OCCURENCE AND EXPOSURE ASSESSMENT OF POLYCHLORINATED BIPHENYLS (PCBs) AND ORGANOCHLORINE PESTICIDE (OCPs) VIA BABY FOOD CONSUMPTION IN KOREA

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Introduction

Persistent organic pollutants (POPs) are globally distributed in various environmental multimedia[1,2]. In 2001, dirty dozen of POPs including polychlorinated biphenyls (PCBs) and organochlorine pesticide (OCPs) were registered by the United Nations Environment Programme (UNEP) under the Stockholm Convention [3,4]. Organochlorines (OCs) such as PCBs and OCPs have been used for past decades with large volume in many countries[5]. OCs elicit adverse health effects such as immunotoxicity, reproductive disorders and carcinogenesis [6,7]. Food consumption contributed over 90% of the total human exposure to OCs for general population[8]. Because of toxicities and exposure status of OCs, there are several guidelines of these contaminants. Although the use of OCs has been banned or restricted in Korea, PCBs and OCPs are still present in coastal environments[9,10] and have been found in human tissues[11]. Infants are biologically sensitive group to OCs because of the low detoxify capacity with lower body burden than adults[12,13]. Most of Korean infants traditionally consume home-made baby food. Based on the Korean government report, hypoallergenic foods such as rice, vegetable and fruit are recommended for 6 month infants. Considering essential ingredients for growth and health of infants, consumption of greasy food such as fish and meat is recommended for over 12 months. In Korea, a consumption rate of breast milk feeding is lower than other developed countries baby food could be a major source of OC exposure to infants. However, no data are available on OC exposure in baby food for Korean infants. Therefore, the objectives of this study were to investigate the occurrence of PCBs and OCPs in homemade baby food and to assess potential risks to Korean infants by the exposure of these contaminants. In our knowledge, this is the first report on OC measurement in home-made baby food.

Materials and methods

Sample collection

Baby food samples (*n*=100) were collected from four regions of Korea in 2012. Collected baby food samples were divided into four subject groups according to the infant age; (1) food for 6 month infant (n=22); (2) food for 9 month infant (n=29); (3) food for 12 month infant (n=37); (4) food for 15 month infant (n=12). We measured intake amount of baby food and infant body weight for each subject group, to obtain actual exposure status of PCBs and OCPs through baby food consumption.

Chemical and instrumental analysis

PCBs and OCPs were measured in baby food samples following methods described elsewhere[14,15].In brief, approximately 25 g of baby food samples were homogenized with anhydrous Na_2SO_4 and extracted with mixed solvents of DCM:hexane (3:1) using Soxhlet apparatus for 16 h. The extract was concentrated to 11 mL, and an aliquot (1 mL) was taken for gravimetric determination of lipid content. Remained aliquot was spiked with PCBs and OCPs internal standard and cleaned by a multi-layered silica gel column with 150 mL of 15% DCM in hexane. The eluted fractions were concentrated to 1 mL and were dissolved in 100 µL of nonane for instrumental analysis. PCBs and OCPs were measured using a high resolution gas chromatography interfaced with high resolution mass spectrometry. The HRMS was operated electron ionization (EI) mode and ions were monitored by selected ion monitoring. The recoveries spiked ^{13}C-labelled CBs 28, 52, 118, 153, 180, 202, 206 were 73 ± 9.4% (average ± SD), 68 ± 8.9%, 83 ± 8.1%, 77 ± 7.8%, 88 ± 9.4%, 78 ± 8.3% and 99 ± 9.3% respectively. The recoveries spiked ^{13}C-labelled DDTs, HCHs, CHLs, HCB, heptachlor expxide and mirex were 99 ± 18% (average ± SD), 73 ± 12%, 91 ± 17%, 87 ± 6.3%, 94 ± 19% and 93 ± 8.2%, respectively. Limit of quantification (LOQ) was calculated as ten times of the signal to noise ratio, which ranged from 0.4 to 1.0 pg/g fw for PCBs and from 0.5 to 5.0 for OCPs.

