Estimation of Dietary Intake of Dechlorane Flame Retardants in Japan, FY 2016

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Introduction

Dechlorane flame retardants have the potential for bioaccumulation and persistence in the environment because of its highly chlorinated chemical structure and high lipophilic property. Dechlorane Plus (DP), which has a log K_{ow} value of 9.3[1)], is used as a substitute for Dechlorane (Mirex) which was already regulated for use in the 1970s. Environmental DP levels have mainly been investigated in the areas around DP manufacturing plants, both in North America and China, and it has been identified in various environmental matrices including air, soil, sediment and fish[2)3)]. As DP and related 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 their 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)]. However, data on the presence of DP and related compounds in environmental media in Japan are currently very limited, as are data in foodstuffs[5)6)], and human dietary exposure to them[7)]. Previously, we performed a preliminary investigation of the concentration of DP and related compounds, including Dechlorane (Mirex), Chlordene Plus (CP), Dechlorane 602 (Dec 602), Dechlorane 603 (Dec 603), and Dechlorane 604 (Dec 604), in market-basket study samples prepared in Fukuoka, in the Kyushu district of Japan, and estimated the individual dietary exposure to the chemicals[8)]. In the present study, we determined concentrations of Dechloranes in market-basket study samples prepared in four regions of Japan, in FY 2016, to estimate potential dietary intakes of the chemicals.

Materials and methods

In 2016, we prepared market-basket study samples in ten different regions across Japan, and began to analyze four sample sets (region A, B, C and D) selected in the year. Table 1 shows the classification of foods into 13 groups and their mean daily consumption in the region A as an example. As a result, 166 common retail foods were collected in the region, and weighed according to consumption data from Japan's National Nutrition Survey. These food samples were cooked in ways typical of the Japanese diet, and the samples were then blended to prepare 13 food group composites.

Figure 1 presents an analytical method used in this study. A total of 10 g of the market-basket samples was mixed in a bottle tube with 20 g of glass beads, which varied in particle diameter from 0.991–1.397 mm. After freeze dry treatment, the sample was spiked with a labeled standards mixture, and was extracted using an ASE-350 extractor (Thermofisher Scientific, MA) under conditions of 1,500 psi, with hexane as an the extraction solvent. The extracts were 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-2,2',3,4,4',5,5'-heptabromodiphenylether (^{13}C-PBDE180) as a syringe spike. Finally, the volume was adjusted to 50 µL with nonane.

Table 1 Classification of food samples and their average daily consumption in region A

Group No.	Composition	Number of food stuffs	Daily intake (g/day/person)
I	Rice and rice products	6	344.7
II	Cereals, seeds and potatoes	19	162.6
III	Sugar and confectionary	12	32.8
IV	Oils and fats	5	9.5
V	Pulses	11	59.2
VI	Fruits	15	96.7
VII	Green vegetables	13	89.1
VIII	Other vegetables, mushrooms and seeweed	19	191.7
IX	Beverages	10	678.8
X	Fish and shellfish	21	71.1
XI	Meat and eggs	9	126.9
XII	Milk and dairy products	9	113.0
XIII	Seasonings	17	89.0

The determination of Dechloranes 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. The limit of detection for Dec 602 was 0.05 pg/g, for Dec 603, 0.06 pg/g, for Dec 604, 0.8 pg/g, for Dechlorane (Mirex), 0.03 pg/g, and for CP, 0.03 pg/g, respectively, all on a wet weight basis (S/N=3). Because the method blank value for each *syn*- and *anti*-DP isomer was not negligible, the data on each compound are not available at present.

