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Levels of polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in breast milk in Shanghai, China: A temporal upward trend

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HIGHLIGHTS

- A TEQs uptrend over time was observed in breast milk samples from Shanghai mothers.
- Exposure signatures were linked with rapid industrialization and urbanization.
- Mothers well represented the population for exposure in their birth and grown-up areas.
- Consumption of higher amounts of meats caused higher exposure in mothers.
- Breastfed infants have high EDIs of PCDD/Fs and DL-PCBs in Shanghai.

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ABSTRACT

Human milk samples were collected from 150 mothers in 2011 and 2012 in Shanghai, China and analyzed for 17 polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) and 12 dioxin-like polychlorinated biphenyls (DL-PCBs). The up-bound Toxic Equivalent Quantity (TEQ) ranged from 0.27 to 16.8 pg TEQ/g lipid (mean 5.4 pg TEQ/g lipid) for ∑PCDD/Fs and from 0.75 to 10.2 pg TEQ/g lipid (mean 2.9 pg TEQ/g lipid) for ∑DL-PCBs. TEQs in our study were lower than those in most countries worldwide, and displayed a notable uptrend, in contrast with those in China's national survey in 2007. TEQs in mother milks from urban areas were higher than those from rural areas, and an orderly distribution was found in four geographical regions: Eastern China > Central China ≈ Southwestern China > Northwestern China. Levels of analytes in Shanghai native mothers' milk ranked the first among those from all provinces and cities investigated. Migrant mothers to Shanghai from other inland provinces could potentially represent the population for exposure and risk assessment in their birth and grown-up places. Both the distribution and the uptrend were associated with release of these pollutants due to rapid industrialization and urbanization in China. Fine correlations were observed between TEQs and age of mothers, and weak correlations between TEQs and consumption of meat & meat products. Participants, who preferred both fresh water and marine fish to freshwater fish only, were prone to be exposed to higher level of PCBs. The estimated daily intake (EDI) doses for breastfed neonates entirely exceeded the tolerable intake dose by WHO.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (PCBs) are ubiquitous persistent organic pollutants (POPs). They disperse to almost every corner in the environment from the sites where they occurred, even to the remote arctic areas. Due to their persistence and lipophilic tendency, these POPs tend to be bioaccumulated through food chains and potentially cause adverse health effects on biota and even human (Lakind, 2007).

A downward trend of these POPs were observed in many industrialized countries due to a restriction on their release from

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industrial practices (US EPA, 2004; Lakind, 2007; Focant et al., 2013; Mannetje et al., 2013; Ryan and Rawn, 2014). However, their environmental issues in China have become more and more concerned due to China's rapid industrialization and urbanization since early 1980s and a considerable amount of their release. Uncontrolled e-waste recycling (Lau et al., 2012) has resulted in a high accumulation of these pollutants in human body via inhalation of contaminated air and consumption of contaminated local food (Lau et al., 2012; Chan and Wong, 2013). A preliminary estimation by China's government showed that 10,237 g Toxic Equivalent Quantities (TEQs) of dioxins were released in 2004 and were much higher than the values in other countries (Lv et al., 2008).

Increasing efforts toward monitoring of environmental chemicals has been made over the last decade, but studies on biomonitoring of PCDD/Fs and DL-PCBs in human milk was limited in China (Lau et al., 2012). For examples, PCDD/Fs and DL-PCBs were investigated in 24 pooled samples of 1237 individual human milk samples from 12 provinces of China in 2007 (Li et al., 2009b). Other studies were focused on the local populations in Zhejiang (Shen et al., 2012), Shijiazhuang and Tangshan (Sun et al., 2006), north China (Shijiazhuang, Tianjin and Yantai) (Sun et al., 2010) and Shenzhen (Deng et al., 2012). An upward trend for the levels of PCDD/Fs and DL-PCBs was observed in human milk samples in Shijiazhuang from 2002 to 2007 (Sun et al., 2011). Human milk has high lipid contents and a larger volume of human milk can be sampled in a short period via a non invasive way, in contrast with blood sampling. The World Health Organization (WHO) has considered human milk as an ideal matrix for generally measuring POPs exposure (WHO, 2007). Levels of these POPs in human milk can help us observe unexpected or unnoticed exposure of mothers to these pollutants. As the most vulnerable population, infants suffer from higher POPs levels on a body-weight basis than adults. Therefore, biomonitoring of these pollutants in human milk is especially important for assessing exposure of breast-fed infants (US EPA, 2004).

This study investigated levels of PCDD/Fs and DL-PCBs in 150 human breast milk samples, which were collected from 147 migrant mothers to Shanghai, and 3 Shanghai native mothers, who were born and raised in the city. Our focus was to examine the temporal trends of PCDD/Fs and DL-PCBs, and the association of the exposure levels with participants' birth and grown-up places and residential areas (urban and rural areas).

