blank preparation over the whole procedure as well as reference samples. Blank values have been below the quantification limits given.

Results and discussion
The analytical data are given as mean, median, minimum and maximum concentration in pg/g TEQ $_{WHO\ 2005}$ in Table 1 for all groups of samples.

Table 1: PCDD/Fs (pg/g TEQ $_{WHO\ 2005}$) in various Paprika/Pepper and Marigold products, samples were analyzed between 2008 and 2014

	n	Mean	Median	Min	Max
Paprika					
Raw material, meal, powder	35	0,296	0,163	0,007	2,83
Oleoresin, extract	128	3,81	1,92	0,238	41,8
Marigold					
Raw material, meal, powder	23	0,458	0,212	0,041	4,87
Oleoresin, extract	170	9,68	0,754	0,102	90,8

Paprika samples show a wide range of concentrations, ranging between 0,01 and 42 pg/g TEQ$_{WHO\ 2005}$. In contrast to paprika samples marigold products range between 0,04 and 91 pg TEQ$_{WHO\ 2005}$/g sample. An important question was to find out the reason for the observed dioxin contamination of the products analyzed here.
For an estimation of the origin of the observed Dioxins it is possible to compare the profiles of the 2,3,7,8-substituted Dioxins (congener pattern) from different chemicals and processes. Hagenmaier et al. 1994 [6] demonstrated the occurrence of typical congener patterns for chemicals like PCP, PCBs, sludge from electrode at chlorine production and other chemical processes. On the other side dioxin patterns observed for thermal processes like incineration, ambient air and car exhaust are quite different. All patterns observed for thermal processes are very similar among each other.
Using this information the analytical data were transferred into graphs as presented in Figures 3 and 4. This offers the possibility to compare the graphical analytical data with published patterns from Hagenmaier [6].

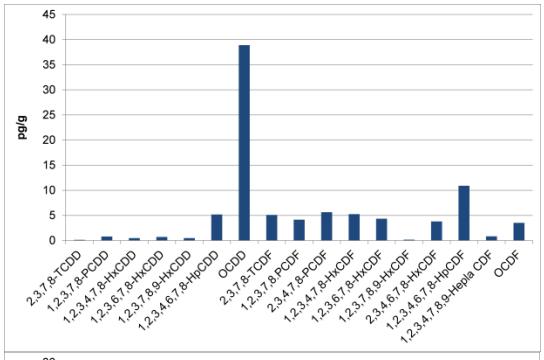

Figure 3:
Typical profile of 2,3,7,8–substituted Dioxins in Oleoresin **Paprika**, $TEQ_{WHO\ 2005}$ (upper-bound PCDD/Fs only, 4,98 pg/g)

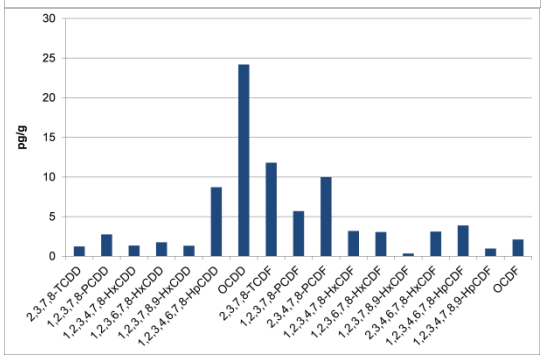

Figure 4:
Typical profile of 2,3,7,8–substituted Dioxins in Oleoresin **Marigold,** $TEQ_{WHO\ 2005}$ (upper-bound, PCDD/Fs only, 9,93 pg/g)

We compared typical patterns of Paprika Oleoresin (Figure 3) and Marigold Oleoresin (Figure 4) with patterns observed for other products. In Figures 5 to 7 typical congener profiles for spruce needles, Green cabbage and Sugar beet chips (dried over open fire) are presented. Spruce needles and green cabbage show a typical congener pattern for ambient air as reported by Hagenmaier [6]. Ambient air represents the typical distribution of dioxins originating from thermal processes. Dioxins are part of toxic contaminants of air: they are distributed in the air in gaseous phase – and in particle phase. Plants can adsorb/absorb these components from the air. Looking at specific plants, dioxins can be observed in "surface reach" plants like e.g. green cabbage and in spruce and/or pine needles (with high wax content on the surface) showing the patterns as demonstrated in Figure 5 and 6.