Statistical analysis

All chemical data are presented on fresh weight basis. The concentrations of PCBs and OCPs detected in > 60% of samples were used for statistical analysis. Any sample wherein PCBs and OCPs were not detected was given as of LOQ deviding with root 2. Analysis of Variance (ANOVA) was used to determine significant differences in the concentrations and EDIs between subject groups. Statistical significance was based on the level of $p < 0.05$. All statistical analyses were performed using SPSS version 18.0.

Estimated daily intake

Daily intakes of PCBs and OCPs through baby food consumption were estimated using the following equation:

$$EDI = C \times Intake / BW$$

where EDI (ng/kg bw/day) is estimated daily intake, C (ng/g fresh weight) is the measured concentrations of target compounds. Average and 95th percentiles of each compound concentration were used to calculate the EDI. Intake is the daily consumption rate of food (g/day) and BW (kg) is body weight of baby. Respective food intake and body weight for each infant age of subject groups were estimated to be 95.9 g/day and 8.53 kg for 6 month, 161 g/day and 9.47 kg for 9 month, 222 g/day and 9.98 kg for 12 month, and 310 g/day and 10.5 kg for 15 month.

Results and discussion

Concentrations of PCB and OCP in baby food

The concentrations of PCBs and OCPs in baby food samples from 4 subject groups are summarized in Table 1. Six congeners of PCBs and 8 compounds of OCPs were detected in > 60% of baby food samples. However, six PCB congeners (CBs 128, 187, 194, 195, 199 and 206) and two OCP compounds (*δ*-HCH and HCB) were not detected in any baby food samples.

Table 1. Concentrations of PCBs and OCPs (pg/g fresh weight) in baby food samples (n=100) collected from Korea in 2012

Compound	Mean ± SD	50th	95th	Range (outlier)	Detection Frequency (%)	LOQ
CB 28	8.80 ± 17.1	2.08	51.2	0.35-91.6 (176)	94	0.50
CB 33	2.97 ± 6.10	0.37	18.4	0.35-32.3 (115)	75	0.50
CB 44	2.20 ± 4.87	0.35	14.8	0.35-29.4	60	0.50
CB 52	3.45 ± 7.06	0.53	17.0	0.35-37.8	76	0.50
CB 118	1.49 ± 5.34	0.35	4.80	0.35-52.4	61	0.50
CB 153	3.60 ± 11.9	0.71	11.9	0.71-111 (154)	74	1.00
∑PCB[a]	37.5 ± 57.7	16.5	171	7.78-270		
p,p'-DDE	51.6 ± 117	10.1	217	0.71-1010	97	1.00
p,p'-DDT	24.5 ± 125	2.34	86.2	0.71-1228	86	1.00
∑DDT[b]	96.6 ± 328	19.4	301	3.57-3159		
α-HCH	4.28 ± 8.72	0.71	20.2	0.71-70.8	87	1.00
β-HCH	14.4 ± 34.6	2.52	56.1	0.71-230	87	1.00
γ-HCH	6.62 ± 13.3	1.12	39.8	0.71-73.1 (619)	90	1.00
∑HCH[c]	26.0 ± 48.8	7.01	108	2.83-375		
trans-CHL	6.43 ± 14.4	1.01	27.4	0.28-99.9	82	0.40
cis-CHL	3.26 ± 7.83	0.42	18.2	0.28-46.5 (141)	87	0.40
trans-NonaCHL	3.48 ± 8.51	0.52	15.0	0.28-63.0 (174)	83	0.40
∑CHL[d]	13.2 ± 28.0	3.03	67.8	1.41-175		
Heptachlor epoxide	1.28 ± 2.24	0.71	3.92	0.71-15.2	20	1.00
Mirex	0.37 ± 0.08	0.35	0.37	0.35-0.99	16	0.50
∑OCP	140 ± 365	48.8	405	9.58-3380		

[a]Sum of 19 PCB congeners (PCB 18, 28, 33, 44, 52, 70, 101, 105, 118, 128, 138, 153, 170, 180, 187, 194, 195, 199, 206 and 209); [b]Sum of *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT; [c]Sum of α-, β-, γ- and δ-HCH; [d]Sum of *oxy*-CHL, *trans*-CHL, *cis*-CHL, *trans*-NonaCHL and *cis*-NonaCHL.

