CONCENTRATION OF DECHLORANE PLUS IN FISH SAMPLES COLLECTED IN KYUSHU DISTRICT, WESTERN JAPAN

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Introduction

Dechlorane Plus (DP) is an additive chlorinated flame retardant that is used as a substitute for Mirex, which was already regulated for use in the 1970s. DP has the potential for persistence in the environment and bioaccumulation because of its highly chlorinated chemical structure and high lipophilic property, with a log K_{ow} value of 9.3[1)]. DP has been mainly investigated in the area 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 have been reported to be sold and used worldwide, the occurrence of this compound in the environment is not considered to be a local subject 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 and on human dietary exposure to DP.

In this report, we present data on the concentration of DP residue in seafood samples collected in Fukuoka, in the western region of Japan.

Materials and methods

In the year 2013, 20 fresh fish items were purchased in markets in Fukuoka prefecture. As shown in Table 1, they were caught and produced along Japan's western coast including Kyushu and Chugoku-Shikoku, except for one item from the Tohoku region in eastern Japan. Edible parts of individual fish items were chopped and homogenized using a food processor.

Non-labeled and ^{13}C-labeled standards for individual *syn*- and *anti*-DP were purchased from Cambridge Isotope Laboratories (MA), which were preserved at room temperature to avoid reduction of the concentration of the DP isomer[4)]. The florisil cartridge column used was Sep-pak Vac RC (500mg) from Waters.

Our analytical method is shown in Fig. 1. A total of 10 g of fish homogenates was weighed and mixed with 20 g of diatomaceous earth powder in a bottle tube. After mixing, the sample was spiked with labeled *syn*- and *anti*-standards, and was extracted using an ASE-350 (Dionex, CA) under conditions of 1,500 psi, with hexane as an extraction solvent. The extracts were washed with 5% NaCl aq. and concentrated to dryness in order to determine the lipid content gravimetrically. The lipid extracted was dissolved with hexane and purified with a sulfuric acid treatment, followed by florisil column cleanup[4)]. The eluent was concentrated and fortified with ^{13}C-PCB111 as syringe spike, and finally the volume was adjusted to 50 µl with nonane.

The determination of DP isomers was performed by 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, and 2 µl of the sample was injected to HRGC/HRMS. The limit of detection for the individual DP isomer was 1 pg/g on a wet weight basis.

Recovery rates of non-labeled *syn*-/*anti*-DP standards were evaluated using the homogenized edible parts of shrimp purchased at a fish market in Japan.

Results and discussion

The recovery test of *syn*-/*anti*-DP standards was performed using schrimp homogenates. As a result, the mean recovery rate for *syn*-DP was found to be 99%, ranging from 98% to 101%, and for *anti*-DP it was 93%, ranging from 92% to 94% (n=4).

An example of an HRGC/HRMS chromatogram of DP in a fish sample is shown in Fig. 2. As a result of the analysis of 20 fish samples, no interference was observed in any of the chromatograms.

The concentrations of DP in fish samples are presented in Table 3. Both *syn*- and *anti*-DP were detected in 15 of the samples, while only *anti*-DP was detected in two samples (Nos. 9 and 20), and neither of the isomers was detected in three samples (Nos. 3, 15 and 17).

The concentrations of *syn*-DP observed during this study ranged from ND to a maximum of 7.0 pg/g, and the mean concentration was 2.2 pg/g when ND was assumed to be a concentration of zero. The concentrations of *anti*-DP ranged from ND to a maximum of 13 pg/g, and the mean concentration was 3.7 pg/g. The mean total DP isomers concentration was 3.7 pg/g, ranging from ND to a maximum of 20 pg/g; the latter value was measured in Amberjack-1, No. 4.

We observed a weak correration between the total DP concentration on a whole wet basis and the fat content (%) (R^2=0.212). The DP levels obtained in the present study were similar to those in a recent study in which the concentrations of DP in 20 fish samples from Japanese market were found to range from ND (< 0.2 pg/g) to a maximum of 14.2 pg/g[5].

