

## Occurrence of dioxin-like Polychlorinated biphenyls in animal food samples in the east of China

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### Abstract

The Pollution status of dioxin-like Polychlorinated biphenyls (DL-PCBs) in 87 animal food samples collected from 40 cities in ten provinces along oceans in the east of China were investigated. The total TEQs for DL-PCBs in collected samples were 0.4 to 471 pg TEQ kg<sup>-1</sup> wet weight (ww), which much lower than the level 4.0 pg TEQ g<sup>-1</sup> ww regulated by EU. The results shows that most of food samples collected in east of China are less contaminated with DL-PCBs than other recent reports. Terricolous animal foods were found to possess a lower level comparing to aquicolous ones.

### Introduction

Dioxin-like Polychlorinated biphenyls (DL-PCBs) in foods and environment have been of great concern due to their toxicity and potential health risks. DL-PCBs belong to persistent organic pollutions with long half-life, long-distance transport and intensive bioaccumulation in tissue cells.<sup>1</sup> Food consumption has been identified as the major pathway of human exposure, contributing over 90% of total exposure. The major food sources of DL-PCBs have been reported to be fat-containing animal origin food and fish.<sup>2</sup> Occurrence of DL-PCBs in the food has attracted growing global public attention. However, there are few data reported according to DL-PCBs in food in China. Thus, DL-PCBs in 85 food samples collected from 40 cities in ten provinces along oceans in the east of China, including Hainan, Guangdong, Fujian, Zhejiang, Jiangsu, Shandong, Hebei, Liaoning, Jilin, Heilongjiang and Jiangxi provinces, were investigated. These data will be used to evaluate DL-PCBs levels in animal food in east China and human health assessment.

### Materials and Methods

Eighty-seven animal food samples were collected in ten provinces located in east of China. Information of the samples was list in Table 1 in detail.

All solvents were ultra resi-analyzed grade and were purchased from J.T. Baker. Silica column (PCB-HCDS-ABN or PCBs-ABN-STD), alumina column (PCB-ABA-S011) and carbon column (PCBC-CEE-034) were obtained from Fluid Management Systems, Inc.. Standard solutions of the WHO-specified DL-PCBs were purchased from Wellington Laboratories. Certified reference WMF-01 and quality control test materials T0623 were obtained from Wellington Laboratories and Food Analysis Performance Assessment Scheme (FAPAS) of Central Science Laboratory (CSL).

The analytical procedure was presented briefly as follows. Briefly, the food sample was spiked with <sup>13</sup>C-labeled surrogate standards prior to Accelerated Solvent Extraction 300 (ASE 300) with 60-milliliter toluene. The extract was concentrated to dryness and the residue was dissolved with hexane. After the treatment with concentrated sulphuric acid, the extract was sequentially subjected to silica gel, alumina and carbon columns for cleanup by Fluid Management Systems (FMS), an automated extraction and clean-up system. Recovery standard of DL-PCBs was added prior to the GC injection.

The quantification of DL-PCBs was performed on an Agilent 6890 gas chromatography coupled with an Autospec

Ultima mass spectrometer operating with EI source in SIM mode. 2 µl of sample extract was injected with splitless mode into a DB-5MS fused silica capillary column (60 m × 250 µm i.d. × 0.25 µm film thickness) with helium as carrier gas. The details of the MS analysis and quality control are described in the EPA method 1668A.

Method performance was evaluated with quality control samples during the food sample analyses. Method blank were analyzed along with the samples. Certified materials, WMF01 and T062, were analyzed to validate the method used in this investigation. In addition, proficiency test 0628 organized by FAPAS was participated.

## Results and Discussion

### 1. Quality control and quality assurance

Method performance was also evaluated with quality control samples during the animal food sample analyses. Method blank and spiked matrix samples were analyzed along with samples. The performances met the criteria specified in the US-EPA method 1668A.

Certified materials, WMF01 and T062, were analyzed to validate the method used in this paper. All results are accord with reference concentrations and recoveries competent specified in EPA method 1668A. Cod oil T0623 was analyzed for three times and the results were satisfied with relative standard deviation (RSD) ranging from 2.0% to 9.0%. The average recoveries (with RSD) of the  $^{13}\text{C}_{12}$ -labelled DL-PCBs were in the range of 87-95% (8-13%), which met the criteria specified in US-EPA method 1668A.

In addition, the method was used to participate proficiency test 0628 organized by FAPAS in 2006. The results reported by our lab are satisfied with z-score being 0.0 and 0.4, respectively.

### 2. Dioxin like PCBs concentration in collected samples

The TEQ levels of DL-PCBs in animal foods are summarized in Table 1, respectively. The total TEQs for DL-PCBs in collected samples ranged from 0.4 to 471 pg TEQ kg<sup>-1</sup> wet weight (ww), which much lower than 4.0 pg TEQ g<sup>-1</sup> ww regulated by EU. The ranking based on fresh weight is in increasing order of squid 0.4, hog casing 13, crab 44, shrimp 73, poultry fat 94, lobster 111, prawn 136, fish 148 and eel 203 pg TEQ/g ww. Among these samples, terricolous animal foods possessed a lower level comparing to that of the aquicolous, which is in accord with recent studies.<sup>3,4</sup>

Table 1 Concentrations of DL-PCBs (pg TEQ/g wet weight) and number of analyzed samples

Samples	Number of samples	Sampling locations	DL-PCBs(TEQ, pg TEQ/g ww)		
			Max.	Min.	Mean value
Lobster	10	Shandong, Zhejiang, Jiangsu, Hunan provinces	268	2.3	111
Shrimp	27	Zhejiang, Shandong, Hainan, Guangdong, Fujian provinces	422	11	73
Prawn	4	Shandong, Guangdong provinces	169	109	136
Squid	1	Shandong province	0.4	0.4	0.4
Crab	1	Shandong province	44	44	44
Hog casing	2	Jiangsu province	23	3.2	13
Poultry fat	16	Liaoning, Shandong, Jilin provinces	298	0.8	94
Eel	20	Guangdong, Jiangxi, Jiangsu, Fujian provinces	471	24	203
Fish	6	Guangdong, Jiangsu provinces	285	33	148

The pollution levels of DL-PCBs in animal foods collected in this study were not significant. Table 2 lists the comparison occurrence of DL-PCBs with international studies. Though different species contained various lipid percentage, excepting pollution source, may also lead to different levels of DL-PCBs, occurrence of DL-PCBs in collected samples in China are not higher than Egypt, Sweden and Spain as listing in Table 2. With the mean level of DL-PCBs being 94 pg TEQ/g ww, poultry fats collected in China are less contaminated with DL-PCBs than that collected in Egypt.<sup>3</sup> The concentration of DL-PCBs in squid and crab collected in China were also found to be lower than that from Spain and Egypt.<sup>3,5</sup> In addition, higher levels were determined in shrimp in China comparing to Spain.<sup>5</sup>

Table 2 Comparison occurrence of DL-PCBs with international studies

Samples	Country	DL-PCBS(pg TEQ kg <sup>-1</sup> ww)	reference
Lobster	China	2.3-268	This study
Shrimp		11-422	
Prawn		109-169	
Squid		0.4	
Crab		44	
Poultry fats		0.8-298	
Eel		24-471	
Fish		33-285	
Chicken	Ismailia(Egypt)	120-240	3
Mullet fish		760-820	
Bolti fish		310-320	
Crab		310-700	
Bivalves		310-330	
Fish	Sweden	380-586	4
Meat		25-44	
Fats		141-141	
Fish	Catalan (Spain)	240-4150	5
Cuttlefish		20	
Squid		610	
Shrimp		30	

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