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SURVEY OF DIOXINs/DIBENZOFURANs IN PIZZAS AND NOODLES FROM KOREA

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Abstract : The present study focused on determining the polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofurans (PCDD/Fs) levels in fast food, such as pizza and noodles, which are currently very popular among Korean young people. The total level of PCDD/Fs in pizza were found to be 3.064~12.066 pg/g-wet-weight. For half and half pizza, the total concentrations for two different brands were 3.064 pg/g-wet-weight and 8.627 pg/g-wet-weight, respectively. For noodles, the total concentrations per sample ranged between 6.905~48.546 pg/g-wet-weight for cup noodles and 7.659~29.502 pg/g-wet-weight for packet noodles. The TEQ levels in the fast food samples ranged between 0.108~0.354 pg TEQ/g-wet-weight in pizza, while the residue of PCDD/Fs in noodles ranged from 0.101~0.545 pg TEQ/g-wet-weight for cup noodles and 0.077~0.108 pg TEQ/g-wet-weight for packet noodles. As such, higher TEQ levels were found in noodles than in pizza, with higher levels in cup noodles than in packet noodles. In terms of the congener distribution, octa dibenzo-p-dioxin was predominant in almost all the samples analyzed.

Key Words : congener profile, Korean fast food, PCDD/Fs, TEQ

INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have a very low water solubility, high octanol-water partition coefficients, low vapor pressure, and high toxicity.[1,2] Although never intentionally manufactured, they have a significant presence throughout the environment due to their chemical and physical properties. As final consumers in the food chain, humans accumulate these compounds in their bodies through diet, ingestion, inhalation, adsorption from soil and water, etc.[3] Numerous reports are available on the levels of PCDD/Fs in various edible foods, which were surveyed to estimate the daily intake of dioxins.[4~11] Furthermore, food is generally recognized as the main source of human intake of PCDD/Fs and dioxin-like PCBs; more than 90% of the total daily intake of these contaminants is generally derived from food. To evaluate the risk for humans, several surveys in various countries have determined the intake of PCDD/Fs and dioxin-like PCBs from total diet study samples and individuals.[12~14] However, relatively limited data is available on the PCDD/Fs levels in fast food products despite of their popularity and the identification of food as the primary source of non-occupational human exposure.[15~17] In Korea, the consumption of fast food is steadily increasing in popularity, as in many other countries. However, the currently available literature is insufficient

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to understand the daily intake of dioxins through fast food in Korea. Accordingly, the main objective of the present study was to investigate the levels of PCDD/Fs in representative types of fast food, such as pizza and noodles (ramyun: Korean brand).

Based on recent statistics compiled by the Korean Health Industry Development Institute (KHIDI), young people between the ages of 7~29 have a daily fast food intake of approximately 59~83 g per day, including ramyun, indicating a significant increase. In Korea, noodles, particularly ramyun, are very popular as they are quick and easy to prepare. Therefore, the current study also focused on investigating the residue levels of PCDD/Fs in Korean noodles.

MATERIAL AND METHODS

Sampling Method and Sample Preparation

Five kinds of pizza (D company, P company) and five kinds of noodle that are especially popular among Korean youngsters were selected as the samples. The pizzas were purchased from the franchise store, while the noodles were obtained from a supermarket in Seoul, Korea, between March and October 1999. The samples were collected in triplicate from randomly selected locations.

Representative samples should be collected in order to determine the levels of contaminant. For example, dioxin levels vary widely due to their various kinds of topping materials used during the preparation of ingredients such as powder soup used in noodles. However, our aim was focused on determining the concentration of fast food itself that is consumed rather than the various types of components used during preparation. Additionally, cup and packet type noodles were grouped and then analyzed because it was anticipated that the levels of dioxins is contributed due to the difference that the lipid content possess.

Table 1 provides detailed information pertaining to each individual sample. After collection, the samples were frozen until they were delivered to the analytical laboratory.

