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INVESTIGATION OF DIETARY EXPOSURE TO DECHLORANE PLUS AND RELATED COMPOUNDS IN KYUSHU DISTRICT, JAPAN

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Introduction

Dechlorane Plus (DP) is an additive chlorinated flame retardant that is used as a substitute for Dechlorane (Mirex), which was already regulated for use in the 1970s. DP has the potential for bioaccumulation and persistence in the environment because of its highly chlorinated chemical structure and high lipophilic property, with a log Kow value of 9.3[1)]. DP has mainly been investigated in the areas around DP manufacturing plants, both in North America and China, and has been identified in various environmental matrices including air, soil, sediment and fish[2)3)]. As DP products are reportedly sold and used worldwide, the occurrence of this compound in the environment should not be considered simply a local issue related to DP production sites.

Sakiyama et al. (2012) first reported on the existence of DP in environmental samples in Japan, including soil, sediment, and dust samples collected in domestic urban regions[4)]. Thus, data on the presence of DP in environmental media in Japan are currently very limited, as are data on DP in foodstuffs[5)6)], and human dietary exposure to DP[7)].

In this report, we present data on the concentration of DP and related compounds, including Dechlorane (Mirex), Chlordene Plus (CP), Dechlorane 602 (Dec602), Dechlorane 603 (Dec603), and Dechlorane 604 (Dec604), in market-basket study samples prepared in Fukuoka, in the Kyushu district of Japan, and on the estimation of dietary exposure to the chemicals.

Materials and methods

In 2015, we collected 167 common retail foods in Fukuoka prefecture selected according to the results of the National Nutrition Survey, conducted by the Ministry of Health, Labor and Welfare, Japan. These food samples were weighed according to the official consumption data of each, and cooked in ways typical of the Japanese diet. Samples were then blended to form 13 official food group composites. Table 1 shows the classification of the 13 food groups and their daily consumption in the Kyushu district.

Figure 1 presents our analytical method. Non-labeled and ^{13}C-labeled standards for individual syn- and anti-DP were purchased from Cambridge Isotope Laboratories (MA), and preserved at room temperature to avoid reduction of the concentration of the DP isomer[4)]. A total of 10 g of the market-basket samples was weighed and mixed in a bottle tube with 20 g of glass beads, which varied in particle diameter from 0.991–1.397 mm. After mixing, the sample was spiked with labeled standards mixture, and was extracted using an ASE-350 (Dionex, CA) under conditions of 1500 psi, with hexane as an the extraction solvent. The extracts were washed with 5% NaCl aq., and concentrated to dryness in order to determine the lipid content gravimetrically. The lipid extract was dissolved with hexane and purified with a sulfuric acid treatment. The solution was purified with a Sep-pak Vac RC (500 mg) florisil column, and then re-purified with a Supelclean Sulfoxide (3 g) column[4)]. The eluent was concentrated and fortified with ^{13}C-PCB111 as a syringe spike. Finally, the volume was adjusted to 50 µl with nonane.

The determination of DP and other dechlorane compounds was performed using an Agilent 6890 GC equipped with an Autospec-Premier MS (HRGC/HRMS). Details of the operating conditions of the system are shown in Table 2. 2 µl of the sample was injected to HRGC/HRMS. The limit of detection for each DP isomer was 0.2 pg/g, for Dec602 was 0.05 pg/g, for Dec603 was 0.06 pg/g, for Dec604 was 0.8 pg/g, for Declorane (Mirex) was 0.01 pg/g, and for CP was 0.03 pg/g on a wet weight basis, respectively (S/N=3).

Results and discussion

As shown in Table 3, both syn-DP and anti-DP were detected in all market-basket samples. The concentrations of syn-DP observed during this study ranged from 0.72 to a maximum of 2.4 pg/g-wet, with a mean concentration of 1.5 pg/g-wet. Concentrations of anti-DP ranged from 2.6 to a maximum of 7.8 pg/g-wet, with a mean concentration of 3.8 pg/g-wet. The mean total DP isomers (ΣDP) concentration

was 5.2 pg/g-wet, ranging from 3.3 to a maximum of 9.8 pg/g; the latter value was measured in food group No.4 (oil and fats). The concentrations of the syn-DP and anti-DP in group No. 10 (fish and shelfish) were 1.9 and 5.6, respectively; these values were similar to mean concentration of 2.2 pg/g-wet for syn-DP and 3.7 pg/g-wet for anti-DP, respectively, in 20 marketed fish samples collected in western Japan, 2013[6].

