Estimation of Dietary Intake of Dechlorane Plus and Related Compounds in a Japanese National Survey

Yasutake D[1], Sato T[1], Hori T[1], Watanabe T[2]

[1] Fukuoka Institute of Health and Environmental Sciences, 39 Mukaizano Dazaifu-shi, Fukuoka, Japan, 818-0136, yasutake@fihes.pref.fukuoka.jp; [2] National Institute of Health Sciences, 3-25-26 Tonomachi, Kawasaki-ku, Kawasaki-shi, Kanagawa, Japan, 210-9501

Introduction

Chlorinated flame retardants have the potential for bioaccumulation and persistence in the environment because of their highly chlorinated chemical structures and high lipophilia. Dechlorane Plus (DP), which has a log K_{ow} value of 9.3[1)], is used as a substitute for Dechlorane (Mirex), whose use has been regulated since the 1970s. Environmental DP levels have been investigated mainly in areas around DP manufacturing plants in North America and China, and DP has been identified in various environmental matrices including those of air, soil, sediment, and fish[2)3)]. As DP and related products are sold and used worldwide, the occurrence of these compounds in the environment should not be considered simply a local issue related to their production sites. Sakiyama et al. (2012) first reported on the presence of DP in environmental samples in Japan, including soil, sediment, and dust samples collected in residential urban regions[4)]. However, data on the presence of DP and related compounds in environmental media and food items in Japan are currently very limited[5)6)], as are data about human dietary exposure to them[7)]. Previously, we performed a preliminary investigation into concentrations of DP and related compounds, including Dechlorane 602 (Dec 602), Dechlorane 603 (Dec 603), Dechlorane 604 (Dec 604), Chlordene Plus (CP), and Dechlorane (Mirex), in market-basket (MB) samples prepared in Fukuoka, in the Kyushu district, located at south west of Japan, and estimated dietary exposure to these chemicals[8)]. In this study, we determined concentrations of seven dechlorane related compound including Dec 602, Dec 603, Dec604, *syn*-DP, *anti*-DP, CP, and Dechlorane (whole of these seven compounds referred as "Dechloranes") in MB-samples prepared in ten different regions and estimated the dietary intake of Dechloranes in Japan.

Materials and methods

In 2016, we prepared MB-samples in ten different regions of Japan under the project in which the local governmental-institutes participated. Table 1 shows the classification of food items into 13 groups and, as an example, the mean per capita daily consumption of them in a region. In this example, we collected 166 common retail food items and cooked them in typical Japanese way if necessary. According to the consumption data from Japan's National Nutrition Survey, the foods were weighed and blended to prepare a composite sample, i.e. MB samples for each of the 13 food groups.

Figure 1 presents an analytical method used in this study. A total of about 5 g of each MB-sample was mixed in a bottle tube with glass beads that ranged in diameter from 0.991 to 1.397 mm. The samples were freeze-dried, spiked with a labeled standards mixture, and extracted using an ASE-350 extractor (Thermo Fisher Scientific, Waltham, MA, USA) at 1,500 psi, with hexane as 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 consecutively purified with a Supelclean sulfoxide (3 g)

Table 1 Classification of market-basket samples and average daily comsumption in a regions

Group No.	Composition	Number of food items	Dairy intake (g/day)
I	Rice and rice products	6	345
II	Cereals, seeds and potatoes	19	163
III	Suger and confectionary	12	33
IV	Oils and fats	5	10
V	Pulses	11	59
VI	Fruits	15	97
VII	Green vegetables	13	89
VIII	Other vegetables, mushrooms and seaweeds	18	192
IX	Beverages	10	679
X	Fish and shellfish	21	71
XI	Meat and eggs	9	127
XII	Milk and dairy products	9	113
XIII	Seasonings	17	89

column (Sigma-Aldrich, St. Louis, MO, USA) [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 25 µL with nonane. The Dechloranes were identified and quantified using an Agilent 6890 gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) equipped with an Autospec-Premier mass spectrometer (HRGC/HRMS; Waters, Milford, MA, USA). Details of the operating conditions of the system are shown in Table 2.

