MONITORING AND DAILY INTAKE ESTIMATION OF DIOXINS (PCDDs, PCDFs AND DIOXIN-LIKE PCBs) FROM MAJOR SIX FRUITS IN KOREA

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Introduction

Persistent organic pollutants (POPs) are organic compounds that are non-degradable, long-range transportable and bioaccumulated toxic chemicals. They include several organochlorine pesticides and industrial byproducts such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).[1] Among of them, PCDD/Fs and dioxin-like PCBs (DL-PCBs) are highly considered as organochlorine POPs due to their notable toxicities, thus World Health Organization (WHO) set a tolerable daily intake (TDI) for dioxins at 4 pg-TEQ_{WHO}/kg body weight (b.w.)/day as well as Korean Food and Drug Administration (KFDA).[2] The main source of dioxin exposure for human is known as food contamination in non-occupationally exposure person.[3,4] Thus, number of researchers investigated the contamination of PCDD/Fs and DL-PCBs in livestock products, dairy products, marine products, and farm products.[5-10]

However, only scare information on background concentration level of dioxins and dietary intake of human beings in agricultural fresh food is available for Korean, because the survey was mostly focused on meat, fish, dairy product and cereals but not fresh fruits.

As part of these ongoing studies on dioxins contamination in Korean fresh food, the present study was to determine the levels of 17 PCDD/Fs, 12 DL-PCBs by HRGC/HRMS in the six major Korean fruits (apple, grape, mandarin orange, peach, pear and persimmon) that were collected from 36 orchards at 2009 in Korea.

Materials and methods

Samples

The six major fruits represent the most consumed in Korea, and they are around 74 % of total Korean fruits consumption.[11] In this research, total number of samples was 36 (7 apples, 6 grapes, 3 mandarin orange, 6 peach, 7 pears and 7 persimmons) from each major producing district in Korea, and collected sample was used whole part without peeling and washing except peach that its core was removed. It was chopped and stored in freezer before analysis.

Analysis

All the analytical samples for dioxins were prepared according to the method of Kim *et al.*[12] with several modifications. Briefly, 50 g of samples were extracted by homogenization with acetone/n-hexane and filtered, and then all samples were spiked with a mixture of $^{13}C_{12}$-labelled 29 PCDD/Fs and DL-PCBs congeners (Wellington Laboratories, Ontario, Canada). The extract was transferred to separation funnel, after which the organic phase was washed with saturated sodium chloride, and concentrated sulfuric acid was added to the organic phase and mixed for the elimination of pigment. Then the organic phase was washed with distilled water and concentrated under reduced pressure. Clean-up procedure was performed with the PowerPrep automated system (Fluid Management System Inc., Waltham, Massachusetts). The system was equipped with three types of columns with silica, alumina and activated carbon. After washing with hexane, mono- and di-ortho PCBs were eluted with 2% and 50% dichloromethane in hexane respectively (Fraction 1). PCDD/Fs and non-ortho PCBs were eluted with toluene (Fraction 2). Then as injection standard solution, $^{13}C_{12}$-labeled PCBs IUPAC 70, 111

and 138 were spiked to Fraction 1. For Fraction 2, 1,2,3,4,6-PentaCDF and 1,2,3,4,6,8,9-HeptaCDF with above labeled PCB congeners were added.
Quantification and identification of PCDD/Fs and DL-PCBs were performed with HRGC-HRMS system. The analysis was conducted with DB-5MS (60 m × 0.25 mm × 0.25 μm) and SP-2331 (60 m × 0.25 mm × 0.25 μm). The HRGC-HRMS program was operated in electron impact ionization (EI) mode at a resolution of more than 10,000 using multiple ion detection (MID). We used the non-detects as equal to zero. TEQ levels of dioxins were expressed in pg-TEQ_{WHO}/gram using the appropriate WHO toxic equivalent factor (WHO-TEF).

Results and discussion

The contamination level of PCDD/Fs and DL-PCBs were 0.0042 and 0.0932 pg/g fresh weight (f.w.) in the apple, 0.0094 and 0.2649 pg/g f.w. in the grape, 0.1843 and 1.5437 pg/g f.w. in the mandarin orange, 0.2282 and 0.1942 pg/g f.w. in the peach, 0.1491 and 0.4591 pg/g f.w. in the pear, and 0.1330 and 0.4396 pg/g f.w. in the persimmon. The average contamination residues of PCDD/Fs were sequenced in the ascending order of peach, mandarin orange, pear, persimmon, grape and apple (Figure 1). Mandarin orange was showed the highest average residue of DL-PCBs. The most abundant contaminant was 1,2,3,7,8-PeCDD for PCDDs, 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF for PCDFs, and 3,3',4,4'-TeCB (PCB 77) for DL-PCBs. In this experiments, 1,2,3,4,7,8,9-HpCDF and OCDF in PCDD/Fs, and 2,3,3',4,4'-PeCB (PCB 105), 2,3,4,4',5-PeCB (PCB 114), 2',3,4,4',5-PeCB (PCB 123), 2,3,3',4,4',5-HxCB (PCB 156), 2,3,3',4,4',5'-HxCB (PCB 157), 2,3',4,4',5,5'-HxCB (PCB 167) and 2,3,3',4,4',5,5'-HpCB (PCB 189) were not detected on the major fruits.

In comparison with atmospheric dioxins contamination results in South Korea by Shin *et al.*,[13] the congener pattern of PCDD/Fs and DL-PCBs in fruits was similar to the atmosphere's congener pattern. They reported that DL-PCBs didn't show significant seasonal and spatial variations in the congener profile, whereas the congener patterns of 17 PCDD/Fs were different by sampling season and area.

