PCBs CONCENTRATIONS IN THREE KINDS OF LIVESTOCK MEAT FROM SHENZHEN, CHINA

Wang Chunlei[1,2], Zhang Jianqing [2,*] ,Yang Dacheng[1], Jiang Yousheng[2],Zhou Jian[2],Fang Daokui[2],Huang Haiyan[2]

[1]School of Chemistry and Chemical Engineering,Southwest University,Chongqing, 400715, China
[2]Shenzhen Center for Disease Control and Prevention, Shenzhen, Guangdong, PR,518020 ,China

Abstract

Food intake is the main source of exposure to dioxin-like compounds for humans, meat accounts for a large portion in human daily diet. To protect the people's health and explore the pollution level of polychlorinated biphenyls(PCBs) in meat, 28 samples of three kind of retail livestock meat were investigated. The research included beef, pork and mutton. After extraction, extracts were cleaned up by FMS and analyzed by isotope dilution high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The results showed that the highest level for the median of DL-PCBs was 0.84 pg WHO-TEQ/g fat in beef, followed by 0.28pg/g fat in mutton, 0.15pg/g fat in pork. In all samples, PCB118 was the greatest contributor to the total contaminated concentration, and PCB126 was the dominant contributor to the TEQ concentration. From the results of dioxin content in six samples exceeded the EU action level limit and four of the six samples also exceeded the EU maximum level limit, PCBs contamination existed in livestock meat products in China, it was suggested that policy decision maker and superviser should pay more attention to this circumstance.

Introduction

Polychlorobiphenyls (PCBs) are the family of compounds which include 209 kind of congeners. Since its good chemical stability, high boiling point and electrical insulation, PCBs are widely used in transformer insulating liquids, pesticides, paints, lubricants and other products of additives, heat transfer systems in the past decades. PCBs have become a global pollutant because the slowly degradation in the environment, the relocation of the environment, and the bioaccumulation and toxicity .So that they are one object of 12 highly toxic persistent organic pollutants in the Stockholm Convention. Data shows that China had produced 10,000 tons of PCB products from 1966 to 1975 , and long-term using and shortcomings in management and disposal had caused a very serious environmental pollution. PCBs in food comes mainly from environmental pollution, food containers, contaminated packaging materials and equipment containing PCBs accident [1]. Food intake is the main route to PCB exposure for human being. However, the data on pollution levels of PCBs in food in Shenzhen of south of China is also inadequate due to detection fee and equipment restrict. As Special Economic Zone of China, there are have1400 population in Shenzhen . In order to ensure food safety, it is very necessary to study the pollution levels of PCBs in food. To explore the contamination levels of PCBs in some food in Shenzhen of China, three kind of livestock (beef, pork and mutton) which people often consume was chosen to detect the level of PCBs totally including of 6 indicator PCBs and 12 Dioxin-like PCBs.

Materials and methods

Food samples

28 Samples of three kind of meat (beef, pork and mutton) were randomly acquired in local markets from Shenzhen city in China, which including 14 pork samples, 10 beef samples and 4 mutton samples. The samples were

* Corresponding auther: Zhang Jianqing, e-mail: zhjianqing95@gmail.com

kept at -20°C until they were processed

.

Sample preparation

All solvents for trace determination analysis were purchased from Merck (Darmstadt, Germany). Calibration standard solutions, ^{13}C-labeled surrogate standards, cleanup standards and injection standards specified in US EPA Method 1668A for PCBs analysis were purchased from Cambridge Isotope Laboratories Co.(Andover, MA, USA).

All the samples were grounded, then freeze-dried and processed the preparation step individually. Soxhlet extraction was used for the samples extraction. With hexane/dichloromethane (1:1) as solvent extracted the sample at least 24 h. Extracts were concentrated by rotary evaporator (BUCHI, Switzerland) and subjected to a three-stage clean-up procedure using PowerPrep automated system (Fluid Management Systems, Inc. Waltham, MA, USA). A set of disposable columns consisting of a multi-layer silica column, a basic alumina column and a carbon column have been used to purify. Analytical procedures used in this study are described in detail previously [2].

HRGC/MS Analysis

Six indicator PCB congeners(IUPAC No. 28, 52, 101, 138, 153 and 180), the non-ortho PCB congeners (IUPAC No. 77, 81, 126 and 169), as well as the mono-ortho PCB congeners (IUPAC No. 105, 114, 118, 123, 156, 157, 167, 189) were analyzed by HRGC/HRMS according to the US EPA 1668A method. A DB5-MS (J and W Scientific, USA) fused silica capillary column (60 m×0.25 mm id., 0.25 μm film thickness) was used with helium as the carrier gas. The temperature program was from 90 °C (held for 1 min) to 180 °C (held for1 min) at 20 °C/min, to 300 °C (held for 3 min) at 3 °C/min for PCBs using the splitless injection mode. The ion source and interface temperatures were 260 °C and 280 °C, respectively; ionization energy 60 eV (electron ionization mode), and trap current 0.9 mA. The resolving power was kept at 10,000 (10% valley definition), using selected ion monitoring (SIM) in isotopic dilution.

