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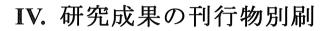
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III. 研究成果の刊行に関する一覧表

# 研究成果に関する刊行物一覧表

整理番号	発表者氏名	論文タイトル	発表誌名	巻号	ページ	出版年
1	Watanabe T, Kikuchi H, Matsuda R, Tomoko Hayashi T, Akaki K and Teshima R.	Performance evaluation of an improved GC-MS method to quantify methylmercury in fish	J. Hood Hyg. Soc. Japan	in press		
2	Takahashi K, Hori T, Kajiwara J, Watanabe T.	Determination of hexabromocyclododecane in fish samples collected from Japanese markets	Organohalogen Compounds	76	930-933	2014
3	Hori T, Miyawaki T, Takahashi K, Yasutake D, Yamamoto T, Kajiwara J, Watanabe T.	Concentration of Dechlorane Plus in fish samples collected in Kyushu district, western Japan.	Organohalogen Compounds	76	900-903	2014
4	Tsutsumi T, Watanabe T, Matsuda R, Teshima R.	Dietary intake of dioxins in Japan, fiscal year 1998-2013	Organohalogen Compounds	76	1325- 1328	2014
5	畝山智香子	農薬や放射性物質等の食品中 化学物質のリスクについて	小児科臨床	67	2503- 2509	2014
6	畝山智香子	食品中化学物質のリスクについ て	香料	262	33-39	2014
7	畝山智香子, 登田美桜	10年間の食品安全情報で収集した「いわゆる健康食品」についての海外情報の傾向について	日本食品安全 協会会報	9	32-35	2014



# DETERMINATION OF HEXABROMOCYCLODODECANE IN FISH SAMPLES COLLECTED FROM JAPANESE MARKETS

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#### Introduction

Hexabromocyclododecane (HBCD) is a brominated flame retardant (BFR) that for many years has been used in plastics and textile coatings around the world. In Japan, domestic use of HBCDs has recently increased, as it has increasingly replaced or supplemented other BFRs. A total of 2,600 t of HBCD was produced in or imported into Japan in 2011.

HBCD's toxicity and the environmental threat it poses are subjects of current discussion. The chemical has been identified in environmental samples from birds, mammals, fish and other aquatic organisms, as well as in soil and sediment. In October 2012, the Persistent Organic Pollutants Review Committee, a subsidiary of the Stockholm Convention on Persistent Organic Pollutants (POPs), adopted a recommendation to include HBCD in the Convention's Annex A for elimination, with specific exemptions for the expanded and extruded polystyrene needed to give countries time to phase-in safer substitutes.

We previously reported that the Japanese populace is exposed to HBCD mostly via fish among the market-basket food group samples investigated<sup>1,2)</sup>. Therefore, it is important to clarify the status of seafood pollution by HBCD. In the present study, we analyzed HBCD in fish samples collected from Japanese markets.

#### Materials and methods

#### Chemicals

Non-labeled and  $^{13}$ C<sub>12</sub>-labeled  $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCD analytical standards were purchased from Cambridge Isotope Laboratories. Dichloromethane, n-hexane, acetone, methanol and distilled water (washed with hexane) of dioxin or pesticide analysis grade were purchased from Kanto Chemical. A 44% sulfuric acid-impregnated silica gel was purchased from Wako Pure Chemical Industries.

#### Samples

The fish samples for the HBCD analysis were purchased from fish markets in the Kyushu district, western Japan during the period 2013-2014. The edible parts were collected, cut into small pieces and blended. The samples were maintained at temperatures below -20°C until analysis.

#### Sample Preparation

The protocol for the HBCD analysis is illustrated in Fig. 1. Each 5-g fish sample was homogenized with the addition of  $^{13}C_{12}$   $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCD, which were then extracted with methanol, a methanol and dichloromethane/hexane(1:9) mixture, and dichloromethane/hexane(1:9), in turn, using a POLYTRON PT 3100 homogenizer (Kinematica). The extracts were shaken with 5% sodium chloride solution, and the organic layer was dried over anhydrous sodium sulfate and concentrated. The residue was dissolved in 10mL of acetone/cyclohexane(3:7), and 2-mL of this solution was subjected to GPC. HBCD was fractionated over 12.5 to 18.5 min after large molecules such as crude fatty acids eluted in 10 to 12 min. The fraction was concentrated and dissolved in 0.3mL of hexane, re-purified with a 1g 44% sulfuric acid-impregnated silica gel packed minicolumn, and then reconstituted to 50µL using methanol.