Table 1. Samples profiles of fast food

	Items	No. of pools	Weight (g)
Pizza	PZ - 2 (D)	3	45
	PZ - 3 (P)	3	77
	PZ - 4 (D)	3	75
	PZ - 5 (D)	3	55
	PZ - 6 (P)	3	50
Noodle	R - 1 (P.T)	6	60
	R - 3 (P.T)	6	66
	R - 2 (C.T)	6	60
	R - 6 (C.T)	4	60
	R - 4 (C.T)	4	60
	R - 5 (C.T)	6	60

Note: (D) D company, (P) P company, (C.T) cup-type noodles, (P.T) packet-type noodles

The samples were ground and finely homogenized. Equal portions from each sample were then mixed to create a composite sample. The final sample amount was approximately 45 ~77 g.

Analytical Procedure

17 isomers with 2,3,7,8-substitutes were analyzed. The sample extraction and cleanup method was performed per standard method reported in references.[18~20] After the addition of fifteen $^{13}C_{12}$-labelled internal standards, the samples were extracted with toluene for 20 hrs using a Soxhlet/Dean-stark extractor. The extracts were concentrated using a rotary evaporator, dissolved in n-hexane, thoroughly washed with concentrated sulfuric acid until colorless, and finally washed with n-hexane-rinsed water to eliminate all traces of acid. The extracts were then passed through a series of column chromatographic cleanup steps using a silica gel, basic alumina, and activated-carbon-impregnated with silica gel as follows.

The silica-gel column was packed with 1 g of silica-gel that had been activated at 130℃ for 4 hrs and 11 g of 44% silica-gel (w/w; H_2SO_4: silica) that had not been activated, and then capped with 1 g of anhydrous sodium sulfate. After packing, the column was eluted

with n-hexane.

The alumina column was packed with 5 g of basic alumina that had been activated at 190℃ for 22 hrs, and then capped with 1 g of anhydrous sodium sulfate. After packing, the column was first eluted with a 1:50(v/v) ratio of n-hexane and dichloromethane (DCM), followed by a subsequent elution with a 1:1(v/v) ratio of n-hexane and DCM. The second fraction was loaded onto the carbon column that was packed with 0.7 g of activated-carbon-impregnated with silica gel and then capped with 1 g of anhydrous sodium sulfate. After packing, the column was eluted with a 1:4(v/v) ratio of n-hexane and DCM, followed by toluene. The PCDD/Fs were eluted in the second fraction.

The cleanup extracts were allowed to concentrate to approximately 1 mL under a stream of nitrogen gas. The volumes of the fractions eluted from the cleanup columns were also determined so as to recover all the compounds of 4- to 8- chlorinated dioxins and furans.

Prior to the HRGC/HRMS quantifications, the final elute was concentrated with nonane to 25 μL and spiked with a $^{13}C_{12}$-labelled recovery standard for an internal standard recovery calculation. The PCDD/Fs quantifications was carried out by HRGC/HRMS (SIM) using a VG-Autospec Ultima NT instrument equipped with a J&W Scientific DB-5 column(60 m length × 0.25 mm i.d × 0.25 μm film thickness) and Supelco SP2331 column(60 m length × 0.32 mm i.d × 0.20 μm film thickness). The PCDD/Fs levels were expressed in 2,3,7,8-TCDD toxic equivalents using international toxic equivalent factor (I-TEF) calculations.

RESULTS AND DISCUSSION

Concentration and Congener Profile in Noodles and Pizza

For the analysis, the noodles were divided into cup type and packet type. As shown in Table 2, the total PCDD and PCDF concentrations per sample ranged between 6.905~48.546 pg/g-wet-weight for the cup noodles and 7.659~29.502 pg/g-wet-weight for the packet noodles. The TEQ levels were 0.101~0.545 pg TEQ/g-wet-weight for the cup noodles and 0.077~0.108 pg TEQ/g-wet-weight for the packet noodles. Therefore, the cup noodles were found to contain as much as two times the level found in the packet noodles, plus the cup noodles exhibited the higher lipid content. As such, it would appear that the PCDD/Fs values for the noodles were related with their lipid content.