Quality Assurance/Quality Control (QA/QC)

In accordance with the US EPA1668A method[3], the samples quality control process, including the HRGC / HRMS the performance control, method blank, recovery, quality control testing of samples have been done. The laboratory has participated in international quality control studies for the analysis of PCBs at the same period organized by Norway public health institute. The laboratory is also accredited to ISO/IEC 17025 by CNACL of China (No.L2154).

Results and discussion

1. Quality control sample test results

In order to ensure accurate test results and reliability, carrying out the certified reference material (CRM) testing. Using the same testing process for detection of PCBs in fish samples（Carp-2）, to verify the accuracy of the Analysis method. The average of three test results are in the scope of the standard reference values. The three test results of relative standard deviation less than 20%, which could prove the accuracy of this detection method and the stability of inspection system (Table 1).

Table 1
Method validation of international certified reference material Carp-2 for PCBs congeners （National Research Council Canada） *

Compounds	Detection result（n=3）		Certified value (ng/kg wet weight)
	Mean （ng/kg wet weight）	RSD(%)	
PCB28	30.2	17.6	34.0±7.2
PCB52	112.7	14.2	138±43
PCB101	152.1	10.2	145±48
PCB105	52.1	4.5	53.2±15.6
PCB118	124.5	3.2	148±33
PCB138	89.4	11.2	103±30
PCB153	121.4	15.1	105±22
PCB180	58.2	9.8	53.3±13.0

*: note, the concentrations of other congener compounds doesn't be provided in the certification sheet.

2. PCBs concentrations in livestock meat

Table 2 Concentrations of the PCBs in beef, pork and mutton (pg/g fat)

Sample	Con. Of indicator-PCBs	Con. Of Dioxin-like PCBs	Total Con. Of PCBs	Con. Of WHO-TEQ	EU action level standard WHO-TEQ	EU maximum level standard WHO-TEQ
pork （n=14）	389.45	46.37	435.82	0.15	0.5	0.5
beef （n=10）	1151.41	456.19	1607.60	0.84	1	1.5
mutton （n=4）	427.67	77.50	505.17	0.28	1	1.5

Concentrations of the indicator PCBs in three breeding stock meat products are quite different. The highest content was 1151.41 pg/g fat in beef , followed by 427.67 pg/g fat in mutton and 389.45 pg/g fat in pork. The concentration of indicator PCBs in beef was about 3 times of which in the pork and mutton.The DL-PCBs concentration in beef was 456.19 pg/g fat ,followed by77.5 pg/g fat in mutton and 46.37 in pork.The trends total concentration of PCBs is consistent with which of indicator PCBs: beef> mutton> pork.The TEQ concentration of DL-PCBs in three kind of meat were 0.84,0.28 and 0.15 pg/g fat in beef,mutton and pork, respectively .The results showed that TEQ concentration of DL-PCBs (median value) in meat products was lower than the limit value in the EU standard action level[4]. The concentration value in beef samples is about 5.6 and 3 fold of pork and mutton samples, respectively. The study also found the positive samples which exceeded the EU action levels standards and maximum levels standards for PCBs. One pork sample and five beef samples were detected. Among them, the pork sample and three beef samples also exceeded the EU maximum levels standards. the highest WHO-TEQ

concentration of a beef sample was 2.60pg/g fat, about 1.7 times of the maximum levels standard. The study shows that the livestock meat products in China have a certain degree of PCBs pollution.

3. Correlation of the indicator PCBs and dioxin-like PCBs concentrations

The study found a better correlation between the indicator PCBs and DL-PCBs r = 0.6443, P <0.0001 (Figure 1). Compared with the DL-PCBs, indicator PCBs is easily detected and analyzed from food. In this way, the contamination of DL-PCBs (which toxicity is higher, more difficult to detect) in samples can be estimated analysis by detecting the indicator PCBs content in samples. It can not only save cost but also play a role in early warning of monitoring the food.

