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Polychlorinated biphenyl concentrations in pooled serum from people in different age groups from five Chinese cities

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HIGHLIGHTS

- PCBs concentrations in Chinese serum of younger people were higher than in older people.
- Pentachlorobiphenyl were the most abundant PCBs for all age groups.
- TEQs of $\sum_{12}$DL-PCB presented upward trend in Chinese young people.

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ABSTRACT

Polychlorinated biphenyl (PCB) concentrations in human serum samples pooled by donor age and sex (≥60, 50–59, 40–49, 30–39, and 20–29 years old) were determined. The pooled samples were supplied by hospitals in five Chinese cities, which were Yitong (Jilin Province), Weifang (Shandong Province), Ganzi (Sichuan Province), Huaihua (Hunan Province), and Lingshui (Hainan Province). The total PCB concentrations were relatively low compared with concentrations that have been found in other parts of the world. Pentachlorobiphenyls were the dominant PCBs. The total PCB concentrations and the concentrations of most of the pentachlorobiphenyl congeners were slightly higher in the samples from younger donors than in the samples from older donors. The results indicated there is a new source of PCBs in China. Heptachlorobiphenyls in Lingshui may have been transported from Vietnam. Statistical analysis showed that young and old people had been exposed to different sources of PCBs. PCB 126 contributed more than the other dioxin-like PCBs to the total toxic equivalents when the samples were examined as a whole or by city, and the total toxic equivalents were higher in younger people than in older people for the whole sample set and for the Yitong samples.

1. Introduction

Polychlorinated biphenyls (PCBs) are organochlorine compounds that have been widely used as plasticizers, hydraulic and dielectric fluids, fire retardants, and paint additives around the world (Kennisch, 1996). Approximately 1.3×10^6 t of PCBs have been produced worldwide (Breivik et al., 2002). The USA was the dominant producer of PCBs, producing 6.4×10^5 t (48% of the total global production) between 1929 and 1977 (Breivik et al., 2002).

Jensen (1966) was the first to find PCBs in a biological sample, which was from Sweden. Since then, PCBs have been found in various environmental media around the world. PCBs are found around the world because they are persistent in the environment, semi-volatile, and bioaccumulative (Carvalho et al., 2008; Liu et al., 2013; Nhan et al., 1999). PCBs have even been detected in polar bear adipose tissue (Mckinney et al., 2011). Many countries introduced controls on the production and use of PCBs from the 1960s on. The Swedish government took action to prevent the use of PCBs in 1969 (NIP Sweden, 2006). The Japanese government enacted the Chemical Substances Control Law, banning the production and use of PCBs, in 1973 (NIP Japan, 2006). The Chinese government enacted a law restricting the use of PCBs in imported power devices in 1974 (NIP China, 2007). Evidence for positive relationships between PCB concentrations in human serum and adverse effects was gathered in the 1990s (Cogliano, 1998; Rice, 1997; Schantz, 1996).

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International concern led to PCBs being included in the "dirty dozen" persistent organic pollutants required to be controlled under the terms of the Stockholm Convention in 2004.

The analysis of PCBs in human serum is important to allow PCB exposure and adverse health effects to be assessed. American and Spanish researchers recently found that PCB concentrations in human serum decreased as age decreased (Huetos et al., 2014; Pavuk et al., 2014; Wong et al., 2015). However, Chinese researchers have discovered a new source of PCBs, the unintentional production of PCBs in industrial plants. Emissions of unintentionally produced PCBs (UP-PCBs) in China increased rapidly after 2000 (Cui et al., 2015). This has made PCB concentrations and trends in the serum of Chinese people in different age groups unclear.

In the study presented here, human serum samples from people living in different parts of China with different climates and levels of economic development were analyzed with the aim of providing data to help identify the overall trends in PCB concentrations in human serum in China. The PCB concentrations in serum samples from people living in five cities (shown in Fig. S1 in Supplementary Material (SM)) were determined. The cities were, from north to south, Yitong (YT) in Jilin Province, Weifang (WF) in Shandong Province, Ganzi (GZ) in Sichuan Province, Huaihua (HH) in Hunan Province, and Lingshui (LS) in Hainan Province. Detailed information on the cities is shown in Table S1 in SM. The objectives of the study were (1) to determine the PCB concentrations in serum from people living in the five Chinese cities and to compare PCB concentrations between young and old people, (2) to identify the dominant and the distribution of PCB congeners in the whole sample set and in each city samples, and (3) to calculate the toxic equivalents (TEQs) of dioxin-like (DL) PCBs in serum from the inhabitants of the five cities and to compare TEQs of DL-PCBs between young and old people in the whole sample set and in each city samples.

