CONCENTRATIONS OF DECHLORANE COMPOUNDS IN FOODSTUFFS OBTAINED FROM RETAIL MARKETS AND ESTIMATES OF DIETARY INTAKE

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Abstract
A total of 175 samples, composed of 35 different foodstuffs, were obtained from retail markets in Korea and analyzed to investigate the contamination status and dietary intake of dechlorane compounds, including dechlorane plus (DP), mirex, dechlorane (Dec) 602, dechlorane (Dec) 603, and dechlorane (Dec) 604. The concentrations of DP, mirex, Dec 602, and Dec 603 ranged from ND to 169.85 pg/g wet weight (ww), 106.15 pg/g ww, 107.30 pg /g ww, 20.81 pg/g ww, respectively, while Dec 604 was not detected in all samples. The estimated dietary daily intake of DP, 11.2 ng/day, was one to three orders of magnitude higher than other dechloranes. The food group with the highest contribution to dietary daily intake of DP was grain.

Introduction
Dechlorane plus (DP, $C_{18}H_{12}Cl_{12}$) is a highly chlorinated flame retardant that is used in electrical wires, cable coatings, computer connectors, and plastic roofing materials.[1] DP has been used as a substitute for mirex (also called dechlorane, $C_{10}Cl_{12}$), which is employed as an insecticide and a flame retardant. Around the same time, other dechloranes, such as dechlorane 602 (Dec 602, $C_{14}H_4Cl_{12}O$), dechlorane 603 (Dec 603, $C_{17}H_8Cl_{12}$), and dechlorane 604 (Dec 604, $C_{13}H_4Br_4C_{l6}$), were commercialized for the replacement of mirex.[2] DP is classified as a high-production-volume (HPV) chemical by the United States Environmental Protection Agency and is listed on Canada's Domestic Substances List (DSL) by Environment Canada. Furthermore, Dec 602 and 604 are listed on the Non-domestic Substances List by Environment Canada.[3] Although potential toxicity of DP to fish and sediment-bearing organisms was demonstrated by the EPA HPV challenge program, there are no regulations on the production and use of DP.[4]

Although DP has been used widely for over forty years, the existence of DP in the environment was observed recently. Hoh et al. first detected DP in ambient air, sediment, and fish samples from the Great Lakes region.[5] The human exposure pathway to DP has received increased attention. The human exposure pathway to flame retardants includes the inhalation of indoor air, dermal absorption and ingestion of dust, and the intake of foodstuffs.[6] Some studies raised the possibility of human exposure to DP through ingestion of dust.[7,8] The long-range atmospheric transport of DP into Antarctica and its bioaccumulation in the Lake Winnipeg food web were presented; these characteristics agree with those of the legacy POPs.[9,10] In addition, considering the abundance in various matrices and the relatively long usage period, the intake of foodstuffs is likely to contribute to human exposure of DP as it is for legacy POPs. Nevertheless, the dietary exposure of DP has not been investigated until now.

In this study, various foodstuffs, including cereal, vegetable, meat, fish, egg, and dairy products, were analyzed to determine the concentrations of DP and other dechloranes (Dec 602, 603, 604, and mirex). Based on these results, the human daily exposure dose of dechlorane compounds through dietary intake was estimated. This study will provide not only the concentration of dechlorane compounds in foodstuffs from Korea but also the degree of human exposure to them.

Materials and Methods
Sample collection: Thirty-five different foodstuffs were selected. In March 2011, food samples were collected from both supermarkets and traditional markets located in 5 different regions (Seoul, Daejeon, Gangneung, Gwangju, and Busan). A total of 175 food samples were analyzed (5 samples of each foodstuff). After collection,

edible portions of foodstuffs were homogenized using a blender and frozen at -20 ºC until analysis.

