Time Trend and Spatial Distribution of Polybrominated Biphenyl Ethers and Polychlorinated Biphenyls in Human Milk from China under the Stockholm Convention

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Introduction

Polybrominated biphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) are two classes of persistent organic pollutants (POPs). Because of certain characteristics, these chemicals have been massively manufactured and widely used. Due to their toxicological effects, Penta-BDE and Octa-BDE formulations have been phased out and banned on the commercial production and usage in EU and North America since 2004 [1]. PCBs had been once widely employed as dielectric and coolant fluids before ceasing the produce and use in 1980s [2]. However, these chemical pollutants are ubiquitous in environmental and biological matrix, including human samples, because of their persistence and lipophicity [1]. Owing to the non-invasive and lipid-rich, human milk is recommended by WHO as an ideal matrix to assess body burden of lipophilic chemicals in the mothers and the exposure of breast-feeding infants during the lactation [3]. In order to evaluate the body burden, human milk monitoring has been carried out in many countries. China produces and consumes a large quantity of products containing PBDEs, and China is one of the main destinations of electronical wastes, e-waste, from developed countries resulting in high body burden and negative health effects on workers in e-waste dismantling [4]. However, there is still limited information on body burden, temporal trend and spatial distribution of PBDEs and PCBs for non-occupational population in China. In this study, PBDEs and PCBs in these milk samples from the 2nd national human milk monitoring carried out in 2011 were measured, and the major objective was to investigate the current body burden and the temporal trend from 2007 to 2011 as well as the change of profile and spatial distribution.

Materials and methods

The ‘Guideline for Developing a National Protocol’ of the Fourth WHO-Coordinated Survey of Human milk for Persistent Organic Pollutants in Cooperation with UNEP was followed for the selection of volunteering mothers and collection of human milk samples in this study[3]. In 2011, 1760 human milk samples were from 16 provinces of China based on a multistage random cluster sampling method, and these samples were divided into 32 pools based on mother’s residence. All participants were told the objective of this study and

signed the participant information and consent form.

50 mL milk sample was lyophilized. Then, the freeze-dried samples were extracted by using an ASE350 (ThermoScientific, Sunnyvale, CA, USA) after spiking 13C-labeled surrogate standards (P48-M-ES and MBDE-MXFS). The mixture of n-hexane and dichloromethane (1:1, v/v) was applied as solvent. Gravimetric lipid determination was performed after solvent evaporation. The bulk lipid was removed by shaking with acid-modified silica-gel. The Power Prep instrument (Fluid Management Systems, Waltham, MA, USA) with multiple commercial columns was applied for further cleanup. The fraction containing PBDEs and PCBs was collected and concentrated to less than 40 μ. 13C-labeled injection standards were added into the final extract prior to instrumental analysis. PBDEs (BDE-28, 47, 99, 100, 153, 154, and 183) and PCBs (PCB-28, 52, 101, 138, 153, and 180, so-called indicator PCBs) were analyzed by gas chromatography – high resolution mass spectrometry (GC-HRMS) using a Thermo ScientificTM Trace 1300L gas chromatograph (Milan, Italy) coupled to a DFSTM magnetic sector high resolution mass spectrometer (Thermo Scientific, Bremen, Germany) operating in EI mode at 45 eV and a emission current of 0.76 mA. The mass resolution was set at >10000 for the measurement. An AgilentTM DB-5 HT capillary column (15 m × 0.25 mm i.d. × 0.10 μm) and a DB-5 MS capillary column (60 m × 0.25 mm i.d. × 0.25 μm) was equipped to determine PBDEs and PCBs, respectively.

Results and discussion

Fig.1 depicts the concentrations of PBDEs and PCBs in human milk samples from China in 2011. The concentration of $\sum$7PBDEs concentrations was 1.5 ± 0.9 (mean ± standard deviation) ng g^{-1} lipid weight (lw) with a range of 0.3 ng g^{-1} lipid - 4.0 ng g^{-1} lipid. The highest was found in the sample from the rural area of Guangdong, followed by rural area of Sichuan and urban area of Jilin with the concentration of 3.7 ng g^{-1} lipid and 3.6 ng g^{-1} lipid, respectively. And the levels of total PBDEs in human milk from developing regions of China including Neimenggu, Qinghai and Neingxia are notably lower than that from the other provinces. Although notable difference of PBDEs levels was observed between urban and rural area of some province, there was no significant difference across China (paired t-test, $p>0.05$), and the mean of $\sum_7$PBDEs in human milk samples from urban area is comparable to that from rural areas (1.4 ng g^{-1} lipid v.s. 1.5 ng g^{-1} lipid, respectively).