No extraordinary characteristics were observed

Table 2. Levels of dioxins, dibenzofuran, and dioxin TEQs in noodles and pizza

Items		PCDFs	PCDDs	PCDFs/PCDDs	PCDF TEQ	PCDD TEQ	Total TEQ
		(pg/g-wet-weight)			(pg TEQ/g-wet-weight)		
Pizza	PZ-2 (D)	6.370	5.696	12.066	0.196	0.158	0.354
	PZ-3 (P)	3.262	4.548	7.810	0.101	0.095	0.196
	PZ-4 (D)	3.921	6.544	10.464	0.15	0.142	0.292
	PZ-5 (D)	1.287	1.776	3.064	0.068	0.04	0.108
	PZ-6 (P)	3.794	4.833	8.627	0.109	0.082	0.190
Noodle	R-1 (P.T)	0.888	6.771	7.659	0.042	0.035	0.077
	R-3 (P.T)	0.866	28.636	29.502	0.049	0.058	0.108
	R-2 (C.T)	2.687	45.859	48.546	0.104	0.077	0.181
	R-6 (C.T)	0.967	25.205	26.172	0.158	0.064	0.222
	R-4 (C.T)	0.909	16.163	17.072	0.054	0.047	0.101
	R-5 (C.T)	2.945	3.959	6.905	0.441	0.103	0.545

Note: (D) D company, (P) P company, (C.T) cup-type noodles, (P.T) packet-type noodles

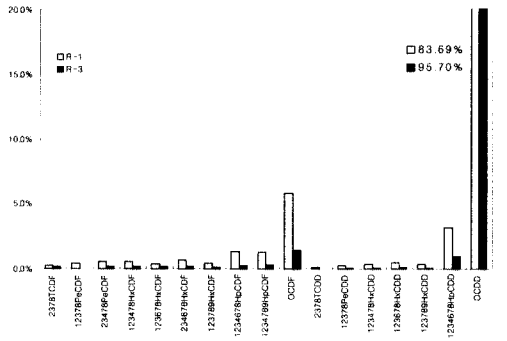


Figure 1. Distribution of 2,3,7,8-substituted PCDD/DFs in packet-type noodles.

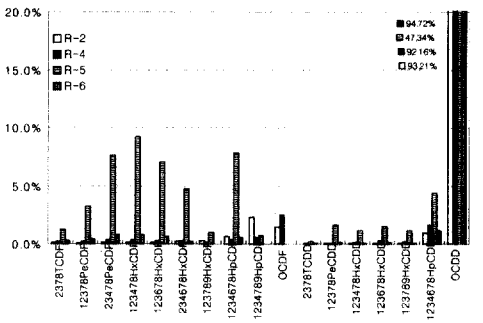


Figure 2. Distribution of 2,3,7,8-substituted PCDD/DFs in cup-type noodles.

as regards the isomeric distribution, however, there was an increased tendency in higher chlorinated compounds of both dioxins and furans.

As shown in Figure 1, a higher proportion of 7 or 8 chlorinated compounds of both dioxins and furans was found in the packet noodles. In particular, octa-chlorinated dibenzo-dioxin made up 83 and 95% in the R-1 and R-3 samples, respectively. In addition, the congener profile of the cup noodles also exhibited an increased proportion of higher chlorinated compounds, as in Figure 2, except for the R-5 sample. Meanwhile, the R-5 sample of cup noodles revealed higher levels of 5~7 dibenzo-p-dioxins and a lower OCDD percentage at 47 compared with the other samples.

In the pizza samples, little difference was found between the congeners, as shown in Figure 3. Yet most of the samples exhibited a similar tendency of high proportions of higher

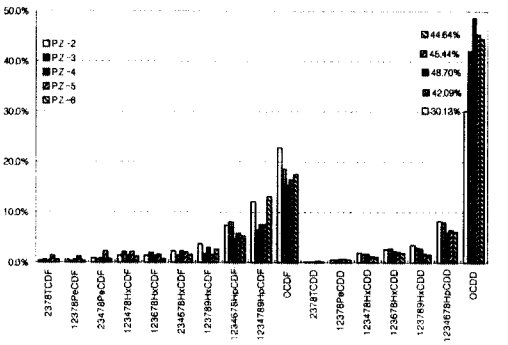


Figure 3. Distribution of 2,3,7,8-substituted PCDD/DFs in pizza.