Sample analysis: With the exception of liquid samples, such as milk and ice cream, every food sample was weighed (approximately 5g) and mixed with the same amount of anhydrous sodium sulfate (Na_2SO_4). Then, the internal standard (^{13}C-mirex) was added. Ultrasonication was employed to extract the samples for thirty minutes; this process was repeated. Cleanup of the samples was then performed with multi-layer silica gel columns. The column was eluted with 100 mL of hexane, followed by 100 mL of hexane:dichloromethane (1:1). After evaporating the solvent, the recovery standard (^{13}C-PCB 70) was added to the sample. Liquid-liquid extraction was performed for the liquid food samples, such as milk and ice cream. DP and other dechloranes were analyzed using a JMS-800D high-resolution mass spectrometer (JEOL, Japan) coupled with a 6890N gas chromatograph (Agilent Technologies, USA).

Chemicals: Syn- and anti-DP were purchased from Wellington Laboratories Inc. (Guelph, On, Canada), and Dec 602, Dec 603, and Dec 604 were purchased from Toronto Research Chemical Inc. (Toronto, On, Canada). Mirex was supplied by Cambridge Isotope Laboratories Inc. (Cambridge, MA, USA). The mass-labeled ^{13}C-mirex and ^{13}C-PCB 70 were supplied by Cambridge Isotope Laboratories Inc. (Cambridge, MA, USA) and used as internal and recovery standards, respectively.

Results and Discussion

Concentration of DP

The concentrations of mirex, Dec 602, Dec 603, syn-DP, anti-DP, ∑DPs (sum of syn- and anti-DP), and fanti (the fractional abundance of the anti-isomer) in foodstuffs based on the wet weight are shown in Table 1; Dec 604 was below its detection limit in all samples. The concentrations based on the lipid weight are described in Table S2. The concentrations were calculated using zero for no detection (ND).

The mean ∑DPs ranged from ND to 169.85 pg/g wet weight (ww). The syn- and anti-DP concentrations were detected to be 83.4% and 79.4% in all foodstuffs, respectively. The highest mean concentration of ∑DPs was detected in bovine liver with 169.85 pg/g ww, followed by Spanish mackerel, oyster, and dried anchovy with 134.50, 80.78, and 77.79 pg/g ww, respectively. Previous studies related to DP were principally focused on marine species, such as oysters and fishes, and birds, including their eggs.[1,11,12,13,14] However, in this study, we analyzed all foodstuffs, including vegetables, dairy products, meats, and fishes. Thus, we could observe the contamination status of DP in various matrices. The significant finding, which was displayed in every food group, was a similar concentration of ∑DPs and is important evidence of the wide-spread exposure to DP in Korea's environments.

Concentration of other dechloranes

Mirex was not registered in Korea as a pesticide. In this study, however, mirex was detected in dairy products, meats, fishes, and shellfishes. Baek et al. also detected a relatively lower concentration of mirex in Korea than in China.[15] Mirex is still used as an insecticide in China. Consequently, long-range transport of mirex from China could influence the environment around Korea. Fish and shellfish samples showed a relatively higher concentration of mirex than meat and dairy product samples. The concentration of mirex in fatty fishes, such as Spanish mackerel and mackerel, was especially high among the fish samples.

There was no information about the use or import of Dec 602 and 603 in Korea. However, in this study, Dec 602 and 603 were detected in some samples. Concentrations of Dec 602 and 603 were much lower than that of DP, which meant that these chemicals might be used in small amounts in Korea, or like mirex, could be transported from China. Jia et al. observed a higher concentration of Dec 602 and 603 in oyster samples from the northern China coastal areas.[12]