Results and discussion:

Concentration of Dechloranes in the MB-samples

The mean concentration of each of Dechloranes in ten regions is shown in Table 3. The concentrations of each compound in all 130 MB-samples (i.e., 13 food groups in ten regions) were within the following ranges. Dec 602 : ND-63 pg/g wet weight (ww), Dec 603 : ND-1.3 pg/g ww, Dec 604 : ND-1.4 pg/g ww, *syn*-DP : ND-10 pg/g ww, *anti*-DP : ND-36 pg/g ww, CP : ND-0.83 pg/g ww, Dechlorane : ND-7.4 pg/g ww. As shown in Table 3, Dec 602, *syn*-DP, *anti*-DP, and Dechlorane were detected in almost all MB-samples. Dec 603 was detected in the MB samples except for the sample for food groups with low fat contents, such as groups VI (fruits), VII (green vegetables), VIII (other vegetables and seaweeds), and IV (beverages). Dec 602 and Dechlorane concentrations were highest in group X (fish and shellfish). We attribute this to the high bioaccumulation levels of Dec 602 and Dechlorane. Dec 604 was detected in only 3 samples, all in groups VI and XI. Dec 604 and CP were rarely detected in the samples and their concentrations were quite low. CP was detected in 26 MB-samples, mainly in groups X and XI (meat and eggs).

Dietary intake of Dechloranes

The estimated mean dietary intake of each of Dechloranes in ten regions is shown in Table 4. The estimate was assumed to be zero when the concentration was under the detection limit (ND=0). The dietary intake ranges of Dec 602, Dec 603, Dec 604, *syn*-DP, *anti*-DP, CP, and Dechlorane in the ten regions were 2.7-4.9 ng/day (mean 3.6 ng/day), 0.045-0.40 ng/day (mean 0.15 ng/day), 0-0.18 ng/day (mean 0.021 ng/day), 0.30-2.0 ng/day (mean 0.99 ng/day), 1.1-3.7 ng/day (mean 2.3 ng/day), 0-0.34 ng/day (mean 0.061 ng/day), and 0.26-0.90 ng/day (mean 0.41 ng/day), respectively. The mean dietary intakes of the Dechloranes by the Japanese general population were estimated to to be 7.6 ng/day, ranging from 4.9 to 9.2 ng/day. The compound of the highest dietary intakes in Dechloranes were in the order of Dec 602, *anti*-DP, and *syn*-DP, those contribution rates were with 47%, 30%, and 13%, respectively. For Dec 602, dietary intake from group X was dominant; the intake from group X accounted for 72% of total Dec 602-intake. For Dec 603, the highest contribution rate (23%) was found in group X. Its contribution rate was equivalent in group I (21%) in which main food item is rice, a staple diet of Japanese, and in group XI (20%) including foods items of livestock origin. For Dechlorane, the highest contribution rate (49%) was found in group X, followed by groups VII, XI, and VIII (19%, 11%, and 9%, respectively). It is interesting that secondary contribution was divided into three groups VII, VIII, and group XI, and each rate was almost the same and relatively high. For *syn*-DP and *anti*-DP, these two compounds were ingested from all food groups and the food group having relatively high contribution rate was not found. Since Dechloranes except for Dec 604 and CP were detected in almost all food groups, it is concluded that Dechloranes have wide distribution in the environment. Information about the amounts of Dechloranes produced, imported, and used are not sufficient, and the routes by which they contaminate food are unknown. The present results strongly suggested that the Dechloranes detected in MB-samples containing various food items prepared in several regions were ingested on a daily basis via meals.

Acknowledgements

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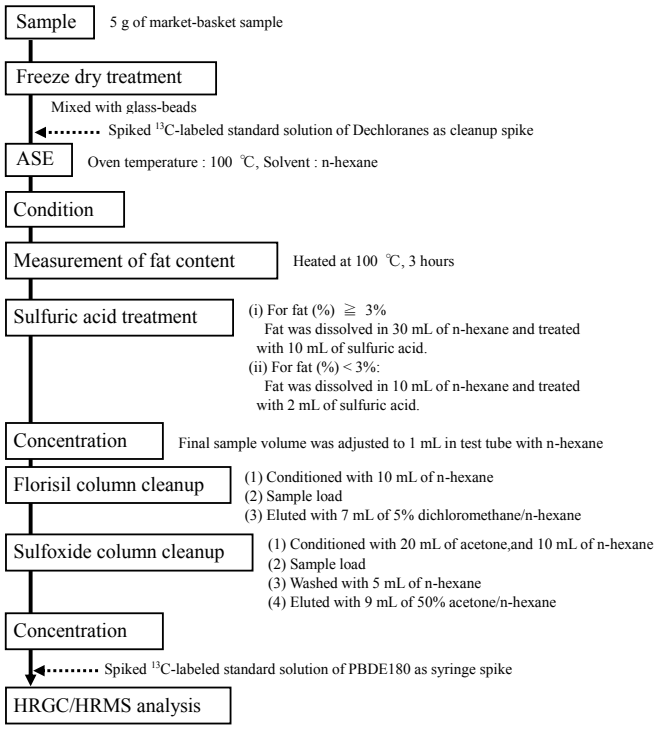

Fig. 1 Analytical method of Dechlorane Plus and related compounds in the market-basket samples