Results and discussion

As shown in Table 3, Dec 602 was detected in all 52 market-basket samples and had the highest levels of all the dechlorane compounds measured in this study. The mean concentration was 2.7 pg/g-wet, ranging from 0.050 to a maximum of 39 pg/g-wet; the latter value was measured in group X (fish and shelfish) of region D. A high detection rate, about 92 %, was also observed for Dechlorane (Mirex), with relatively high concentrations in groups X and XI (meat and eggs). The mean concentration was 0.40 pg/g-wet, ranging from ND to a maximum of 7.4 pg/g-wet. This result indicated that bioaccumulation of the compound in animal-origin food continues after the regulation of use. On the other hand, CP and Dec 604 were rarely detected in the samples and those concentrations were quite low.

The estimated mean dietary intake of Dechloranes is shown in Table 4. The estimate assumed as zero when the concentration was under detection limit (ND=0). The mean dietary intake values of Dec 602 and Dec 603 were 3.2 and 0.26 ng/day, respectively. These are higher than those from the recent survey performed in Korea[9]. The intake of Dec 602 from group X was abundant and it comprised more than 60% of the total Dechloranes intake. In regard to Dechlorane (Mirex) intake, the contribution of group X was about 40% and was almost the same as that of VII (green vegetables). For Dec 603, the largest contribution rate (26%) was found in group I (rice and rice products), the staple diet for the Japanese population, while the contribution rates of animal-origin food groups X and XI were 16% and 19%, respectively.

The dietary intake of all Dechloranes excepting DP isomers by Japanese population were estimated to be 4.0 ng/day, ranging from 3.5 to a maximum of 4.6 ng/day. The mean values were lower than those of our preliminary investigation[8]. The food group X had the highest contribution (approx. 60%) to the dietary intake of Dechloranes. Our result indicated that the major compounds, Dec 602, Dec 603 and Dechlorane (Mirex) extended to a broad range of the environment, and were daily ingested from various sorts of food items in the Japanese market.

Acknowledgements

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References:

1. US EPA; http://www.epa.gov/HPV/pubs/summaries/dechlorp/c15635tp.pdf
2. Hoh E, Zhu L, Hites R.A. (2006); *Environmantal Science and Technoogy*. 40: 1184-1189
3. Wang D.G., Yang M, Qi H, Sverko E, Ma W.L., Li Y.F., Alaee M, Reiner E.J., Shen L. (2010); *Environ. Sci. Technol.* 44: 6608-6613
4. Sakiyama T, Fujimine Y, Nakano T. (2012); *Organohalogen Compounds*. 74: 146-149
5. Kakimoto K, Nagayoshi H, Yoshida J, Akutsu K, Konishi Y, Toriba A, Hayakawa K. (2012); *Chemosphere*. 89:416-419
6. Hori T, Miyawaki T, Takahashi K, Yasutake D, Yamamoto T, Kajiwara J, Watanabe T. (2014); *Organohalogen Compounds*. 76: 900-903
7. Kakimoto K, Nagayoshi H, Takagi S, Akutsu K, Konishi Y, Hayakawa K, Toriba A. (2014); *Ecotoxicology and Environmental Safety*. 99:69-73
8. Takahashi K, Yasutake D, Hori T, Kogiso T, Watanabe T. (2016); *Organohalogen Compounds*. 78: 1191-1195
9. Kim J, Son M. H., Kim J, Suh J, Kang Y, Chang Y. H. (2014) *Journal of Hazardous Materials*. 275: 19-25

