ASSESSMENT OF THE PCDD/PCDF FINGERPRINT OF THE DIOXIN FOOD SCANDAL FROM BIO-DIESEL IN GERMANY AND POSSIBLE PCDD/F SOURCES

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Introduction

In December 2011 the German authorities notified the European Commission through the Rapid Alert System for Food and Feed (RASFF) about PCDD/PCDF contamination of certain animal feeds. The original message referred to one 26 tonnes consignment of contaminated fatty acids being mixed with 500 tonnes of vegetable feed fat. The consignment originated from a company producing biodiesel and was delivered to a feed fat producer, where the mixing occurred. The contaminated fat was then delivered to nine feed manufacturers and the compound feed produced from the contaminated fat was delivered to about 40 farms. As a consequence of the contamination all these farms were quarantined.[1,2]

On Monday 3 January 2011, the German authorities discovered that six other consignments of fatty acids from the biodiesel company were delivered to the feed fat producer. As a precaution, the German authorities decided to consider all fat produced at the feed fat manufacturer since 11 November 2010 (approximately 3000 tonnes) as being potentially contaminated. The German authorities notified that this potentially contaminated feed fat was delivered to 25 compound feed manufacturers. This potentially contaminated feed fat was then mixed into compound feed for laying hens, fattening poultry, cattle and pigs.[1] Up to 4760 farms have been blocked[2] for some time resulting in large economic losses.

The source of the PCDD/F in the fatty acid from the bio-diesel production have not yet been revealed. The pattern of the PCDD/PCDF in the contaminated fatty acid is analysed in this paper and potential sources for this pattern are discussed.

Materials and methods

PCDD/PCDF in a fatty acid sample from the period of the contamination incident has been measured with HRGC/HRMS by a commercial laboratory according to European legislation..

Results and discussion

Assessment of the source of contamination

The contaminated fatty acid samples (in Table 1 a sample with 123 ng TEQ/kg) were dominated by PCDD (with a PCDD:PCDF ratio of about 100) (Figure 1). The dominating homologues were the HexaCDD, HepaCDD and OctaCDD (Figure 1). The main TEQ contribution came from 1,2,3,6,7,8-HexaCDD (ca. 50%), 1,2,3,7,8,9-HexaCDD (ca. 22%), HepaCDD (ca. 15%) and 1,2,3,78,-PentaCDD (ca. 11%) (Table 1).

The detailed assessment of homologue pattern and congener patter reveals the major contamination source from very specific precursors.

The HeptaPCDF isomer showed a specific HeptaCDF pattern with 1,2,3,4,6,8,9-HeptaCDF and 1,2,3,4,6,7,8-HeptaCDF. This is a fingerprint for PCP (and other highly chlorinated chlorophenol mixtures). These two congeners are formed by the condensation of 2,3,4,6-TetraCP and PCP. Also the HexaCDD congeners present as major contaminants and the distribution of the HexaCDD congeners reflected the condensation of 2,3,4,6-TetraCP. The very low concentration of 1,2,3,4,6,8-HexaCDD (formed from PCP and 2,4,6-TCP) show that hardly any 2,4,6-TriCP was involved in the original formation process of these PCDD/PCDF Also the relative low concentration of TetraCDD and PentaCDD (Figure 1) show that lower chlorinated chlorophenols were not significantly involved. Furthermore the TetraCDD and TetraCDF in the sample showed a PCDD/PCDF pattern which was not dominated by a specific chlorophenol pattern but rather a pattern mixture including background also indicating that the specific chlorophenol source did not include significant TriCP and DiCP. However as more then 98% of TEQ stem from the specific chlorophenol pattern (Table 1).