Table 2 Analytical conditions of HRGC/HRMS

GC condition	
Column	DB5 (Agilent, 15m length, 0.25mm i.d., 0.1μm thickness)
Injection mode	Splitless (1μL)
Injector Temperature	280 ℃
Carrier gas (Flow rate)	He (1.0 mL/min)
Oven temperature	120℃(1min)-30℃/min-240℃-5℃/min-275℃-40℃/min-320℃(2.88min)
MS conndituion	
Ionization mode	EI+
Ionization voltage	38 eV
Ion source temperature	280℃
Resolution	10000 <
Monitor Ions	m/z
Dechlorane, Dec 602, DP	271.8102, 273.8072
Dec 603	262.8570, 264.8540
Dec 604	419.7006, 417.7026
$^{13}C_{10}$-Dechlorane, $^{13}C_{10}$-Dec 602	276.8269
$^{13}C_{12}$-2,2',3,4,4',5,5'-heptaBDE	415.9096, 413.8116

Table 3 The mean concentration in ten defferent regions of Dechlorane Plus and related compounds in the market-basket samples

(pg/g wet weight)

No.	Dec602	Dec603	Dec604	*syn*-DP	*anti*-DP	CP	Dechlorane	Total
I	0.23	0.068	ND	0.27	0.78	0.0010	0.011	1.4
II	0.22	0.057	ND	0.47	0.97	0.0049	0.012	1.7
III	0.31	0.10	ND	0.76	1.9	0.0073	0.056	3.1
IV	0.50	0.26	ND	4.5	14	0.020	0.20	20
V	0.33	0.052	ND	0.75	1.5	ND	0.028	2.7
VI	2.9	0.014	0.15	0.33	0.76	0.005	0.019	4.2
VII	0.19	0.025	ND	0.25	0.56	0.023	0.78	1.8
VIII	0.12	0.0025	ND	0.26	0.85	0.00087	0.20	1.4
IX	0.17	0.013	ND	0.28	0.72	0.048	0.012	1.2
X	35	0.46	ND	0.94	1.7	0.21	2.6	41
XI	2.6	0.28	0.022	0.84	2.5	0.042	0.42	6.6
XII	0.38	0.056	ND	0.36	0.76	ND	0.065	1.6
XIII	0.28	0.14	ND	1.2	1.6	0.011	0.16	3.4
Mean	3.3	0.12	0.014	0.86	2.2	0.029	0.35	6.9
Min.	ND	ND	ND	ND	ND	ND	ND	0.024
Max.	63	1.3	1.4	10	36	0.83	7.4	69

I: Rice and rice products, II: Cereals, seeds and potatoes, III: Sugar and confectionary, IV: Oils and fats, V: Pulses, VI: Fruits, VII: Green vegetables, VIII: Other vegetables, mushrooms and seaweeds, IX: Beverages, X: Fish and shellfish, XI: Meat and eggs, XII: Milk and dairy products, XIII: Seasonings.

Table 4 The estimated mean dietary intake of Dechlorane Plus and related compounds in ten defferent regions

(ng/day)

No.	Dec602	Dec603	Dec604	*syn*-DP	*anti*-DP	CP	Dechlorane	Total
I	0.10	0.031	0	0.14	0.36	0.00050	0.0055	0.64
II	0.057	0.016	0	0.12	0.24	0.00092	0.0030	0.44
III	0.012	0.0041	0	0.032	0.076	0.00026	0.0023	0.13
IV	0.0051	0.0027	0	0.044	0.14	0.00017	0.0020	0.19
V	0.020	0.0033	0	0.045	0.091	0	0.0018	0.16
VI	0.29	0.0014	0.019	0.036	0.082	0.00050	0.0020	0.43
VII	0.018	0.0023	0	0.023	0.051	0.0021	0.076	0.17
VIII	0.023	0.00040	0	0.047	0.16	0.00016	0.038	0.27
IX	0.11	0.0087	0	0.18	0.45	0.032	0.0079	0.79
X	2.6	0.035	0	0.074	0.13	0.018	0.20	3.1
XI	0.29	0.030	0.0018	0.095	0.27	0.0046	0.047	0.74
XII	0.047	0.0067	0	0.043	0..093	0	0.0079	0.20
XIII	0..025	0.012	0	0.11	0.14	0.0012	0.015	0.30
Total	3.6	0.15	0.021	0.99	2.3	0.061	0.41	7.6

I: Rice and rice products, II: Cereals, seeds and potatoes, III: Sugar and confectionary, IV: Oils and fats, V: Pulses, VI: Fruits, VII: Green vegetables, VIII: Other vegetables, mushrooms and seaweeds, IX: Beverages, X: Fish and shellfish, XI: Meat and eggs, XII: Milk and dairy products, XIII: Seasonings.