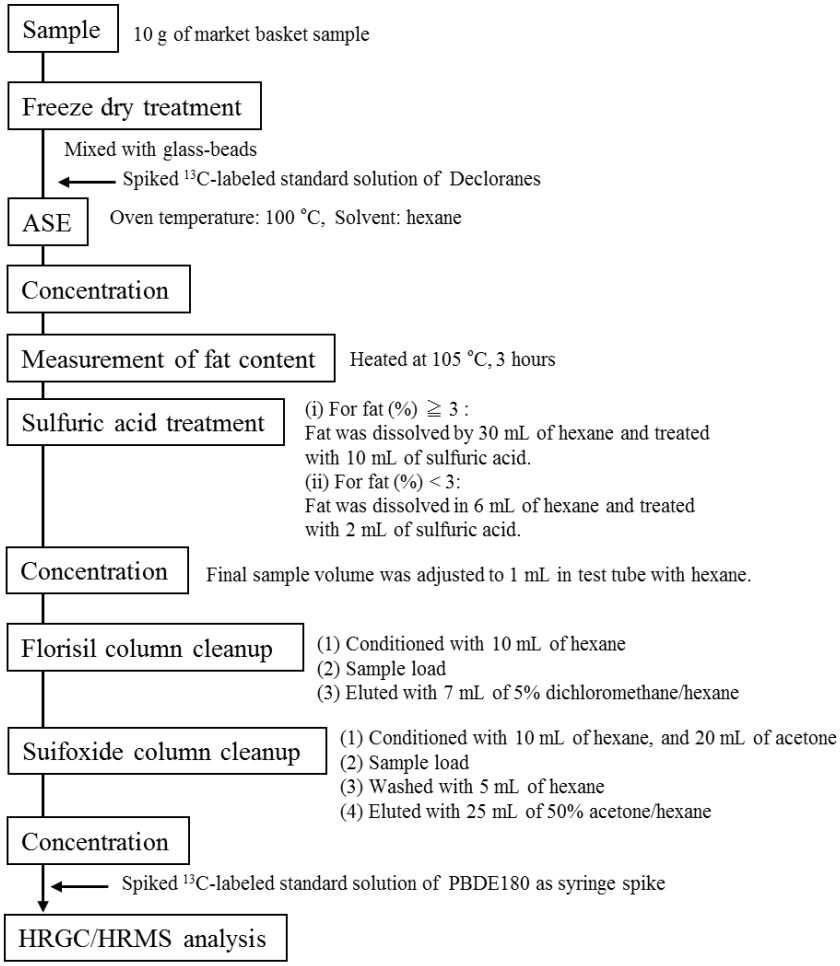

Fig. 1 Analytical method of DP and related compounds in market-basket samples

Table 2 Analytical conditions of HRGC/HRMS

GC condition	
Column	DB5（Agilent, 15m length, 0.25 mm i.d.）
Injection mode (Injection volume)	Split less (2μL)
Injector temperature	280℃
Carrier gas (Flow rate)	He（1.0 mL/min）
Oven temperature	120℃（1min hold）－30℃/min－240℃－5℃/min－275℃－40℃/min－320℃（2.88min hold）
MS condition	
Ionization mode	EI
Ionization voltage	38eV
Ion source temperature	280℃
Resolutiom	10000 <
Monitor ions	
Dechlorane, Dec 602,DP	271.8102, 273.8072
Dec 603	262.8570, 264.8540
Dec 604	419.7006, 417.7026
$^{13}C_{10}$-Dechlorane, $^{13}C_{10}$-Dec602	276.8269
$^{13}C_{12}$-2,2',3,4,4',5,5'-heptaBDE	415.9096, 413.8116

Table 3 Concentrations (pg/g-wet) of Dechloranes in market-basket samples

Region-A (pg/g)

Group No.	Dec602	Dec603	Dec604	CP	Dechlorane	Total
I	0.74	0.48	ND	ND	0.040	1.3
II	0.20	0.050	ND	ND	0.034	0.29
III	0.53	0.26	ND	0.049	0.087	0.92
IV	0.44	ND	ND	ND	0.33	0.77
V	0.19	0.10	ND	ND	0.024	0.32
VI	0.12	0.063	ND	ND	0.020	0.21
VII	0.21	ND	ND	0.034	0.064	0.31
VIII	0.12	ND	ND	ND	0.027	0.15
IX	0.065	0.048	ND	ND	0.017	0.13
X	27	0.41	ND	0.44	2.4	31
XI	3.8	0.32	ND	0.21	0.41	4.7
XII	0.39	0.081	ND	ND	0.047	0.51
XIII	0.12	0.53	ND	ND	0.61	1.3
Total	34	2.4	ND	0.74	4.1	41