Table 1: 2,3,7,8-PCDD/F (ng/kg) in contaminated fatty acid sample from biodiesel production (11.11.2010)

2378-TCDD	12378-PCDD	123478-HxCDD	123678-HxCDD	123789-HxCDD	1234678-HpCDD	OCDD	2378 TCDF	12378-PCDF	23478-PCDF
1.4	14	12	610	270	1800	1200	0.36	<0.1	0.45
123478-HxCDF	123678-HxCDF	123789-HxCDF	123678-HxCDF	1234678-HpCDF	1234789-HpCDF	OCDF		**I-TE**	**WHO**
<0.2	0.35	<0.2	0.54	21	1,2	37		**117**	**123**

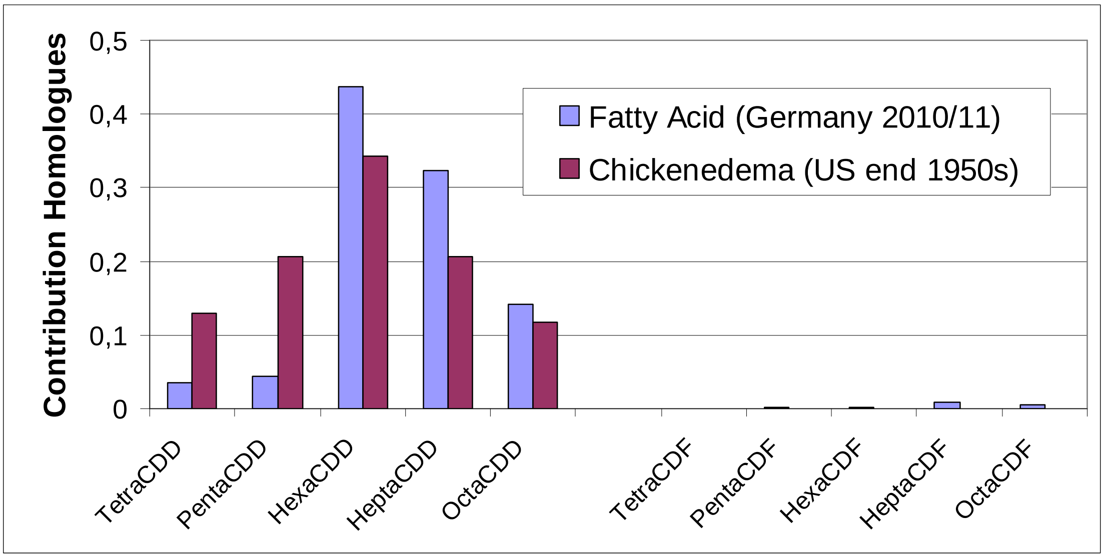

Figure 1: PCDD/F homologue pattern in the contaminated fatty acid from biodiesel (Germany 2010/11) in comparison to the homologue pattern of the chicken edema case US (1950/60) [3]

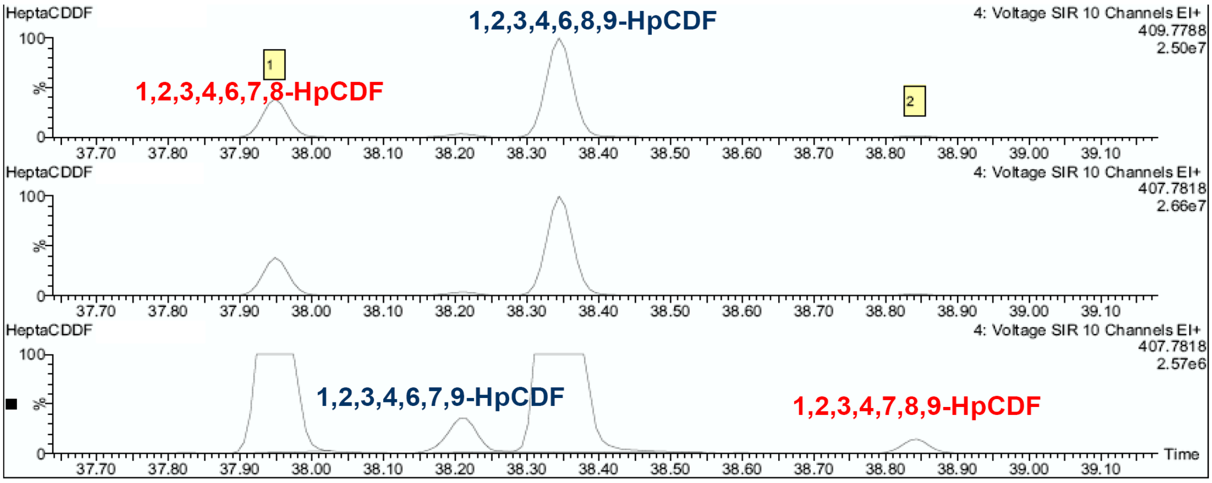

Figure 2: HepaCDF pattern in the high contaminated fatty acid fraction from biodiesel (Germany 2010/11)