The mean concentration ratio of *anti*-DP to total DP (f_{anti}) in 15 fish samples in which both *syn*- and *anti*-DP were present was calculated to be 0.62, ranging from 0.58 to 0.65 (Table 3). It is reported that the f_{anti} values ranged from 0.64 to 0.85 for technical DP manufactured in the United States and from 0.59 to 0.60 for technical DP manufactured in China[1]. Our mean f_{anti} values were close to those of technical DP from China and were lower than those of outdoor dust (0.83), soil (0.81) and sediments (0.81) collected in Japan[4].

Acknowledgements

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Table 1 Fish samples used in the present study

No	Fish	Production region	No	Fish	Production region
1	Sardine	Chugoku-Shikoku	11	Tuna-1	Kyushu
2	Mackerel-1	Kyushu	12	Tuna-2	Kyushu
3	Mackerel-2	Kyushu	13	Horse mackerel-1	Kyushu
4	Amberjack-1	Kyushu	14	Horse mackerel-2	Kyushu
5	Amberjack-2	Kyushu	15	Horse mackerel-3	Kyushu
6	Amberjack-3	Chugoku-Shikoku	16	Horse mackerel-4	Kyushu
7	Sea bass-1	Kyushu	17	Cod	Tohoku
8	Sea bass-2	Kyushu	18	Largehead hairtail	Kyushu
9	Sea bream-1	Chugoku-Shikoku	19	*Yazu* (Young amberjack)	Kyushu
10	Sea bream-2	Kyushu	20	Greater amberjack	Kyushu