2. Materials and methods

2.1. Chemicals and reagents

A total of 15 PCB congeners (PCBs 77, 81, 101, 105, 114, 118, 123, 126, 156, 157, 167, 169, 170, 180, and 189) were analyzed. A $^{13}C_{12}$-labeled PCB internal standard mixture (containing PCBs 77, 81, 101, 105, 114, 118, 123, 126, 156, 157, 167, 169, 170, 180, and 189) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). All organic solvents used were of pesticide analysis grade.

2.2. Sample collection and preparation

A total of 1923 serum samples (918 from females and 1005 from males, see Table S2 in SM) were collected from hospitals in the five selected cities between April and October 2014. The samples were selected from surplus serum samples collected during routine pathology tests with the informed consent of the donors and hospitals. The samples from each city were divided into 10 groups defined by donor age (≥60, 50–59, 40–49, 30–39, and 20–29 years old) and sex. In every group, 0.5 mL human serum from each individual sample was taken as a mixed sample, and then 3 mL from mixed sample was taken as a pooled sample. There were 50 pooled samples, and detailed information on the samples is provided in Table S2 in SM. Each sample was extracted and the extracts cleaned following a method that has been described previously (Hovander et al., 2000). An aliquot of each pooled sample was spiked with internal standards ($^{13}C_{12}$-labeled PCBs 77, 81, 101, 105, 114, 118, 123, 126, 156, 157, 167, 169, 170, 180, and 189), then 1 mL of 6 mol/L hydrochloric acid and 6 mL isopropanol were added and the mixture was extracted with 6 mL of a 1:1 v/v mixture of hexane and methyl *tert*-butyl ether. The sample was completely mixed, then centrifuged at 3000 rpm for 5 min, and then the organic phase was transferred to a glass tube containing 4 mL of aqueous potassium chloride (1% w/w). The sample was then extracted twice more with 1:1 v/v hexane and methyl *tert*-butyl ether, and the organic phase transferred to the glass tube containing the earlier extract. The extract was then centrifuged again, and the organic phase was transferred to a weighed tube. The aqueous phase was extracted with 4 mL of a 1:1 v/v mixture of hexane and methyl *tert*-butyl ether twice, and the organic phase transferred to the weighed tube. The extract was then evaporated to dryness and the lipid residue weight determined. Each sample was weighed five times, and the mean weight was recorded only when the difference between consecutive weights was less than 0.0005 g.

The residue was redissolved in 4 mL hexane, and 2 mL of 0.5 mol/L potassium chloride in a 1:1 v/v mixture of ethanol and water was added. The sample was completely mixed, then centrifuged at 3000 rpm for 5 min, and then the organic phase was transferred to a glass tube. The aqueous phase was then extracted with 3 mL hexane two times and the organic extracts mixed. The extract was then concentrated to approximately 1.0 mL, then cleaned by passing it through a 26 g SX-3 gel permeation chromatography column (300 mm long, 25 mm i.d.). The cleaned extract was evaporated to 1 mL under a stream of high purity nitrogen, then passed through a multilayer silica gel column (containing, from top to bottom, 1.5 g anhydrous sodium sulfate, 0.5 g acidic silica gel, 0.1 g neutral silica gel, and cotton). The multilayer silica gel column was washed with 5 mL hexane before use, and the sample was eluted with 12 mL of a 1:1 v/v mixture of hexane and dichloromethane. The extract was then evaporated to 80 μL.

2.3. Instrumental analysis

The extracts were analyzed using an Agilent 6890N gas chromatograph and an Agilent 5975N mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). The gas chromatograph was fitted with a DB-5MS column (30 m long, 0.25 mm i.d., 0.1 μm film thickness; J&W Scientific., Folsom, CA, USA). The oven temperature program started at 100 °C (held for 3 min), then increased at 5 °C/min to 270 °C, and was held for 1 min. The mass spectrometer was used in selected ion monitoring mode, and two ions were monitored for each PCB congener group. The mass spectrometer was used in negative chemical ionization mode, and the ion source and quadrupole temperatures were both 150 °C. The chemical ionization moderating gas was helium, and the carrier gas was helium, used at a flow rate of 1.0 mL/min. A 1 μL aliquot of a sample was injected in splitless mode. The m/z ratios monitored for each analyte are shown in Table S3 in SM.

2.4. Quality assurance and quality control

An isotope dilution method was used to quantify the target compounds for which $^{13}C_{12}$-labeled standards were available, and an internal standard method was used to quantify the other target compounds. The correlation coefficients of the calibration curves for all of the analytes were >0.9993. The limit of quantification was defined as the concentration giving a signal-to-noise ratio of 10. The limits of quantification for the PCBs in human serum were 0.02–0.4 pg. None of the target compounds were detected in the method blank samples. The recoveries of the labeled PCBs were 71%–99%.

2.5. Statistical analysis

Analysis of variance (using a significance level of $p = 0.05$) was