Intake estimation of dechloranes

The dietary daily intake of dechloranes via selected Korean foodstuffs was estimated, ranging from 35.1 pg/day (Dec 603) to 11.2 ng/day (DP). Among dechloranes, the estimated value of DP was one to three orders of magnitude higher than the others. This value was comparable to the dietary daily intake of PBDEs (a sum of 27 congeners) estimated to 13.0 ng/day in Korea.[16] In the case of DP, rice (3.9 ng/day) had the highest contribution to the dietary daily intake, followed by milk (2.1 ng/day) and pork (1.2 ng/day). The contribution of DP according to various food groups is shown in Figure 1. The principal dietary sources of POPs, such as dioxins, varied according to traditional dietary habits among different countries, e.g., dairy products and meat in the US, and fish in Japan. Traditional Korean dietary habits are characterized by a small contribution from animal-based foods and a large contribution from vegetable-based foods to the total food intake. Consequently, in spite of the relatively low concentration of DP in grain, its strong contribution to dietary daily intake was derived from the traditional Korean dietary habits. Son et al. found that rice contributed to over 50% of the dietary daily intake of 62 PCBs in Korean foodstuffs.[17] In other dechloranes, the contribution of meat, fish and shellfish made up almost all of the daily intake due to their relatively high concentrations.

Table 1

Concentrations (pg/g wet weight) of mirex, Dec 602, Dec 603, *syn*-DP, *anti*-DP, ∑DPs, and f_{anti} in foodstuffs

Food groups	Food items	Mirex	Dec 602	Dec 603	*syn*-DP	*anti*-DP	∑DPs	f_{anti}
Vegetable	Chinese cabbage	ND	ND	ND	0.60 ± 1.20[a]	2.22 ± 4.95	2.82 ± 6.15	0.79
	Onion	ND	ND	ND	ND	ND	ND	-
	Potato	ND	ND	ND	0.67 ± 1.49	3.35± 16.75	4.02 ± 8.98	0.83
Grain	Rice	ND	ND	ND	2.95±3.00	18.73±16.97	21.68 ± 19.75	0.82
Fruit	Apple	ND	ND	ND	0.99 ± 2.22	1.23 ± 2.74	2.22 ± 4.96	0.86
Noodle	Ramen	ND	ND	ND	9.33 ± 6.59	40.83 ± 29.09	50.16 ± 35.69	0.81
Seaweed	Brown seaweed	ND	ND	ND	2.82 ± 2.83	7.11 ± 7.85	9.94 ±10.65	0.72
Legume	Tofu	ND	ND	ND	3.59 ± 5.43	21.05 ± 27.60	24.65 ± 32.99	0.85
Condiment	Soybean paste	ND	ND	ND	4.81 ± 6.07	27.81 ± 27.94	32.62 ± 34.00	0.85
Plant fat	Soy oil	ND	ND	ND	3.32 ± 1.56	15.81 ± 5.63	19.13 ± 7.16	0.83