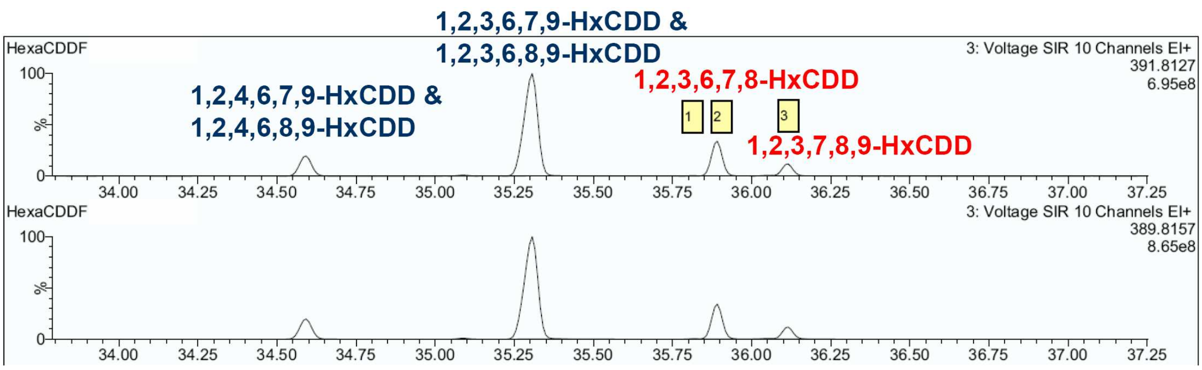

Figure 3: HexaCDD pattern in the high contaminated fatty acid fraction from biodiesel (Germany 2010/11)

Discussion about the possible source

There are several possible PCDD/PCDF sources which could have contaminated the fat and oils used in the biodiesel production or have otherwise entered the process. It is known that the biodiesel company received various oils also from abroad including oil which has been used in deep fat fryers. The high PCDD/F contamination has only been detected between 11. to 25.Nov. 2010[2]

The sources for this PCDD/F contamination are discussed in the order we consider most probable.

a) From application of chlorophenols and pesticides

PCP and less frequent mixtures of TriCP/TetraCP/PCP have been used as main fungicides in wood treatment, leather treatment. and in agriculture. While it is known from literature that in Scandinavia a chlorophenol mixture with predominantly TetraCP was used up to the 1980s it is less widely known that also in India chlorophenols with predominantly TetraCP has been used in the treatment of e.g. leather in the last decade[3]. Also in the US a mixture of 2,4,5-TriCP, 2,3,4,6-TetraCP and PCP[4] were used in the 1950/1960s in the treatment of cow hides after slaughtering. The PCDD/PCDF pattern in commercial TetraCP/PCP depend strongly on the production process[5]. PCDF were dominant in the production process of the "TetraCP" from Finnland but in other PCP samples PCDD;PCDF ratios of up to 100 have been found[5]. Similarly in above example of the US chlorophenol mixture the PCDD dominated with a ratio of PCDD:PCDF above 100 (see Figure 1). It is interesting to note that the PCDD/PCDF from CP application on the cow hides in the US in the 1950s/1960s have entered the human food chain via chicken feed[4]. Here the fat scrapings (tallow) from the chlorophenol treated hides were hyrolysed and the fatty acids were subsequently added to chicken feed[4] and became the first and one of the most (in)famous PCDD/F food/feed cases. This was the chicken edema case where several million chicken died from PCDD/F (and chlorophenol) poisoning via the polluted feed.

In the current case chlorophenols or pesticides could have been applied either as pesticides in plantations for bio-diesel crops or as fungicide for preservation of seeds (oil palm, soya or rape seeds) used for oil production. While in Europe highly chlorinated pesticides are not used e.g. for rape seed and similar production, these highly chlorinated pesticides are still produced and used in developing countries. In 2007 the use of PCP as fungicide on Guar Gum in India (where 80% of Guar Gum seeds are produced) have caused another major food contamination incident. Guar Gum.is used as thickening, emulsifying, binding and gelling additive in a wide range of foodstuff globally.[6] . .