The mean concentration ratio of anti-DP to total DP (f_{anti}) in 13 market-basket samples was calculated to be 0.72, ranging from 0.53–0.79 (Table 2). It has been reported that f_{anti} values ranged from 0.64–0.85 for technical DP manufactured in the United States, and from 0.59–0.60 for technical DP manufactured in China[1]. Our f_{anti} values were relatively close to those of technical DP from the United States, and were close to those of outdoor dust (0.83), soil (0.81) and sediments (0.81) collected in Japan[4].

Dec602 was detected in all food groups and at the highest contributions among all the declorane compounds measured in this study. Mean concentrations were 14 pg/g-wet, ranging from 3.1 to a maximum of 79 pg/g-wet; the latter value was measured in group No.10 (fish and shelfish). On the other hand, the concentrations of CP and Dec604 were obviously low, and were detected in only two and four of the food groups, respectively. Decrorane (Mirex) was detected in all food groups, and relatively high concentrations were measured in groups No.10 and 11 (meat and eggs). This result indicated that bioaccumulation of the compounds in animal-based food continues after its end-useage.

Estimated dietary intake of DP and related compounds is shown in Table 4. The dierary intake values of ΣDP and ΣDechloranes by an average Japanese adult in Kyushu district were estimated to be 8.9 ng/day and 35 ng/day, respectively. The food group beverages (No.9) had the highest contribution (approx. 25%) to the dietary intake in both estimations. The dietary intake value of ΣDP obtained in this study (8.9 ng/day) was higher than that estimated in another survey conducted in Osaka region, Japan (0.58 ng/day)[7], and close to the recent survey performed in Korea (11.2 ng/day)[8].

Acknowledgements

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Table 1 Classification of food samples and their average daily consumption in Kyushu district

Group No.	Composition	No. of food stuffs	Daily intake (g/day/person)
1	Rice and rice products	6	391.7
2	Cereals, seeds and potatoes	19	202.0
3	Sugar and confectionary	12	32.7
4	Oils and fats	5	8.8
5	Pulses	11	62.0
6	Fruits	15	96.5
7	Green vegetables	13	74.9
8	Other vegetables, mushrooms and seeweed	19	169.5
9	Beverages	9	619.8
10	Fish and shellfish	21	66.9
11	Meat and eggs	11	108.9
12	Milk and dairy products	9	108.6
13	Seasonings	17	81.5