To understand the magnitude of contamination by PBDEs, the results from this study are compared with those observed in some recent studies with the sample collection during the period of 2009-2014. Global comparison indicated that the levels observed in the present study are comparable to or slightly lower than that from some European countries and Asian countries as well as Australia, but much lower than that from North America [5-7]. For indicator PCBs, The mean of $\sum_6$PCBs concentrations is 6.6 ng g^{-1} lipid (median: 6.1 ng g^{-1} lipid) with the range of 2.3 ng g^{-1} lipid - 19.0 ng g^{-1} lipid. By comparison with the results from the latest global human milk biomonitoring organized by UNEP/WHO during the period of 2008 - 2012 [8],

levels of indicator PCBs in this study were comparable to those from some countries or regions with very low industrialization like pacific islands, indicating relatively low contamination of PCBs in China which probably result from the limit production and usage of PCBs in the past.

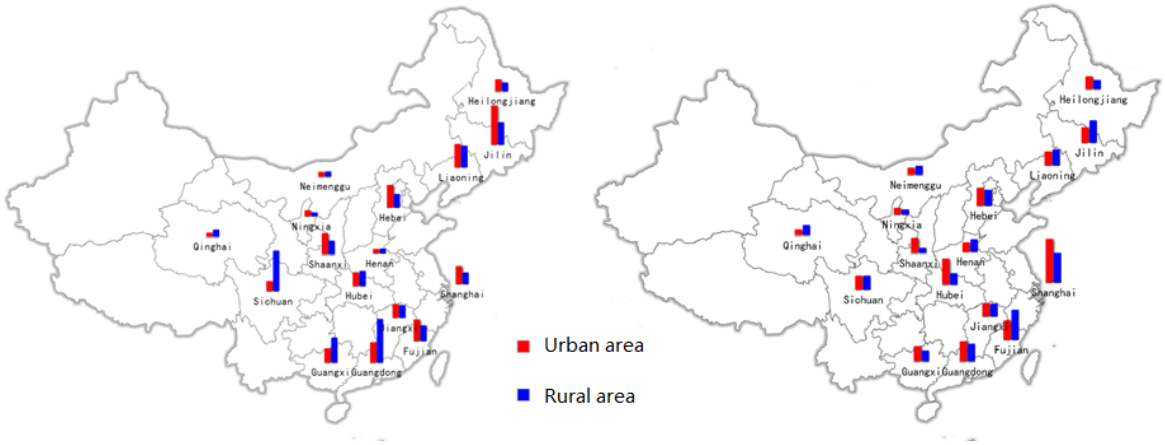

Fig 1 Levels of PBDEs (Left) and indicator PCBs (Right) in human milk samples from various regions of China

There were strongly significant correlation among 5 PBDE congeners including BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154 ($p<0.01$), indicating the similar exposure to these PBDE congeners. While BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154 are mostly present in Penta-BDE commercial mixture. Moreover, in the present study, the levels of BDE-183 were significantly correlated with BDE-99, BDE-100, BDE-153, and BDE-154 with lower coefficients of correlation. BDE-183 is the major ingredient of Octa-BDE formulation. These results indicate that, despite the simultaneous human exposure to PBDEs from products containing Penta-BDE, and Octa-BDE formulations in China, the lack of correlation among some PBDE congeners might suggest the difference of type and quality of consumption of PBDE formulations among various regions of China.

In our previous study, the concentrations of PBDEs and indicator PCBs were determined in human milk sampling in 2007 from 24 regions of China [9]. The mean of $\sum$PBDEs concentrations in human milk in 2011 (1.40 ng g^{-1} lipid) is slightly lower than that in 2007 (1.58 ng g^{-1} lipid), but no statistical difference was found. For individual congeners, there was significant difference of the concentrations of BDE-47, BDE-99, and BDE-100 in human milk between the two studies ($p<0.01$) with a reduction of 45%, 48%, and 46%, respectively, from 2007-2011, indicating the nationwide decline of human body burden on these PBDE congeners in China as a consequence of ban on Penta-BDEs mixtures worldwide. However, there was slight and not statistical reduction of 13% in the mean concentration of BDE-153 in the present study. Moreover, despite no statistical difference, an increase of 56% was found in the mean concentration of BDE-183 from

2007-2011 (p=0.07). In fact, a notable increase of BDE-183 concentrations in human milk was observed in most regions (18/24) with a range of 41% - 728%. For indicator PCBs, there was a significantly difference with a reduction of 41% on average concentration of total indicator PCBs from 2007 - 2011 ($p<0.05$).

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