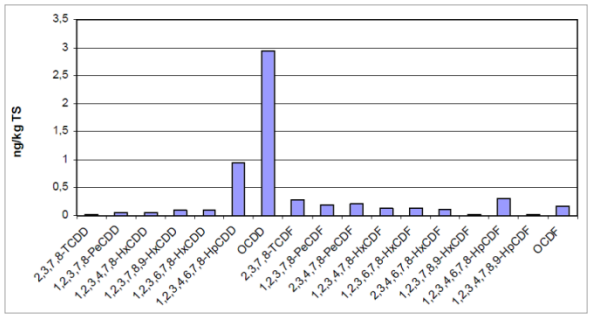

Figure 5:
Mean concentration of PCDD/Fs congeners in Spruce needles, Germany, n = 284 [7]

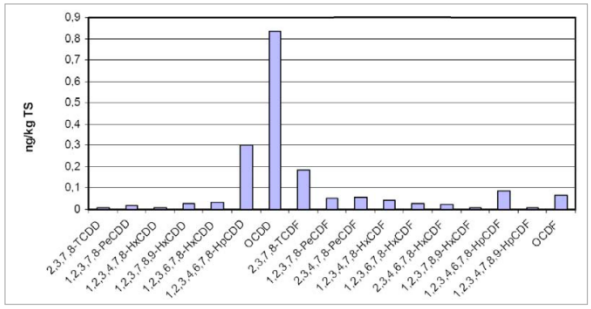

Figure 6:
Mean concentration of PCDD/Fs congeners in Green cabbage, Germany, n = 198 [7, 8]

An additional source for contamination of plant products with dioxins or other products can be expected during the drying process especially during inappropriate drying processes. In the last years dioxin contamination has been observed for “bread meal”, “green meal” and in open fire (coke fire) dried sugar beet chips. As an example for an appropriate drying process in Figure 7 the PCDD/F-pattern for open fire dried sugar beet chips is given [9]. For some samples of oleoresins relatively high values are observed for OCDD. A possible source for this observation might be expected for the use of Pentachlorophenol during the whole process as it was observed for the production of guar gum [10]. On the other hand we could not observe the use or influence of other chemicals in the products analyzed [11].

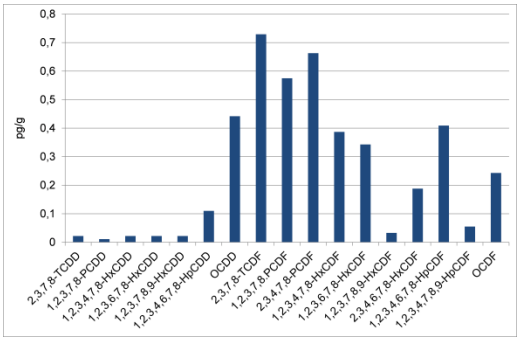

Figure 7:
Concentration of PCDDs/PCDFs in open fire dried sugar beet chips (upper-bound, PCDD/PCDF only, 0,43 pg/g, Bernsmann [9]

The samples analyzed here are received randomly at the laboratory. To reduce the level of contamination of the products in question, a systematic investigation would be needed. Resulting from this, the importance of environmental influences and/or individual process steps could be identified.

Conclusion:

- The Paprika/Marigold samples analyzed in this investigation for PCDD/Fs show congener profiles indicating the influence of thermal processes.
- In general it has to be stated that PCDD/F-congener profiles from thermal processes like municipal waste incineration, general combustion processes, combustion engines for cars, metal production (no electrolytic processes) show a high similarity among each other. These profiles can be observed for ambient air as well.
- The dioxin profiles found in the samples analyzed here show a high similarity to dioxin profiles of other natural products like green cabbage, grass, pine needles and fir needles.

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