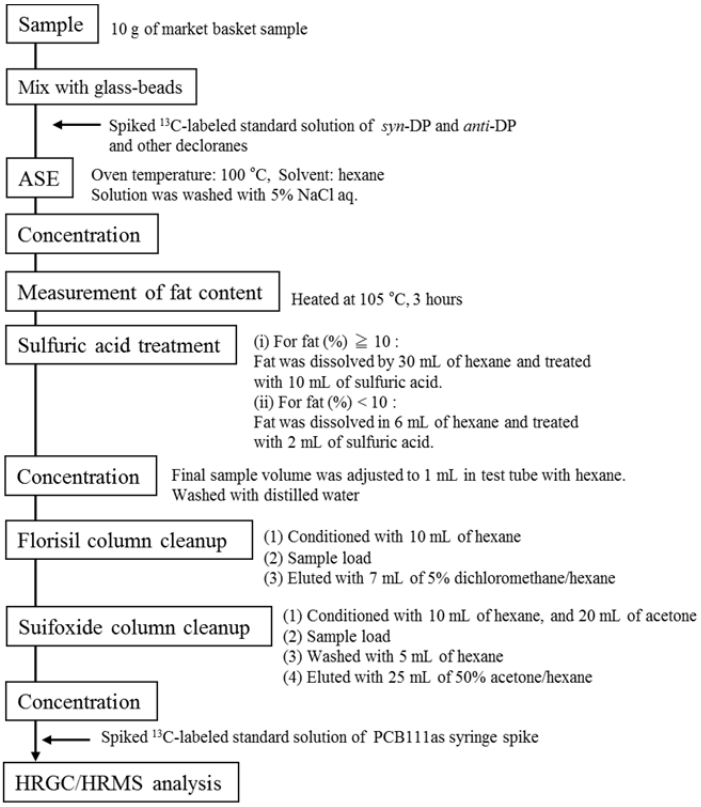

Fig. 1 Analytical method of DP and related compounds in market-basket samples

Table 2 Analytical conditions of HRGC/HRMS

GC condition		
Column	DB-5 (Agilent, 15 m length, 0.25 mm i.d.)	
Injection mode (Injection volume)	Splitless (2 μL)	
Injector temperature	280°C	
Carrier gas (Flow rate)	He (1.0 mL/min)	
Oven temperature	120°C (1 min hold) – 30°C/min – 240°C – 5°C/min – – 275°C – 40°C/min– 320°C (2.88 min hold)	
MS condition		
Ionization mode	EI	
Ionization voltage	38 eV	
Ion source temperature	280°C	
Resolutiom	10000 <	
Monitor ions		
Dechlorane, Dec602, DP	271.8102	273.8072
Dec603	262.8570	264.8540
Dec604	419.7006	417.7026
$^{13}C_{10}$-Dechlorane, $^{13}C_{10}$-Dec602, $^{13}C_{10}$-DP	276.8269	

Table 3 Concentrations (pg/g-wet) of DP and related compounds in market-basket samples

Group No.	Dechlorane	CP	Dec602	Dec603	Dec604	*syn*-DP	*anti*-DP	ΣDP	f_{anti}
1	0.20	ND	3.1	1.1	ND	1.4	3.2	4.6	0.69
2	0.25	ND	4.9	0.98	ND	2.4	2.6	5.0	0.53
3	0.33	0.050	4.6	1.4	0.46	2.2	3.9	6.1	0.64
4	0.48	ND	6.4	2.0	ND	2.0	7.8	9.8	0.79
5	0.20	ND	5.4	1.1	ND	0.90	3.4	4.3	0.79
6	0.35	ND	3.8	0.95	0.18	0.85	2.8	3.6	0.76
7	0.22	ND	5.1	0.89	ND	0.72	2.7	3.4	0.79
8	0.33	ND	4.9	0.78	0.22	1.6	3.2	4.8	0.67
9	0.71	ND	9.7	1.0	0.25	0.73	2.6	3.3	0.78
10	7.2	0.83	79	3.5	ND	1.9	5.6	7.5	0.74
11	2.3	ND	43	4.2	ND	1.9	5.5	7.4	0.75
12	0.65	ND	9.5	0.98	ND	1.5	2.8	4.3	0.65
13	0.36	ND	7.5	1.1	ND	0.83	3.0	3.8	0.78
Mean	1.0	0.068	14	1.5	0.085	1.5	3.8	5.2	0.72
Min.	0.20	ND	3.1	0.78	ND	0.72	2.6	3.3	0.53
Max.	7.2	0.83	79	4.2	0.46	2.4	7.8	9.8	0.79

Table 4 Estimated dietary intake (ng/g) of DP and related compounds in Kyushu district, Japan

Group No.	Dechlorane	CP	Dec602	Dec603	Dec604	*syn*-DP	*anti*-DP	ΣDP	ΣDechloranes
1	0.078	–	1.2	0.43	–	0.55	1.3	1.8	3.5
2	0.050	–	0.99	0.20	–	0.48	0.53	1.0	2.2
3	0.011	0.0016	0.15	0.046	0.015	0.072	0.13	0.20	0.42
4	0.0042	–	0.056	0.018	–	0.018	0.069	0.086	0.16
5	0.012	–	0.33	0.068	–	0.056	0.21	0.27	0.68
6	0.034	–	0.37	0.092	0.017	0.082	0.27	0.35	0.86
7	0.016	–	0.38	0.067	–	0.054	0.20	0.26	0.72
8	0.056	–	0.83	0.13	0.037	0.27	0.54	0.81	1.9
9	0.44	–	6.0	0.62	0.15	0.45	1.6	2.1	9.3
10	0.48	0.055	5.3	0.23	–	0.13	0.37	0.50	6.6
11	0.25	–	4.7	0.46	–	0.21	0.60	0.81	6.2
12	0.071	–	1.0	0.11	–	0.16	0.30	0.47	1.7
13	0.029	–	0.61	0.090	–	0.068	0.24	0.31	1.0
Total	1.5	0.057	22	2.6	0.22	2.6	6.3	8.9	35