2. Materials and methods

2.1. Chemicals and standard solutions

Standard solutions including EDF-9999, EDF-8999, EDF-5999, EDF-5008, EC-5380, EC-5372, EC-5371, EC-4986 and EC-4987 were from Cambridge Isotope Laboratories (Andover, MS, USA). EDF-9999 had five calibration standard solutions in nonane with 17 2,3,7,8-substituted PCDD/F congeners in a concentration range of 0.05–2000 ng/mL. Each solution contained 100 ng/mL of $^{13}C_{12}$-lablled standards except for 200 ng/mL of $^{13}C_{12}$-OCDD. These solutions were diluted to 1/10 their original levels in nonane. EC-5380 contained 4 non-ortho PCBs (CB-77, 81, 126 and 169) and 8 mono-ortho PCBs (CB-105, 114, 118, 123, 156, 157, 167 and 189), of which their concentrations were from 0.1 to 4800 ng/mL for native standards and a constant concentration of 10 ng/mL for $^{13}C_{12}$ labeled standards. A work internal standard solution mixture containing 10 ng/mL of $^{13}C_{12}$-labeled PCDDs/Fs and DL-PCBs (except for 20 ng/mL of OCDD) was prepared from EDF-8999 (100 ng/mL for all PCDD/F congeners except for 200 ng/mL of OCDD) and EC-5372 (100 ng/mL for all PCB congeners). EDF-5999 (including $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD, 200 ng/mL for each) and EC-5371 (including $^{13}C_{12}$-CB-70, 111 and 170, 100 ng/mL for each) were separately diluted to 10 ng/mL in nonane as injection standard solutions. EDF-5008 (100–500 ng/mL for PCDD/F congeners), EC-4986 (10 μg/mL for 4 non-ortho PCBs) and EC-4987 (10 μg/mL for 8 mono-ortho PCBs) were used as spiking standard solutions.

Nonane (anhydrous, ⩾99.0% purity) and anhydrous sodium sulfate (⩾99.0% purity) were from Sigma Aldrich (Steinheim, Germany). Silica gel (0.063–0.100 mm, 100–200 mesh, Merk, Darmstadt, Germany) was rinsed with dichloromethane (DCM) and then activated at 500 °C for 2 h. Acid silica gel (44%, *w*/*w*) was prepared by thoroughly mixing 56 g of the activated silica gel with 44 g of concentrated sulfuric acid. An automate sample clean-up system (ASCS, Polytech Instrument LTD, China) was used for the separation of PCDDs/Fs and DL-PCBs. The system successively consisted of acid multilayer silica columns (PCBS-ABN-STD), basic alumina columns (PCBA-BAS-011) and AX-21 carbon columns (PCBC-CCE-034) (Fluid Management Systems Inc., Waltham, MA, USA). Hexane and DCM (Optima® grade purity) were from Fisher Scientific (New Jersey, USA). Ethyl acetate (EtOAc) and toluene (pesticide grade purity) were from Tedia (Ohio, U.S.A). Certified reference materials included CRM 607 (EU), SRM 1954 (NIST) and a breast milk sample for the Interlaboratory Comparison on Dioxins in Food 2006 (Norwegian Institute of Public Health). Laboratory QC samples were prepared by spiking a pooled mother milk sample (400 g) with analytes at levels of 10–50 pg.

2.2. Sample collection

Sample collection followed the 'Guidelines for Developing a National Protocol' of the Fourth WHO-Coordinated Survey of Human milk for Persistent Organic Pollutants in Cooperation with UNEP (WHO, 2007). The samples were randomly collected from the population with various socioeconomic status and geographic locations. This study recruited three Shanghai native mothers, and 147 migrant mothers who moved to Shanghai from other 15 provinces and settled in Shanghai for 0–3 years before delivery (Table S1, Supplementary Materials). Totally, 150 breast milk samples (⩾50 mL for each) were collected during 2011–2012 from these mothers in Shanghai Pujiang Hospital, China. These participants were all primiparas and aged 18–35 years and had no smoking habit and did not even live or work in the environment associated with highly potential POPs exposure. All milk samples were available during the period of the first week postpartum. With sample collection, all participants were required to complete a consent form and an exposure assessment questionnaire, providing their age, height, body weight, places of birth, and dietary styles (summarized in Table S1) (Lu et al., 2015). The sampling was performed by trained nurses, who cleaned the breast and nipple, and hand squeezed milk out of the way directly into the collection bottle. After sampling, all bottles containing milk samples were wrapped in alumina foil and shipped to the laboratory within 2 h. All samples were stored at −20 °C until chemical analysis.

2.3. Sample preparation

2.3.1. Lyophilization and extraction

The breast milk sample was thawed and homogenized, and then 40 g was lyophilized for 48 h in a freeze dryer (Christ Gamma 1-16/2-16, Osterode am Harz, Germany) at −52 °C and 0.03 mbar. The dried samples were blended with 2.0 g hydromatrix (Agilent, Santa Clara, USA) and then transferred into the 33 mL ASE extraction cells and spiked with 10 μL $^{13}C_{12}$-labeled internal standard solution in each cell. After spiking, the samples were equilibrated