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Lactational exposure to short-chain chlorinated paraffins in China, Korea, and Japan

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HIGHLIGHTS

- SCCPs were detected in breast milk collected from several cities in East Asia.
- Concentration of SCCPs in breast milk (in ng g^{-1} lipid weight) was <20–54.
- The mean exposure of SCCPs in 1-year-olds in Beijing was 337 ng (kg body weight)$^{-1}$ d^{-1}.
- This mean exposure value was significantly higher than those for Korea and Japan.
- Breast milk SCCP content from Beijing differed from that in ambient air and food.

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ABSTRACT

To investigate short-chain chlorinated paraffin (SCCP) levels in human breast milk, pooled breast milk samples (BMSs) collected between 2007 and 2010 from Chinese (Beijing, $n = 17$), Korean (Seoul, Busan, $n = 16$), and Japanese (Kyoto, Sendai, $n = 44$) women were analyzed. SCCPs found in air samples in Beijing ($n = 4$, in 2008) were also analyzed and compared with BMSs to estimate the possible source of contamination in Beijing. The electron-capture negative ionization method demonstrated the different sensitivities for SCCPs, and pentachlorinated alkanes had the highest method detection limit (MDL) among congeners. In Beijing, SCCPs were detected in 8 of 17 pooled BMSs at concentrations more than the highest MDL of each homolog. The total SCCP concentration ranged from below the MDL to 54 ng g^{-1} lipid weight. Among the SCCP homologs, polychlorinated tridecanes were most frequently detected in Beijing. In Korea and Japan, no samples contained detectable total SCCP concentrations at more than the highest MDL. In Seoul, only two samples showed trace levels of polychlorinated undecanes. In Kyoto and Sendai, congeners of polychlorinated dodecanes were most frequently detected. C_{10} components were the major contributors to the SCCPs in the atmosphere of Beijing. Congener profiles in breast milk in Beijing provided a clear contrast to the profiles found in food and air. The unique congener profiles necessitate the monitoring of breast milk for exposure of infants to SCCPs. The calculated mean exposure of SCCPs in 1-year-olds in China was 337 ng (kg body weight)$^{-1}$ d^{-1}. These results demonstrate the body burden of SCCPs in the study areas and potential lactational exposure to SCCPs in Asian countries.

1. Introduction

Chlorinated paraffins (CPs), including short-chain chlorinated paraffins (SCCPs; C_{10-13}), are used in a wide range of industrial applications: plasticizers, flame retardants, cutting fluids, and lubricants (European Chemicals Bureau, 2008; J. Glüge et al., 2016). CPs are produced worldwide, but in China, the production of CPs

Abbreviations: CPs, chlorinated paraffins; SCCPs, short-chain chlorinated paraffins; GC/ECNI/HRMS, gas chromatography and high-resolution mass spectrometry with electron-capture negative ionization; BMSs, breast milk samples; QF, quartz fiber; PUF, polyurethane foam; ACF, activated carbon fiber; MDL, method detection limit.

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has increased rapidly in recent years, reaching 1,000,000 tons in 2009 (Chen et al., 2011; Tong et al., 2009). SCCPs seem to persist in the environment and tend to accumulate in biota (Fisk et al., 1996, 1998; Houde et al., 2008; Iozza et al., 2008; L. M. van Mourik et al., 2016). At high exposure levels, SCCPs have been reported to cause liver toxicities in trout and rats (Cooley et al., 2001; Nilsen et al., 1980). Recently, Geng et al. (2015) found that SCCPs can stimulate β-oxidation, and therefore, SCCPs are considered to be peroxisome proliferators. The International Agency for Research on Cancer has classified SCCPs as group-2B compounds, possibly carcinogenic to humans (IARC, 1990). At present, the risk profile of SCCPs has been adopted by the Persistent Organic Pollutants Review Committee, and SCCPs are being evaluated for global regulation under the Stockholm Convention on Persistent Organic Pollutants (POPRC, 2016).

The release of SCCPs into sewers has been found to result in SCCPs accumulating in sewage sludge and aquatic environments (Gao et al., 2012; Tomy et al., 1997; Zeng et al., 2012). SCCPs have also been found in air samples collected at remote sites in China (Li et al., 2012), such as Chongming Island (Wang et al., 2013a). Furthermore, SCCPs have been detected in bivalves (Yuan et al., 2012), fish (Ma et al., 2014; Reth et al., 2005), birds (Reth et al., 2006), and marine mammals (Tomy et al., 2000), suggesting that SCCPs can be distributed in biota through food chains.

In the previous study, we showed that dietary exposure to SCCPs was higher in a Chinese population than in Japanese and Korean populations (Cao et al., 2015; Harada et al., 2011). In addition, a survey in the United Kingdom demonstrated the presence of SCCPs in human milk fat (Thomas et al., 2006). CP analyses in pooled breast milk samples (BMSs) from Swedish women between 1996 and 2010 showed the mean level of SCCPs was 107 ng/g lipid weight (Darnerud et al., 2012). SCCPs (≈60–70% chlorine by weight) were found at 11–17 ng/g lipid in human breast milk from Inuit women on the Hudson Strait in northern Quebec, Canada (Tomy et al., 1998). Therefore, human breast milk constitutes a source of exposure to SCCPs for infants during lactation. However, little information is available for lactational exposure to SCCPs in Asian countries.

