### CONGENER SPECIFIC DISTRIBUTION OF POLYCHLORINATED DIBENZO-P-DIOXINS, DIBENZOFURANS AND DIOXIN-LIKE POLYCHLORINATED BIPHENYLS IN ANIMAL FEED

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### Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs) are widespread contaminants in the environment. The hazards associated with these compounds arise from their persistence, hydrophobic character, and toxic properties. PCDD/Fs are considered very hazardous chemicals and are known to form during incineration as well as through natural processes. PCBs are synthetic chlorinated compounds that were widely used as dye solvents, plasticizer, dielectric fluids, and hydraulic fluids in the late 1970s; however, the manufacture of PCBs was banned in 1979 in Korea<sup>1</sup>.

Fish, animal meat, and dairy products are considered the most important sources of PCDD/Fs and PCBs in humans. Human exposure to PCDD/Fs and PCBs occurs primarily via low-level food contamination. Concern regarding food for humans and animal feed have been heightened since the food poisoning episode that occurred in Belgium in May 1999<sup>-2</sup>. The major source of human background exposure to PCDD/Fs and PCBs is through food (greater than 90%), with food of animal origin being the predominant source. Several studies have found high levels of PCDD/Fs and PCBs in animals and food resulting from the use of contaminated animal feed <sup>3,4</sup>. This demonstration of a link between contaminated animal feed and food contamination underlines the importance of monitoring the levels of PCDD/Fs and PCBs in animal feed.

The aim of the present research was to evaluate the congener-distribution patterns of PCDD/Fs and dioxin-like PCBs in a range of animal feeds. Twenty-four feed samples were analyzed for PCDD/Fs and thirty-four feed samples were analyzed for dioxin-like PCBs.

### **Methods and Materials**

#### Sampling and storage

Commercially available feed for poultry was used as feed. From June to December 2001, the National Livestock Research Institute sampled and analyzed 24 samples of feed containing PCDD/Fs and 34 samples of feed containing PCBs. The main ingredients of the feed were maize, soybean, wheat and maize gluten, with a total fat content of 3.6 % to 6.9 %. Three different groups of ingredients were analyzed: pigs, poultry, and cattle. The feed was spiked with 1ng of PCDD/Fs standard and 10ng of PCBs standard spiking solution depending on the final matrix amount subjected to analysis.

#### *Extraction and analytical methods*

The extractions were performed on an ASE 200 system (Dionex, USA). The analyses of the PCDD/ Fs and PCBs congeners were carried out on a HP GC 6890 equipped with a JMS-700T and a DB-5MS capillary column (60 m  $\times$  0.25 mm I.D., film thickness 0.25  $\mu$ ).

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#### **Results and Discussion**

#### Congener distribution of PCDD/Fs

The average concentration and pattern of PCDD/Fs congeners (pg I-TEQ per g) in the 24 samples of animal feed is given in Figure 1. Most PCDD congeners are found in the 24 feeds, the exception being 2,3,7,8-TCDD. The mean concentration range of total I-TEQ PCDDs is 0.07-0.09 (pg I-TEQ per g). The most abundant PCDF congeners are 2,3,4,7,8-PeCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,6,7,8-HxCDF, and 2,3,4,6,7,8-HxCDF, which are 0.5, 0.1, 0.1, and 0.1 TEF, respectively. The combined concentration of these four congeners accounts for 78 % of the total I-TEQ PCDFs concentration, and the mean concentration range is 0.19-0.45 (pg I-TEQ per g). The samples analyzed in this study contained elevated levels of PCDFs which correlated with the concentrations of PCDDs, with an average ratio of PCDF: PCDD of about 2.6:1.

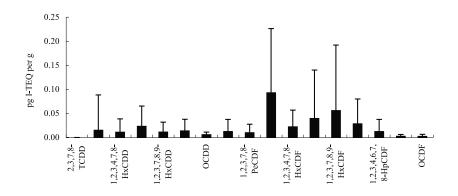
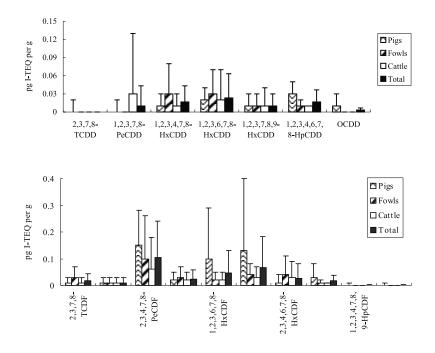


Figure 1. Concentration and Pattern of PCDD/F congeners (pg I-TEQ per g) in feed.