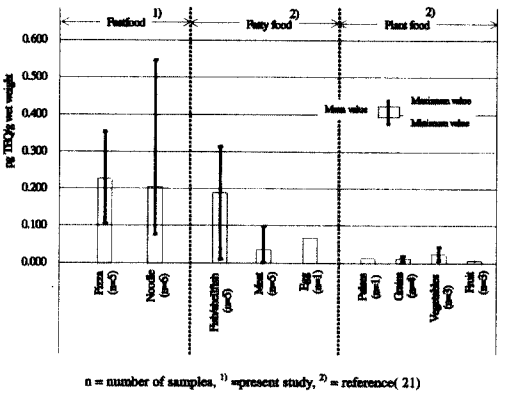
chlorinated compounds.

Comparison with General Food Group

The objective of the current study was to compare and estimate the difference in the TEQ values between general foodstuffs and fast food. The level of PCDD/Fs in Korea retail food is briefly outlined below.[21] Using gathered data, the total concentration of PCDD/Fs in fatty food samples had a whole weight basis ranging between 0.020 to 6.332 pg/g-wet-weight, while plant food samples ranged between 0.369 to 1.614 pg/g-wet-weight. The mean TEQ values of retail food samples were found to be 0.0008~0.315 pg TEQ/g-wet-weight in fatty foods and 0.005~0.042 pg TEQ/g-wet-weight in plant foods. OCDD was found to be the predominant congener among the PCDDs, while 1,2,3,4,6,7,8-HxCDF accounted for the highest value among the PCDFs.

During the present study, the levels of PCDD/Fs found in noodles were relatively higher at mean value 22.64(ranging between 6.905~48.546) pg/g-wet-weight, with mean TEQ values 0.220 (ranging between 0.077~0.545) pg TEQ/g-wet-weight and similarly those of pizzas were 8.41(ranging between 3.064~12.066) pg/g-wet-weight, with mean TEQ values 0.230 (ranging between 0.108~0.354) pg TEQ/g-wet-weight, respectively.

As shown in Figure 4, the PCDD/Fs levels in hamburgers and chicken were similar to



n = number of samples, 1) =present study, 2) = reference(21)

Figure 4. Comparison of TEQ levels between Korean retail food groups and fast food.

those in the animal food groups, yet the mean TEQ values of pizza and noodle were relatively higher than compared with the fish/shellfish groups, which exhibited the highest level among all the general food groups.

Furthermore, the daily intakes of noodles and pizzas obtained from the KHIDI in 1999 were found to be 15.8 and 0.8 g/day, it was assumed that the levels of dioxin intakes through these foods are 3.245 and 0.182 pg TEQ/day at mean values.

The estimated values in the present study record the one-tenth of previous study, when compared with the dietary daily intake of dioxins, which was approximately 37.7 pg TEQ/day.

An earlier study conducted reported, the ratio of the staple food intake for Koreans, such as grains, cereals, and vegetables, was 70%, whereas the ratio of the fish/shellfish intake was only about 7%. Nonetheless, the estimated dioxin intake via fish/shellfish ingestion was reported to be considerably higher at approximately 40%. In the present study, the levels of dioxins were based primarily on the estimated daily intake of fast food only noodles and pizza, it is sought that if a broad range of fast food samples being consumed are considered for future sampling, we might be able to achieve higher levels when compared to the present study.

According to two separate studies on daily intake, when equal proportions of fast food and fish/shellfish were mixed together, similar levels of dietary intakes were noted, even though higher levels of dioxins were observed in the fast food. Although no estimation of fast food was preformed in the previous studies, than compared with the results from the present study it would appear that the fast food groups might be a major controlling group with regard to dioxin intake through fish/shellfish. As such, it is expected that the data from the present study can set a baseline for future research on estimating the total dioxin exposure in Korea.

CONCLUSION

An estimation of the PCDD/Fs levels in fast food was conducted in response to the rising concern over the increased consumption of fast food in Korea.

The TEQ levels of PCDD/Fs in pizza and noodles, as representative fast foods, were found to be 0.108~0.354 pg TEQ/g-wet-weight for pizzas and 0.077~0.545 pg TEQ/g-wet-weight for noodles. The mean TEQ values for pizza and noodles were relatively high when compared with fish/shellfish, known to contain the highest level among general foods.

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