Egg	Egg	ND	ND	ND	3.19 ± 0.41	12.12 ± 1.21	15.31 ± 1.41	0.79
Dairy product	Cheese	0.41 ± 0.21	0.26 ± 0.57	ND	0.61 ± 0.59	3.65 ± 2.92	35.80 ± 3.50	0.86
	Milk	1.53 ± 0.64	ND	ND	5.30 ± 1.66	22.75 ± 8.11	28.05 ± 9.69	0.81
	Ice cream	0.53 ± 0.08	ND	ND	7.36 ± 4.69	31.96 ± 19.66	39.32 ± 24.35	0.81
Meat	Mixed sausage	0.13 ± 0.05	0.39 ± 0.40	ND	2.31 ± 1.51	7.53 ± 6.64	9.84 ± 8.09	0.77
	Chicken	0.51 ± 0.53	0.27 ± 0.60	ND	3.96 ± 4.58	13.56 ± 15.48	17.53 ± 20.02	0.77
	Ham	0.94 ± 0.40	2.49 ± 1.22	ND	11.94 ± 8.79	46.37 ± 34.51	58.31 ± 43.28	0.80
	Pork	1.67 ± 0.61	0.95 ± 1.10	0.41 ± 0.53	9.91 ± 10.65	41.29 ± 43.99	51.20 ± 54.57	0.81
	Pork belly	2.11 ± 0.60	5.27 ± 1.56	ND	6.66 ± 3.71	31.25 ± 21.50	37.91 ± 25.12	0.82
	Beef	5.63 ± 2.96	15.44 ± 11.73	ND	3.45 ± 1.50	14.90 ± 6.17	18.35 ± 7.40	0.81
	Bovine liver	1.00 ± 1.22	ND	ND	43.02 ± 24.75	126.83±79.81	169.85 ± 104.04	0.75
Fish and shellfish	Clam	0.76 ± 1.16	3.46 ± 1.18	0.11 ± 0.25	14.81 ± 7.33	57.84 ± 32.70	72.66 ± 39.95	0.80
	Oyster	0.71 ± 1.59	4.94 ± 1.76	ND	17.49 ± 4.97	63.28 ± 11.22	80.78 ± 16.07	0.78
	Squid	1.20 ± 1.59	2.83 ± 3.48	ND	2.80 ± 1.75	7.90 ± 5.11	10.70 ± 6.43	0.74
	Crab	17.68 ± 8.52	2.89 ± 1.84	ND	2.55 ± 1.66	4.36 ± 5.97	6.91 ± 6.65	0.63
	Fish paste	1.22 ± 1.43	0.23 ± 0.42	ND	6.64 ± 2.14	23.93 ± 5.07	30.56 ± 6.69	0.78
	Spanish mackerel	107.30±39.29	20.81 ± 4.50	ND	28.36 ± 5.09	106.15±23.73	134.50 ± 28.72	0.79
	Hairtail	20.54 ± 12.55	3.29 ± 2.57	ND	1.11 ± 1.58	3.64 ± 6.20	4.75 ± 7.77	0.77
	Pollack	2.69 ± 1.75	0.08 ± 0.19	ND	0.43 ± 0.66	0.14 ± 0.30	0.57 ± 0.95	0.24
	Yellow corvine	36.01 ± 16.22	1.96 ± 0.95	ND	0.56 ± 0.55	2.75 ± 2.77	3.31 ± 3.22	0.83
	Eel	26.19 ± 4.68	0.82 ± 1.83	ND	5.41 ± 3.91	21.07 ± 11.69	26.48 ± 15.38	0.80
	Salmon	35.78 ± 19.44	0.89 ± 1.99	ND	4.45 ± 1.10	20.21 ± 5.63	24.66 ± 6.65	0.82
	Pacific saury	12.79 ± 1.66	4.70 ± 9.06	ND	1.19 ± 1.68	7.30 ± 7.34	8.49 ±8.20	0.86
	Mackerel	81.34 ± 36.14	9.01 ± 3.32	ND	3.31 ± 4.03	23.35 ± 19.82	26.66 ± 23.70	0.88
	Dried anchovy	24.45 ± 7.97	ND	ND	26.39 ± 26.67	51.40 ± 73.49	77.79 ± 99.98	0.66

% detected (n=175)	62.9	41.1	1.1	82.9	78.9		
LOD	0.39	0.42	0.40	0.31	0.40		

[a] mean ± std

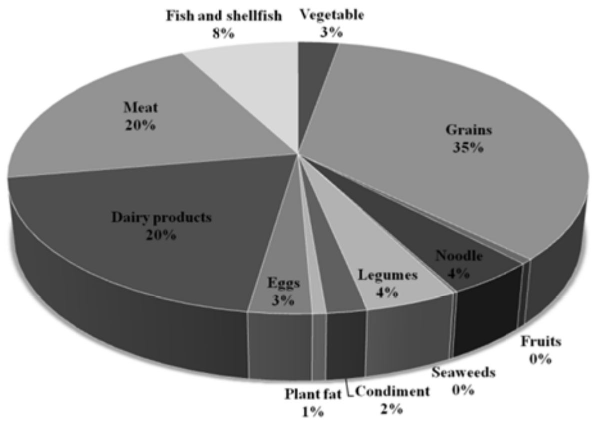

Fig. 1. Percentage contribution of various food groups to daily intake of DP

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