Other pesticides can also contain PCDD/PCDF and chlorophenols are present in phenoxyheribicides and also as intermediates and byproducts and can result in PCDD/F chlorophenol patterns in pesticides. In a recent screening of PCDD/PCDF in current used pesticides PCDD/F have been detected in all pesticides analysed with some pesticide formations containing particularly high levels of PCDD/F [7]. Furthermore mainly PCDD have been formed from certain current used pesticide formulations resulting in PCDD: PCDF ratio of more then 100[8].

b) Production of bio-diesel crops on PCDD/PCDF contaminated sites

The use of contaminated sites for the production of energy crops is suggested as one possible use of brown fields. Such programs are promoted by governments in the EU and elsewhere (see e.g. for. Sweden http://www.swedgeo.se/upload/Publikationer/Varia/pdf/SGI-V599.pdf). There are a large number of areas contaminated by the former application of chlorophenols world wide (e.g. rice growing areas in Asia and wood treatment sites globally) where PCP and other PCDD/PCDF containing pesticides have been used for decades. The extent to which PCDD/F are accumulating in energy crops with high oil content used for biodiesel production on such sites has not yet been assessed.

c) PCDD/F possibly present in other additives of the process

Another less probable source for PCDD/PCDF contamination in this German case could be chemicals used in the biodiesel production. Sodium hydroxide or sulphuric acids are used for the cracking of fatty acids for example. Although sodium hydroxide is produced via the chloralkali production process and could possibly be associated with PCDD/F such contamination is not reported in the literature and the chloroalkali electolysis pattern is normally dominated by PCDF. Also Sulphuric acid is used in some processes in the chlorine and organochlorine industry it is possible that PCDD/F contaminated sulphuric acid could have been recycled for such simple uses. In 2006 a PCDD/F contaminated hydrochloric acid has contaminated gelatine.[9]. . .

d) Possible modification of the PCDD/PCDF pattern during the biodiesel production process

In technical processes at temperatures above 200ºC the PCDD/F pattern can be changed by processes including. dechlorination. In the biodiesel production distillation processes with temperatures above 200ºC are used for separation of the fatty acids. Considering the Heptafuran pattern a dechlorination is very unlikely since in particular the 1.9-substituted PCDF are dechlorinated first. However a shift in the homologue pattern by this distillation process can not be excluded.

Some lessions learned from the current case

The case demonstrate that even in a country with established legislation and control system which prohibit e.g. the mixing of industrial fat with fat for feed then regulations can be systematically undermined. Some companies producing animal feed have diluted here suspected PCDD/PCDF containing (industrial) fat waste (in this case the fatty acid) known to possibly be contaminated into the feed (2 to 10%) in order to maximize profits. It is likely that such activities are also occurring in other countries - particular those with weaker regulations – and the extent of this should be assessed.

Furthermore the German case shows that fatty acids generated as waste from biodiesel production can be contaminated with PCDD/PCDF and possibly other contaminants including pesticides. The pesticide intensive production of "Biodiesel" production has increased tremendously in recent years and residues from such productions have grown commensurately. As shown here, thes waste need to be controlled and assessed in order to ensure that possible contaminants do not enter the feed and food chain.

Further action taken by the German authorities

Due to the experience of this case, the German Federal Ministry for food, agriculture and consumer protection has established an action plan for a better protection of the food and feed chain Main action points included[2]:

1) Duty of feed producers to obtain authorisation

Manufacturers of fats for feed will in future have to apply for authorisation;

2) Separation of production flows

Stipulation of a new regulations that fats and fatty acids for feed must not be manufactured in facilities that are also used to produce substances for the technical industry.

3) Expansion of legal requirements in respect of feed controls

The duty of feed operators to control their products will be made more stringent.

4) Duty of private laboratories to report

Private laboratories that test food or feed and ascertain undesirable substances in quantities that give cause for concern will in future have to report these results to the competent authorities.

5) A binding positive list of feedstuffs

6) Coverage of the risk of liability

We will require feed operators in Germany to take out an employer and product liability insurance or equivalent cover against the risk of liability.

7) Revision of the system of penalties in respect of infringements of the Food and Feed Code.

8) Improvement of the quality of food and feed controls and inspection of federal state authorities

9) Transparency for consumers

The competent authorities will be required to publish without delay the results of official food controls and inspections on all infringements caused by limit values being exceeded.

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