The predominant PCB congeners were CBs 28, 153, 52, 33, 18 and 44, collectively accounting for 63% of total PCBs concentrations. Similar PCB contamination pattern was found for a previous study for Korean dietary exposure. Lower chlorinated CBs such as CBs 28 and 52 in rice and vegetable from Korea contributed over 50% to the ΣPCB concentrations[21].The PCB concentrations measured in our study were similar to those reported for fish-based commercial baby food from Spain[16]. The predominant ΣOCP were *p,p'*-DDE, *p,p'*-DDT, *β*-HCH and *p,p'*-DDD, collectively accounting for 74% of the ΣOCP concentrations. The predominant *p,p'*-DDE concentration is similar pattern with food from developed countries including seafood, meat, poultry, daily products, fruits and vegetables which can be an ingredient of baby food[18,19]. Compared to infant formulae from European Union countries[13], Korean baby food showed different OCPs compound contribution. In Korea, HCB was not detected in any of samples while infant formulae from EU market showed high contribution of HCB (51 %). It might be the effect of historical usage pattern that Korea have never been imported and produced the HCB[20].

Comparisons between each infant age

Total concentrations of PCBs, DDTs, HCHs and CHLs in baby food samples measured in each consumption month are shown in Figure 1. No statistically significant differences in the concentrations of OCs for infant age ($p > 0.05$), suggesting the contents of baby foods are not variable in each infant age. Pandelova et al. (2011) reported that infant formulae from EU market also showed no difference between starting infant formulae and follow on infant formulae. The highest mean value of DDT concentration was found at the sample of 15 months followed by 12 months, 9 months and 6 months. The highest value of DDTs was found in 12 month baby food, which included high lipid content food such as fish, egg and daily products. The highest value of PCBs, HCHs and CHLs were found in the 6 month baby food, each was different sample. The lowest mean and 95th percentile value of PCBs, HCHs and CHLs were detected in 15 month. The 95th percentile concentration in each month has high lipid content (3-5%, total mean value: 1%) which contains beef, fish soup, fried fish, cheese, bread, snack, chicken and rice based on questionnaires from the mother of subject group.

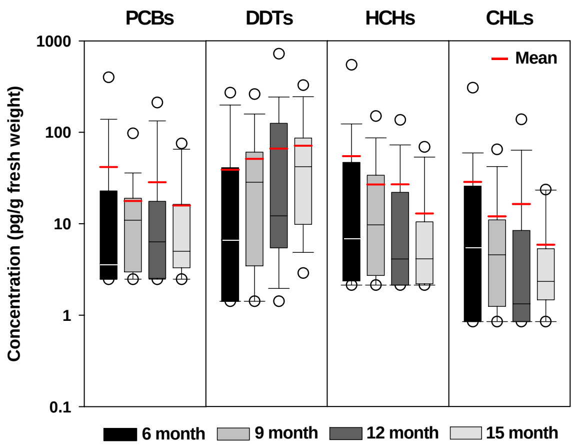

Figure 1. Total concentrations of PCBs, DDTs, HCHs and CHLs in baby food samples measured in different consumption month (6, 9, 12 and 15 month). The box plot shows 10th, 25th, 50th and 90th percentiles with error bars. The arithmetic mean concentrations are given as red bars. The circles are 5th percentile (lower) and 95th percentile (upper).