The present study aimed to investigate the levels of SCCPs in human breast milk in East Asian countries (Korea, China, and Japan) collected between 2007 and 2010. The concentrations of SCCPs were determined semi-quantitatively by gas chromatography and high-resolution mass spectrometry with electron-capture negative ionization (GC/ECNI/HRMS). SCCPs have elicited the most concern due to their higher toxicity relative to MCCPs, and therefore, in the present study, only SCCPs were analyzed. Profiles of SCCP congeners in milk samples were also compared with those in samples of ambient air and food in Beijing (China).

2. Materials and methods

2.1. Sampling and preparation of BMSs

The Ethics Committee of Kyoto University (Kyoto, Japan) approved the study protocol (E25). Written informed consent was obtained from all study participants.

BMSs from the Human Specimen Bank of Kyoto University were used for the evaluation (Koizumi et al., 2005, 2009). These BMSs were stored at −30 °C, and it was assumed that SCCPs in frozen BMSs did not change during storage.

Each participant had been requested to donate a BMS when the woman and her baby visited the hospital for health checkups within 4 weeks after delivery. A total of 385 BMSs were collected from Kyoto and Sendai in Japan; Beijing in China; and Seoul and Busan in Korea (Table 1). Collected BMSs were stored in acetone-washed polypropylene tubes. BMSs from five subjects (2 mL per-subject) were treated as one pooled sample, resulting in 77 pooled samples that were subjected to chemical analyses.

2.2. Sampling of ambient air

Air samples were collected on quartz fiber (QF) filters (8″ × 10″; QR-100, Sibata, Saitama, Japan) for the particulate phase and glass columns (90 mm i.d.) with a polyurethane foam (PUF; 50 mm i.d.) followed by activated carbon fiber (ACF; 10 mm i.d.; KF-1700F, Toyobo, Osaka, Japan) felts for the gaseous phase by using high-volume air samplers (HV-700F; Sibata) at approximate flow rates of 700 L min^{-1} for 24 h. QF filters and ACF and PUF slices were prepared by washing in toluene using a Soxhlet extractor, followed by drying under vacuum. All sampling media were wrapped in polyethylene bags and transported to the sampling site.

During 18–21 October 2008, four air samples were collected from two locations in the center of Beijing. The volume collected was 865.9–1008 m^3. Field blanks (ACF, PUF, QF with no air stream) were sent to sampling sites with each set of samples, placed in the same sites for 24 h, and returned with environmental samples.

2.3. Analytical methods

The same analytical protocols as used in our previous study (Harada et al., 2011) are described in detail in the Supplementary Material. In brief, pooled BMSs were stirred, and a 5-g aliquot of sample was extracted twice with 5 mL of 1:1 (*v*/*v*) acetone/hexane. Extracts were combined and washed with 25 mL of hexane-washed distilled water. The aqueous layer was extracted twice with 5 mL of hexane. Organic layers were combined and washed again with 5 mL of hexane-washed distilled water. The organic fraction was dried over with anhydrous sodium sulfate and evaporated to 5 mL. An aliquot of the crude extract was dried on a balance, and the weight of the residue was evaluated as fat content. Air sampling media were combined and extracted with 200 mL of 1:4 acetone/toluene using a Soxhlet extractor for 12 h. The extracts were concentrated to 5 mL using a rotary evaporator.

A 4-mL aliquot of the crude extract of milk and air samples was loaded onto an 8-g activated Florisil® PR (Wako Pure Chemicals Industries Ltd, Osaka, Japan) column that had been preconditioned with 90 mL of 1:4 (*v*/*v*) mixture of dichloromethane/hexane. SCCPs were eluted with 90 mL of 1:4 mixture of dichloromethane/hexane. The eluate was concentrated to 50 μL of decane and spiked with 250 pg of $^{13}C_{12}$-2,3,3′,5,5′-pentachlorobiphenyl (CB-111; Cambridge Isotope Laboratories, Andover, MA, USA) as an internal standard before GC/ECNI/HRMS (Table S1).

SCCPs were separated on a short, thin film capillary (DB-5MS; 15 m × 0.25 mm i.d., 0.1-μm film thickness; Agilent Technologies, Palo Alto, CA, USA). Although the separation of congeners is essential because of the interference from various fragment ions of SCCPs (Yuan et al., 2016), a short, thin film capillary provided good separation, as reported previously by Harada et al. (2011). Electron-capture negative ionization was performed using methane as the reagent gas. A 1:1:1 mixture of reference solutions containing SCCPs with chloride contents of 45%, 55%, and 65% (Dr. Ehrenstorfer, Augsburg, Germany) was prepared for each carbon chain length (C_{10}–C_{13}). The congener composition of these mixtures was analyzed by electron impact ionization, and the data were used to construct a calibration curve for each carbon chain length and chloride content. The peak of the $[M-Cl]^-$ ion was monitored for each SCCP chain length and chloride content in ECNI. The calibration curves were linear, and the correlation coefficients were >0.998. The method detection limit (MDL) was defined as the concentration of analyte that gave a signal with a signal-to-noise