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Concentrations of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and polychlorinated biphenyls in blood and breast milk collected from pregnant women in Sapporo City, Japan

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ABSTRACT

We measured the concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), dioxin-like polychlorinated biphenyls (PCBs), and non-dioxin-like PCBs in paired samples of blood and breast milk collected from 67 secundiparas in Sapporo City, Japan, and combined this data with those of the 30 secundiparas previously measured. The arithmetic mean total toxic equivalents (TEQ-WHO) concentrations of PCDDs, PCDFs, non-*ortho* PCBs, and mono-*ortho* PCBs in blood and breast milk of the 97 secundiparous subjects were 3.0–23 (mean: 13, median: 14) and 2.7–20 (mean: 8.6, median: 8.5) pg TEQ g^{-1} lipid, respectively. The sums of the concentrations of 56 non-dioxin-like PCB congeners that were measured in the subjects' blood and breast milk were 16–326 (mean: 107, median: 100) and 12–252 (mean: 73, median: 67) ng g^{-1} lipid, respectively. The partitioning ratios of individual congeners of PCDDs, PCDFs, dioxin-like PCBs, and non-dioxin-like PCBs from blood to breast milk in secundiparas were almost the same as those of primiparas that have been recently reported, suggesting that the partitioning ratios of these compounds from maternal blood to breast milk in women is little affected by delivery. Furthermore, the partition of PCB congeners with chlorine at the 2-, 3-, 4′-, and 5-positions or the 2-, 4-, 4′-, and 5-positions of the biphenyl ring from the blood to the breast milk tended to occur at a higher level than that of other congeners. In particular, the levels of tetraCB-74 and hexaCB-146 in the breast milk for both primiparous and secundiparous mothers were slightly higher than those in the blood.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) are highly toxic environmental pollutants. These pollutants are distributed worldwide, and their lipophilic compounds are highly resistant to biodegradation in the environment, becoming concentrated in the food chain and accumulating in the fatty tissues of animals and humans (Liem et al., 2000; Schecter and Gasiewicz, 2003). PCDDs, PCDFs, and PCBs accumulated in the maternal body have been reported to be transferred from the mother to her fetus via the placenta during pregnancy and from mothers to infant via breast milk (Wang et al., 2004; Nakano et al., 2005). Human exposure to PCDDs, PCDFs, and PCBs result in many adverse health effects, including growth retardation in fetuses and infants (Yonemoto, 2000), thyroid deficiency (Pavuk et al., 2003), immune deficiency (Weisglas-kuperus et al., 2000), reproductive effects (Guo et al., 2000), and carcinogenic effects (Steenland et al., 1999; Demers et al., 2002). Moreover, several epidemiological studies have demonstrated the adverse effects of environmental exposure to these dioxin-like compounds on the neurobehavioral development of children (Schantz et al., 2003). Because fetuses and infants are considered to be significantly more sensitive to a variety of PCDDs, PCDFs, and PCBs compared with adults, the adverse effects of these toxicants on these fetuses and infants are of grave concern (Needham and Sexton, 2000; Charnley and Putzrath, 2001; Branum et al., 2003). To elucidate the influence

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of PCDDs, PCDFs, dioxin-like PCBs, and non-dioxin-like PCBs on the health of fetuses and infants, researchers have conducted exposure surveys of these compounds in maternal blood and breast milk in various countries. However, exposure studies of dioxin-like compounds and non-dioxin-like PCBs regarding maternal blood are limited in comparison with studies of breast milk, and comparisons of the concentrations of PCDDs, PCDFs, dioxin-like PCBs, and non-dioxin-like PCBs in blood and breast milk collected from the same mothers have been performed in only a few trials (Schecter et al., 1998; Wang et al., 2004; Nakano et al., 2005; Wittsiepe et al., 2007; Nakamura et al., 2008). Therefore, few exposure studies have compared the levels of dioxin-like compounds and non-dioxin-like PCBs in paired samples of blood and breast milk collected from primiparous mothers with those from secundiparous mothers. The data obtained by the study will help us understand the partitioning ratios of individual congeners of these compounds from blood to breast milk in primiparous and secundiparous mothers and the effect of delivery on the partitioning ratios. We previously measured the concentrations of dioxin-like compounds and non-dioxin-like PCBs in paired samples of blood and breast milk collected from 30 primiparous and 30 secundiparous mothers living in Sapporo City, Hokkaido Prefecture, Japan (Hori et al., 2007; Todaka et al., 2008a). Subsequently, we measured the concentrations of these compounds in paired samples of blood and breast milk collected from 89 primiparas living in the same area, and reported the concentrations of these compounds in blood and breast milk for the total 119 (89 + 30 previous) primparas (Todaka et al., 2010).