Relative contribution of each compound to total concentrations in 6, 9, 12 and 15 months are shown in Figure 2. DDTs were the major contributor in every consumption month. HCHs and CHLs concentration were decreased from 6 months to 15 months while PCBs concentration showed almost constant contribution in each month.

Total diet study (TDS) from China conducted in 2007[21] measured the contribution of various food groups including meats, eggs, aquatic foods, milk, fruits and vegetables to dietary OCPs intake. According to the result of Zhou et al. (2012), main contributors of DDTs concentration were aquatic food and meats, HCHs concentration were meats and vegetables and CHLs concentration were vegetables. In our result, with the month increasing, foods were changed from hypoallergenic food such as vegetables and fruits to greasy food such as seafood and meats which are sufficient for baby activities. As a result, DDTs contribution in each month increased because of the meat and seafood additives. Thus, through baby food consumption, babies can be exposed to contaminants mainly DDTs.

Estimated daily intake

The estimated daily intake calculated for each month. We used the mean and 95th percentile value in each month group to represent average and high exposure scenarios, respectively. The highest mean and 95th percentile EDI values were ∑DDT in 15 which are comparable to EDI of total PCB in highest exposure scenario. The EDI values of CBs 118, ∑DDTs and γ-HCH were increased with the month while ∑PCBs, *β*-HCH, and ∑CHLs were decreased from 12 months to 15 months. The dietary exposure to PCBs and OCPs in our study was three or four orders of magnitudes lower than oral reference dose recommended by US EPA, Health Canada and WHO. In Korea, contribution of ∑OCPs dietary intake is higher than ∑PCBs suggesting Korean baby can be mainly exposed to OCPs by consumption of baby food.

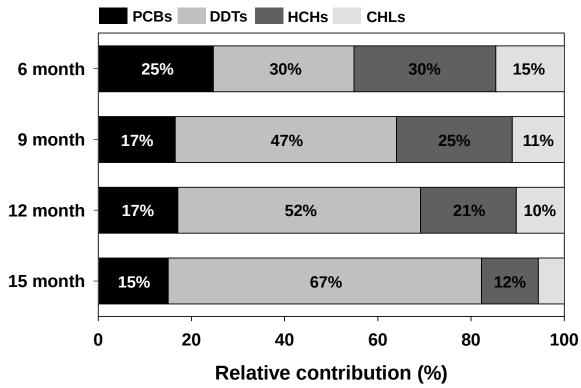

Figure 2. Relative contribution of PCBs, DDTs, HCHs and CHLs in baby food samples from each infant age; 6, 9, 12 and 15 months.

Simultaneous exposure from baby food and breast milk consumption

Considering the lowest baby food intake in 6 months, there might be a simultaneous breast feeding for fed a baby. We also measured the PCBs and OCPs concentration in breast milk which was the same subject group. To estimate individual contribution of baby food and breast milk to daily dietary intake, same compounds except for *β*- and *γ*-HCH were selected to calculation. According to WHO (2001), the consumption ratio of breast milk and baby food (3.5 : 1) is sufficient to 6 months baby, using this ratio to calculate the dietary intake of PCBs and OCPs concentration via simultaneous intake of breast milk and baby food. For 6 months baby, the calculated dietary intake of breast milk and baby food were as shown below; PCB 118 (9.3 ng/kg bw/day), ∑PCB (98.9 ng/kg bw/day), ∑DDT (701 ng/kg bw/day), ∑CHL (55.3 ng/kg bw/day), mirex (0.65 ng/kg bw/day), heptachlor epoxide (24.0 ng/kg bw/day) and ∑OCP (979.4 ng/kg bw/day). Among the compounds, heptachlor epoxide exceeded the reference dose proposed by US EPA (13 ng/kg bw/day) with a high contribution of breast milk. It can be suggested that while babies are fed with breast milk and baby food concurrently, there will be additional health effect to babies.

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