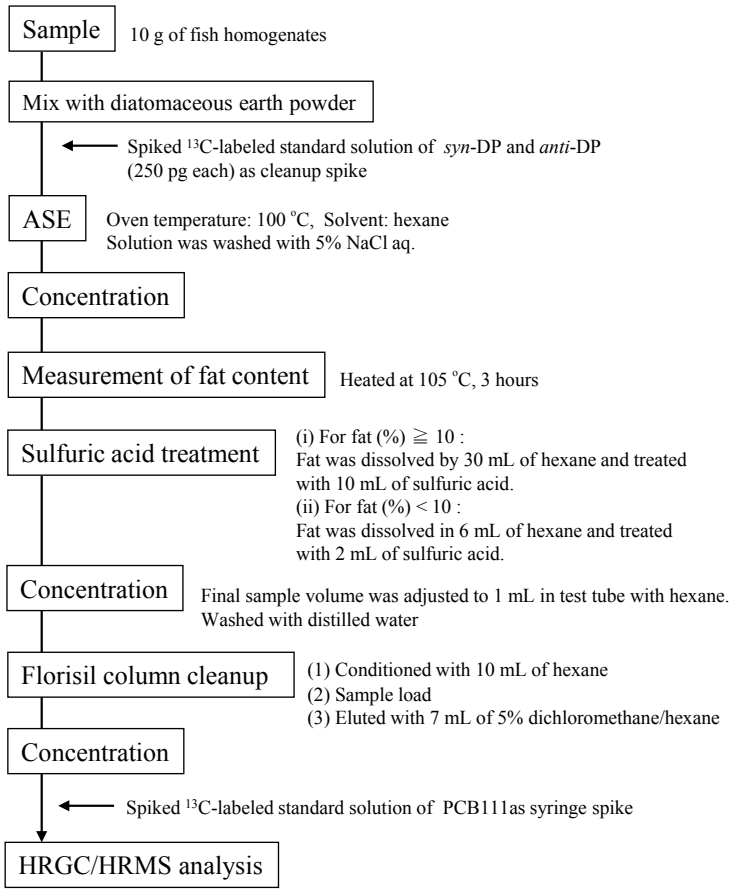

Fig. 1 Analytical method of DP in fish samples

Table 2 Analytical conditions of HRGC/HRMS

GC condition	
Column	HT8-PCB（Kanto Chemical, 60m length, 0.25mm i.d.）
Injection mode（Injection volume）	Split less（2 μL）
Injector temperature	290 °C
Carrier gas（Flow rate）	He（1.0 mL/min）
Oven temperature	130 °C（2min hold）－20 °C/min－340 °C（17.5min hold）
MS Condition	
Ionization mode	EI
Ion source temperature	290 °C
Resolution	10000 <
Monitor ions	Non-labeled DP: 271.8102, 273.8072
	Labeled DP: 276.8269, 278.8240
	Syringe spike: 337.9207, 339.9626
	Lock mass (PFK): 292.9824

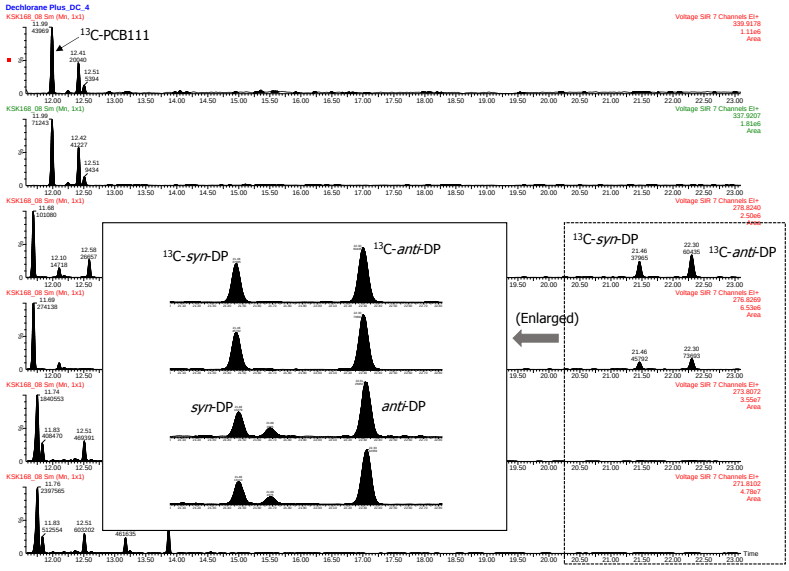

Fig. 2 HRGC/HRMS profiles of DP in an Amberjack-1

Table 3 Concentarions of DP isomers in fish samples

No.	Sample name	Fat (%)	Conc (pg/g-wet)			f_{anti}
			syn-DP	*anti*-DP	Total DP	
1	Sardine	1.3	3.6	5.6	9.2	0.61
2	Mackerel-1	3.8	2.3	3.4	5.6	0.60
3	Mackerel-2	4.1	ND	ND	-	-
4	Amberjack-1	3.5	7.0	13	20	0.64
5	Amberjack-2	11	2.4	4.4	6.8	0.65
6	Amberjack-3	1.7	2.2	3.9	6.0	0.64
7	Sea bass-1	0.54	3.2	5.8	9.0	0.65
8	Sea bass-2	0.41	2.8	5.0	7.8	0.64
9	Sea bream-1	5.0	ND	1.0	1.0	-
10	Sea bream-2	0.96	1.5	2.7	4.2	0.65
11	Tuna-1	18	6.9	9.4	16	0.58
12	Tuna-2	2.8	2.6	4.6	7.2	0.64
13	Horse mackerel-1	0.39	2.7	4.7	7.4	0.64
14	Horse mackerel-2	0.11	1.2	1.8	3.0	0.59
15	Horse mackerel-3	0.32	ND	ND	-	-
16	Horse mackerel-4	1.4	1.4	2.7	4.1	0.65
17	Cod	0.078	ND	ND	-	-
18	Largehead hairtail	2.9	1.8	2.5	4.3	0.59
19	*Yazu* (Young amberjack)	0.14	1.8	2.7	4.5	0.60
20	Greater amberjack	0.029	ND	1.0	1.0	-

ND: <1pg/g