In the present study, we measured the concentrations of PCDDs, PCDFs, dioxin-like PCBs, and non-dioxin-like PCBs in blood and breast milk collected from 67 secundiparous mothers in Sapporo City, Japan, and combined this data with those of the 30 secundiparous mothers previously collected. The objectives of our primary study were: (1) to study the relationships of these compounds between blood and breast milk for the total 97 secundiparas and (2) to compare our findings with the concentrations of these compounds in those for 119 primiparas.

2. Materials and methods

2.1. Sampling

In 2002, the Hokkaido University Graduate School of Medicine established a hospital-based prospective cohort study entitled the "Hokkaido Study on Environment and Children's Health" to investigate the possible adverse effects of PCBs, PCDDs/PCDFs, perfluopinated chemicals, and many other environmental contaminants on fetal growth and newrodevelopment. 514 pregnant women were enrolled in this cohort study between July 2002 and October 2005. All the subjects participating in this study were native Japanese and residents of Sapporo City or the surrounding area. Blood, cord blood and breast milk specimens were collected from mothers, after obtaining informed consent from them. After collection, the specimens were frozen and stored at −80 °C until analysis. Between June 2004 and June 2008, we measured the levels of PCDDs, PCDFs, dioxin-like PCBs, and non-dioxin-like PCBs in 462 maternal blood samples and 250 breast milk specimens. In the present study, blood samples in 67 subjects were taken from the maternal peripheral vein after the 2nd trimester during their second pregnancy. In the previous 30 cases, blood samples were taken during the first 1 week after birth (Todaka et al., 2008a). The breast milk specimens were collected during 28–30 days after delivery. The ages of the secundiparas examined in the present study were within 22–41 years (mean: 31.9 years, median: 32.0 years).

2.2. Materials

Native congeners of PCDDs, PCDFs, dioxin-like PCBs, and non-dioxin-like PCBs were purchased from Wellington Laboratories (Guelph, Canada). [$^{13}C_{12}$]-congeners of PCDDs, PCDFs, dioxin-like PCBs, and non-dioxin-like PCBs as internal standards, were also purchased from Wellington Laboratories. An active carbon column was prepared as follows: active carbon was purchased from Nacalai Tesque (Kyoto, Japan), refluxed 3 times with toluene for 1 h, and dried in vacuum, after which 500 mg of the active carbon was mixed with 500 g of anhydrous sodium sulfate (Wako Pure Chemical Industries, Ltd., Tokyo, Japan). A silver nitrate/silica gel was purchased from Wako Pure Chemical Industries, Ltd. An active carbon-dispersed silica gel was purchased from Kanto Chemical Industries, Ltd., Tokyo, Japan. All reagents and solvents used in this experiment were of the analytic grade of dioxin that is commercially available.

2.3. Analysis of PCDDs, PCDFs, dioxin-like PCBs, and non-dioxin-like PCBs

The extraction and purification of PCDDs, PCDFs, dioxin-like PCBs, and non-dioxin-like PCBs from blood and breast milk specimens were performed using a previously reported method (Iida and Todaka, 2003; Todaka et al., 2008a,b). Concentrations of the PCDDs, PCDFs, non-*ortho* PCBs, and mono-*ortho* PCBs and concentrations of 56 non-dioxin-like PCB congeners were also performed using a previously reported method (Iida and Todaka, 2003; Todaka et al., 2008a,b).

2.4. Quality control

To evaluate the accuracy and reliability of the analysis of PCDDs, PCDFs, and dioxin-like PCBs, our laboratory completed quality control studies for the analysis of these compounds. Our laboratory has participated in a quality control study for the analysis of these dioxin-like compounds in dried milk powder (BCRRM 534), assisted by a Grant-in-Aid for scientific research from the Ministry of Health, Labour, and Welfare, Japan, in 2003. In our results, the difference between values of our laboratory and certification values in the reference material was within 10% of certification values. In 2004 and 2006, we prepared human blood samples using blood collected from five volunteers and attempted to carry out a quality control study of the analysis of PCDDs, PCDFs, and dioxin-like PCBs in human blood. In both studies, the average variation among the TEQ values in samples obtained by all participating laboratories was within 10% (Iida et al., 2004). In 2007, our laboratory prepared human blood samples using blood collected from five volunteers and breast milk samples prepared using 10 randomly selected specimens from 250 breast milk samples collected in this cohort study. In both samples, measurements of 56 non-dioxin-like PCBs congeners that were measured in the present study among 197 non-dioxin-like PCBs congeners requested from three different analysis organizations and their results were compared with our results. The average variation among the total non-dioxin-like PCBs levels in human blood and breast milk samples obtained by the four participating laboratories was within 10% and was considered acceptable (Kajiwara et al., 2008, 2009, 2010). These results indicated that our laboratory's analytical methods for PCDDs, PCDFs, dioxin-like PCBs, and non-dioxin-like PCBs in human blood and breast milk specimens provided correct results.

2.5. Data analysis

To estimate the TEQ concentrations, we introduced ND (less than the detection limit) values to half values of the detection limit