Region-B (pg/g)

Group No.	Dec602	Dec603	Dec604	CP	Dechlorane	Total
I	0.18	0.050	ND	ND	0.023	0.25
II	0.71	0.038	ND	ND	0.0069	0.75
III	0.33	0.12	ND	ND	0.068	0.52
IV	0.55	0.72	ND	ND	ND	1.3
V	0.45	0.10	ND	ND	0.027	0.58
VI	19	0.038	ND	ND	0.023	19
VII	0.19	0.053	ND	ND	7.4	7.7
VIII	0.20	ND	ND	ND	0.040	0.24
IX	0.068	ND	ND	ND	ND	0.068
X	13	0.17	ND	ND	0.90	14
XI	1.1	0.11	ND	ND	0.28	1.5
XII	0.39	0.077	ND	ND	0.21	0.68
XIII	0.13	ND	ND	ND	0.011	0.14
Total	36	1.5	ND	ND	9.0	47

Region-C (pg/g)

Group No.	Dec602	Dec603	Dec604	CP	Dechlorane	Total
I	0.11	ND	ND	ND	0.023	0.14
II	0.16	0.061	ND	ND	0.033	0.25
III	0.47	0.036	ND	ND	0.041	0.54
IV	0.41	ND	ND	ND	0.27	0.68
V	0.69	0.042	ND	ND	0.013	0.74
VI	0.11	ND	ND	ND	0.031	0.14
VII	0.52	0.058	ND	0.058	0.032	0.67
VIII	0.16	ND	ND	ND	0.022	0.18
IX	0.17	0.052	ND	ND	0.014	0.24
X	21	0.44	ND	0.56	2.2	24
XI	1.7	0.57	ND	0.20	0.22	2.7
XII	0.40	0.11	ND	ND	0.086	0.60
XIII	0.35	0.11	ND	ND	0.10	0.56
Total	26	1.5	ND	0.82	3.1	31

Region-D (pg/g)

Group No.	Dec602	Dec603	Dec604	CP	Dechlorane	Total
I	0.094	0.050	ND	ND	0.0085	0.15
II	0.15	0.25	ND	ND	ND	0.41
III	0.36	0.15	ND	ND	0.095	0.61
IV	0.55	ND	ND	ND	0.20	0.75
V	0.088	0.15	ND	ND	0.079	0.31
VI	0.16	ND	ND	ND	ND	0.16
VII	0.12	ND	ND	0.089	0.038	0.25
VIII	0.12	ND	ND	ND	0.043	0.16
IX	0.054	ND	ND	ND	0.026	0.080
X	39	0.94	ND	0.83	3.5	44
XI	1.7	0.91	0.22	0.15	0.31	3.3
XII	0.45	0.16	ND	ND	0.15	0.76
XIII	0.050	0.18	ND	ND	0.074	0.30
Total	43	2.8	0.22	1.1	4.5	51

Table 4 Estimated mean dietary intake (ng/day) of Dechloranes in FY 2016

(ng/day)

Group No.	Dec602	Dec603	Dec604	CP	Dechlorane	Total
I	0.14	0.067	0	0	0.012	0.21
II	0.088	0.032	0	0	0.0043	0.12
III	0.019	0.0060	0	0.00043	0.0032	0.028
IV	0.0047	0.0018	0	0	0.0019	0.0084
V	0.023	0.0065	0	0	0.0023	0.032
VI	0.46	0.0024	0	0	0.0020	0.47
VII	0.025	0.0028	0	0.0041	0.18	0.22
VIII	0.028	0	0	0	0.0060	0.034
IX	0.061	0.018	0	0	0.0095	0.088
X	2.1	0.042	0	0.040	0.19	2.4
XI	0.23	0.050	0.0046	0.015	0.034	0.33
XII	0.048	0.013	0	0	0.015	0.075
XIII	0.013	0.018	0	0	0.018	0.049
Total	3.2	0.26	0.0046	0.060	0.48	4.0