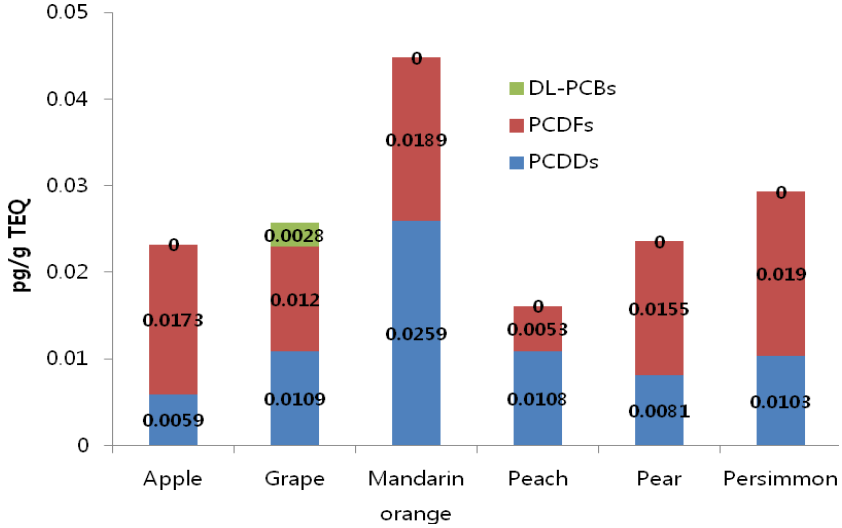

Figure 1. The average TEQ contribution of dioxins (PCDDs, PCDFs and DL-PCBs) in the six major Korean fruits.

Estimated daily intake (EDI) for population were calculated by multiplying the measured TEQ concentration based on the food consumption data of the local residents that were investigated for Korean, and the results were divided by 60 to obtain average daily exposure per kg of body weight (Table 1). The total daily intake of dioxins from apple, grape, mandarin orange, peach, pear and persimmon were estimated 0.72, 0.30, 1.47, 0.22, 0.52 and 0.60 pg-TEQ_{WHO}/day respectively, and the total EDI of dioxins from the six fruits were 3.83 pg-TEQ_{WHO}/day for Korean. From the result, the dioxins exposure of Korean male person was estimated 0.0638 pg-TEQ_{WHO}/kg b.w./day from the six fruits, and the fruits contributed 1.60 % of Korean TDI. However, the real

dietary exposure of dioxins would be lower than the estimated ratio because the TEQ levels in this experiment were investigated with whole fruits including edible and inedible portion.

Table 1 Estimated daily intake (EDI) to the dioxins of Korean fruits

	Daily Intake*	EDI dioxins (pg-TEQ_{WHO}/day/person)			
		PCDDs	PCDFs	DL-PCBs	Total
Apple	31.1 g	0.18	0.54	0	0.72
Grape	11.6 g	0.13	0.14	0.03	0.30
Mandarin Orange	32.7 g	0.85	0.62	0	1.47
Peach	13.5 g	0.15	0.07	0	0.22
Pear	22.0 g	0.18	0.34	0	0.52
Persimmon	20.3 g	0.21	0.39	0	0.60
Total TEQ		1.70	2.10	0.03	3.83

* Daily intake values were referenced from Korea National Health and Nutrition Examination Survey in 2007 [Korean CDC, 2008]

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References:

1. Grassi P, Fattore E, Generoso C, Fanelli R, Arvati M, and Zuccato E (2010) *Chemosphere* 79, 292-298.
2. Kim YS, Eun HS, Cho HS, Kim KS, Watanabe E, Baba K, and Katase T (2008) *Journal of Hazardous Materials* 154, 756–765.
3. Baars AJ, Bakker MI, Baumann RA, Boon PE, Freijer JI, Hoogenboom LAP, Hoogerbrugge R, van Klaveren JD, Liem AKD, Traag WA, and de Vries J (2004) *Toxicology Letters* **151**, 51-61.
4. Parzefall W (2002) *Food and Chemical Toxicology* **40**, 1185-1189.
5. Bernard A, Hermans C, Broeckaert F, De Poorter G, De Cock A, and Houins G (1999) *Nature* **401**, 231-232.
6. Guruge KS, Seike N, Yamanaka N, and Miyazaki S (2005) *Chemosphere* **58**, 883-889.
7. De Mul A, Bakker MI, Zeilmaker MJ, Traag WA, van Leeuwen SPJ, Hoogenboom RLAP, Boon PE, and van Klaveren JD (2008) *Regulatory Toxicology and Pharmacology* **51**, 278-287.
8. Edwards R (2004) *New Scientist* **181**, 8-8.
9. Moon HB, Kannan K, Choi HG, An YR, Choi SG, Park JY, and Kim ZG (2010) *Chemosphere* **79**, 733-739.
10. Tard A, Gallotti S, Leblanc JC, and Volatier JL (2007) *Food Additives and Contaminants* **24**, 1007-1017.
11. Korean CDC (2008) In *Korea National Health and Nutrition Examination Survey (KNHANES IV) 2007 - Health Examination*. p. 116, Seoul: Ministry of Health and Welfare, Korean CDC
12. Kim M, Choi SW, and Kim DG (2008) *Food Additives and Contaminants Part A-Chemistry Analysis Control Exposure & Risk Assessment* **25**, 1278-1282.
13. Shin SK, Jin GZ, Kim WI, Kim BH, Hwang SM, Hong JP, and Park JS (2011) *Chemosphere* **83**, 1339-1344.