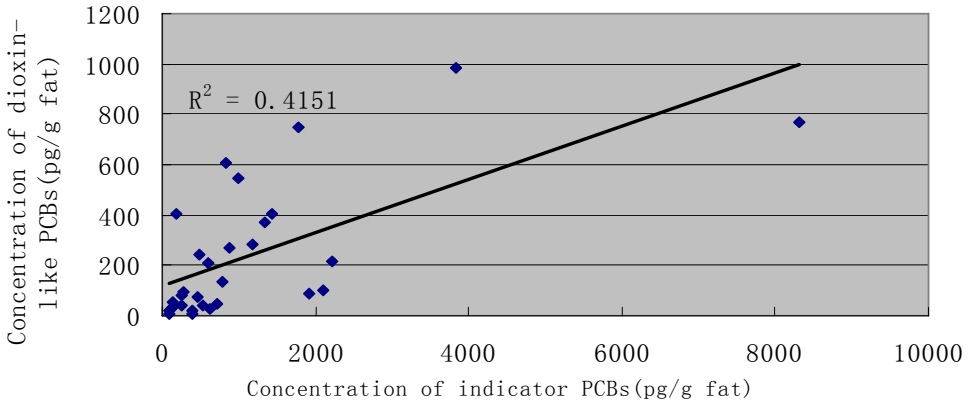

Fig.1. Distribution of indicator PCBs and DL-PCBs concentrations in meats

4. Pollution characteristics of DL-PCBs in three sorts of livestock food

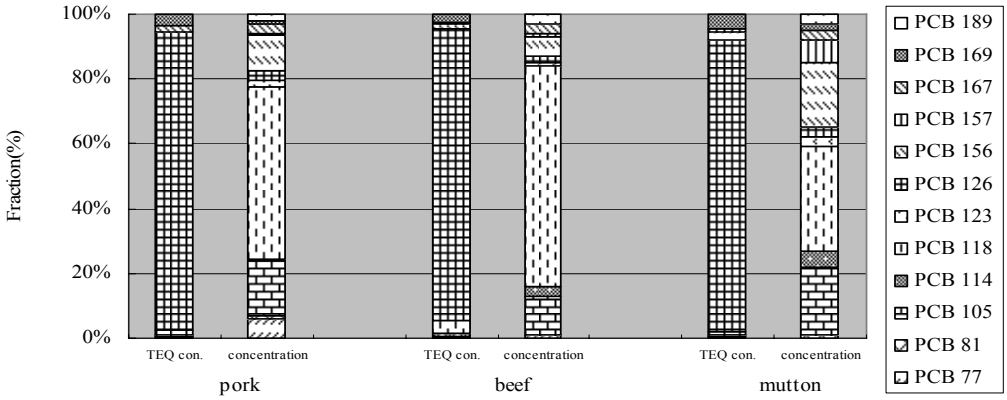

Fig.2. Pollution characteristics of the dioxin-like PCBs

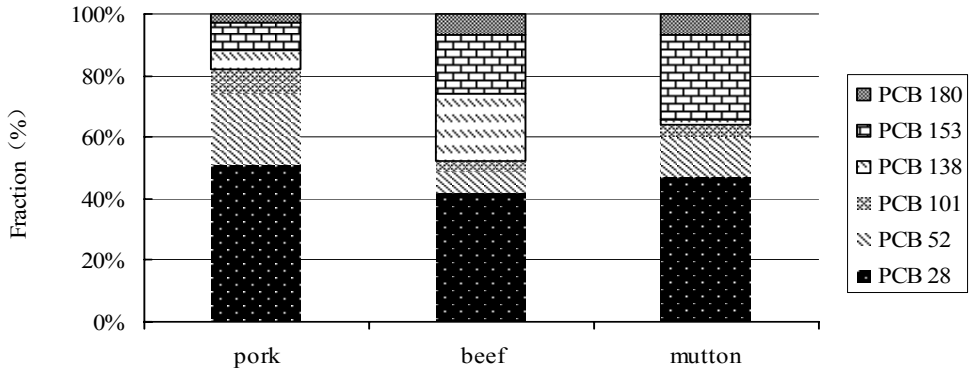

Fig.3. Pollution characteristics of the in dicator PCBs

Pollution characteristics of the DL- PCBs are shown in Fig.2. In all samples, PCB118 was the main contributor to the total concentration, between 32%-68%; followed by PCB105 and PCB156. Compared the total PCB118 concentration in three samples, beef in the highest proportion, followed by pork and mutton was minimum. Different from other congeners contribution trends, concentrations of PCB105 and PCB156 in mutton were higher than pork and beef, about 20% contribution. However PCB126 was found to be the main contributor to the WHO-TEQ concentration in the three kind of samples, accounting for nearly 90% ~ 92% of TEQ concentration.

Indicator PCBs were analyzed simultaneously Fig.3. PCB 28 is the predominant contributor to the total concentration accounted for 40%-50% in the three kind samples. Other contributor to total concentration was different based on different food groups. The sum of PCB 52 and PCB 153 accounted for more than 30% in pork , sum of PCB138 and PCB153 accounted for more than 40% in beef ,and sum of PCB53 and PCB153 accounted for more than 40% in mutton.