Bioaccumulation potential is expressed as the log of the octanal/water partition constant (log  $K_{ow}$ ). Generally, congeners with log  $K_{ow}$ <6 are easily biodegraded or excreted by aquatic organisms and those with log  $K_{ow}$ >6 are accumulate with difficulty due to their solubility in water and steric constraints. The penta- and hexa-CDD/Fs detected abundantly in this study have log  $K_{ow}$  values of 6-7.The PCDD/F congener distribution pattern found in the feed samples was similar to that found previously in Belgian feed samples, but differed from that of other matrix samples <sup>5</sup>.Our survey of the PCDD/Fs contamination in animal feed confirmed that the total I-TEQ PCDDs and total I-TEQ PCDFs in the samples analyzed were up to 0.52 and 2.07 pg I-TEQ per g fat, respectively. Both of these values are within the tolerance level for PCDD and PCDF (5 pg I-TEQ per g fat).

Figures 2 shows the mean concentrations of PCDD and PCDF congeners in the samples of pig feed, poultry feed, and cattle feed.

The I-TEQ PCDD values for the three types of animal feed show a similar pattern in terms of the overall I-TEQ value and concentration, with the most prevalent congeners being hexa- and hepta-CDD (Figure 2). The combined concentration of the hexa- and hepta-PCDDs accounts for about 83% of the total PCDD concentration in the three types of feed. The most abundant PCDD congeners were 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, and 1,2,3,4,6,7,8-HpCDD; these congeners account for about 71% of the total PCDD concentration in the feed.



**Figure 2.** Comparison of PCDD/PCDF congeners concentration (pg I-TEQ per g) according to three different feeds.

The I-TEQ PCDF values of the three types of feed indicate that the I-TEQ value of the pig feed was higher than that of the poultry and cattle feed. The concentration of PCDFs in the pig feed accounts for about 50 % of total PCDF concentration in the three types of feed. The most abundant PCDF congeners in the pig feed are 2,3,4,7,8-PeCDF, 1,2,3,6,7,8-HxCDF, and 1,2,3,7,8,9-HxCDF; these congeners account for about 84 % of the total PCDF concentration in the pig feed.

The most abundant congeners in feed are penta- and hexa-CBs such as 118, 156, 157, and 169, which correspond to 23'44'5, 233'44'5, 233'44'5', and 33'44'55' chlorinated substitution and have toxicities of 0.0001, 0.0005, 0.0005, and 0.01 TEF, respectively. The combined concentration of these congeners accounts for about 80% of the total I-TEQ PCB concentration. The hexa- and penta-CBs detected abundantly in this study all have log  $K_{ow}$  values of 6-7.

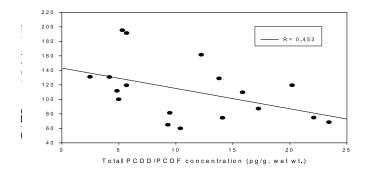
The PCBs homologue distribution pattern found in the feed samples differed from that found in other matrix samples.

Our survey of PCB contamination in animal feed confirmed that total PCBs were present at levels up to 0.39 pg I-TEQ per g, which is within the tolerance level for PCBs (0.5 pg I-TEQ per g).

Figure 3 shows the total PCDD/DFs concentration plotted against total dioxin-like PCB concentration on this feed samples. The correlation coefficient (r) was calculated to be 0.453.

We found that the concentrations of total PCDD/Fs and total PCBs are below the existing tolerance limits (5 pg I-TEQ per g fat for PCDD/Fs and 0.5 pg I-TEQ per g fat for PCBs) in all of the feed samples analyzed. Specifically, we confirmed that total I-TEQ PCDDs, total I-TEQ PCDFs, and total I-TEQ PCBs are present in concentrations up to 0.49, 2.93, and 0.39 pg I-TEQ per g fat, respectively.

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**Figure 3.** Correlation PCDD/F concentration vs. dioxin-like PCB concentration. \* Total PCBs: PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189

Investigation of the correlations among the concentrations of PCDDs, PCDFs, and PCBs showed that samples containing increased amounts of PCDFs also had higher concentrations of PCDDs, with an average ratio of PCDF: PCDD of about 2.6:1. The correlation between the concentrations of PCDD/ Fs and PCBs was found to be negative but not significant.

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