4. Conclusion

The study involved in three kind of meat samples, the total concentration of PCBs in beef samples were significantly higher than pork and mutton. The concentration of indicator PCBs and DL-PCBs have good consistency and correlation. It can be found that the PCB polluted level in beef is still the highest compared to the others. However, the median concentration of TEQ for three samples did not exceed the EU standards for PCBs. In Taiwan [5] survies of the related beef, mutton and pork in the TEQ concentrations of PCBs were 0.363, 0.189 and 0.145pg/g fat, respectively. In some European studies[6,7,8]showed that the TEQ concentration were 0.02-0.69 pg/g fat, 0.13-1.22 and 1.22 pg /g fat in pork ,beef and mutton, respectively. The results of this study showed that the TEQ concentration of beef is closed to European and higher than Taiwan's investigative levels; mutton is closed to Taiwan, but lower than the European studies levels, and pork with the concentration of research near to Taiwan and lower than the similar studies in Europe. PCBs content in three kind of meat trend that is consistent with other studies: beef> mutton> pork. The content of indicator PCBs in beef is the highest, which was similar to those of other studies[9,10]. This study shows that, PCB118 is still the most polluted monomer, the main contributor to TEQ concentration is PCB126, which is consistent with the results of other studies [11,12].

In this study, some positive samples were detected. It shows that some retail meat products have been contaminated in this city. At present, the domestic meat animals are reared closely and some feed additive were used for feeding in China. Therefore, the meat may have been contaminated by polychlorinated biphenyls feed additives, which entered animals' body through enrichment. Because the meat products in Shenzhen produced from different feeding base, there is a certain extent of risk of PCBs contamination in our country. More monitoring to PCBs pollution on meat products should be carried out in order to guarantee the food security and people's health.

5 .References

1.Liu qian.Chinese Occup Health2007;23(13):1145-1148.

2.Zhang JianQing, Li Jiangguang, Wu Yongning, Jiang jie Jiangyousheng, Zhou Jian. Chinese J Anal Chem 2005;33(3):296–300.

3.United States Environmental Protection Agency. Method 1668,Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/ HRMS. 1999, December.

4.a.COMMISSION RECOMMENDATION (EC) of 6 February 2006 on the reduction of the presence of dioxins, furans and PCBs in feedingstuffs and foodstuffs. Official Journal of the European Union,2006.2.14.
b.COMMISSION REGULATION (EC) No 199/2006of 3 February 2006 amending Regulation (EC) No 466/2001 setting maximum levels for certain contaminants infoodstuffs as regards dioxins and dioxin-like PCBs. Official Journal of the European Union,2006.2.4.

5.Ming-Sheng Hsu, Kuang-Yi Hsu, Shih-Min Wang, Ukai Chou, Shih-Yun Chen,Nai-Chun Huang, Chia-Yi Liao, Tsae-Pyng Yu, Yong-Chien Ling. Chemosphere2007;67 :S65–S70.

6.Anika De Mul, Martine I. Bakker, Marco J. Zeilmaker, Wim A. Traag, Stefan P.J. van Leeuwen,Ron L.A.P. Hoogenboom, Polly E. Boon , Jacob D. van Klaveren. Regulatory Toxicology and Pharmacology 2008;51 : 278–287.

7.Elena Fattore1,Roberto Fanelli,Aida Turrini and Alessandro di Domenico.Mol.Nutr. Food Res.2006;50:915 – 921.

8.Athanasios Papadopoulos a, Irene Vassiliadou a, Danae Costopoulou,et al.Levels of dioxins and dioxin-like PCBs in food samples on the Greek market[J]. Chemosphere 2004,57 :413–419.

9.A.J. Baars, M.I. Bakker, R. A. Baumann ,et al. Dioxins, dioxin-like PCBs and non-dioxin-like PCBs in foodstuffs: occurrence and dietary intake in The Netherlands[J].Toxicology Letters 2004,151:51–61.

10.MeeKyung Kim , Sooyeon Kim, Seonjong Yun, Myoungheon Lee,Byunghoon Cho, Jongmyung Park, Seongwan Son, Okkyung Kim. Chemosphere2004;54:1533–1538.

11.N.Loutfy,M.Fuerhacker, P.Tundo, S.Raccanelli, M.Tawfic Ahmed.Chemosphere2007;66 :1962–1970.

12.E.Zuccato, P.Grassi , E. Davoli, L. Valdicelli , D. Wood , G. Reitano, R. Fanelli.Food and Chemical Toxicology 2008;46: 1062–1067.