#### Analytical Methods and Instrumentation

HBCD concentrations were determined using liquid chromatography/mass spectrometry (LC/MS) performed on a Quattro Ultima Pt (Waters) connected to a 2695 LC (Waters). The HPLC column was a 150mm x 2.1mm i.d. 5 $\mu$ m Inertsil ODS-3 (GL-Science). The detection limit of both  $\alpha$ - and  $\gamma$ -HBCD was 0.02 ng/g wet weight (ww); that for  $\beta$ -HBCD was 0.01 ng/g ww.

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#### Results and discussion

Table 2 presents the results of the HBCD analysis of the fish samples. HBCD was detected in all fish samples collected in this study. The concentrations of detected total HBCD were 0.12 ng/g -22 ng/g wet weight; mean concentration was 3.1 ng/g when ND was assumed to be zero. The HBCD levels found in this study were higher than those in our previous study of same region  $(ND -1.4 \text{ ng/g})^3$ . Fig. 2 shows the concentrations for all the samples. In this study, tuna, yellowtail and one of a mackerel samples showed particularly high concentrations relative to other fish species.

Fig. 3 shows the ratio of HBCD isomers in fish samples. The analysis of isomers detected  $\alpha$ -HBCD in all 20 samples, but  $\gamma$ - and  $\beta$ -HBCD in only 11 and 6 samples, respectively. The concentrations of the isomers of all fish samples were in the order:  $\alpha - \gamma - \gamma > \beta$ -HBCD.

The relationship between total HBCD concentration in the whole wet basis and the fat content (%) is shown in Fig. 4. We observed a correlation between the HBCD concentration and fat content ( $R^2$ =0.529).

#### Acknowledgements

This study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Health, Labor, and Welfare, Japan.

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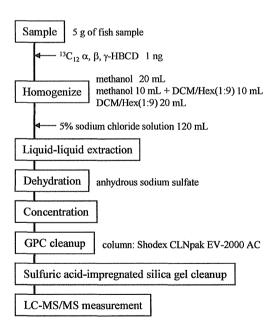


Fig.1 Protocol for HBCD analysis

Table 1 Concentrations of HBCD in fish samples

No.	Fish	Production regions of Japan	Fat content (%)	α-HBCD (ng/g ww)	β-HBCD (ng/g ww)	γ-HBCD (ng/g ww)	Total HBCD (ng/g ww)
1	Sardine	Chugoku-Shikoku	1.3	0.33	ND	0.02	0.35
2	Mackerel -1	Kyushu	3.8	0.60	0.01	0.06	0.67
3	Mackerel -2	Kyushu	4.1	14	0.11	5.2	19
4	Yellowtail -1	Kyushu	3.5	4.2	ND	0.02	4.2
5	Yellowtail -2	Kyushu	11	3.5	0.02	0.15	3.7
6	Yellowtail -3	Chugoku-Shikoku	1.7	2.9	0.01	0.15	3.1
7	Japanese seabass -1	Kyushu	0.54	0.22	ND	0.02	0.24
8	Japanese seabass -2	Kyushu	0.41	0.62	ND	0.04	0.66
9	Sea bream -1	Chugoku-Shikoku	5.0	0.34	ND	ND	0.35
10	Sea bream -2	Kyushu	0.96	0.13	ND	ND	0.13
11	Tuna -1	Kyushu	18	16	0.10	6.2	22
12	Tuna -2	Kyushu	2.8	3.3	0.02	1.1	4.4
13	Horse mackerel -1	Kyushu	0.39	0.12	ND	ND	0.12
14	Horse mackerel -2	Kyushu	0.11	0.20	ND	ND	0.20
15	Horse mackerel -3	Kyushu	0.32	0.23	ND	ND	0.23
16	Horse mackerel -4	Kyushu	1.4	0.70	ND	ND	0.70
17	Cod	Tohoku	0.078	0.18	ND	ND	0.18
18	Largehead hairtail	Kyushu	2.9	0.21	ND	0.02	0.23
19	Young yellowtail	Kyushu	0.14	0.42	ND	ND	0.42
20	Greater amberjack	Kyushu	0.029	0.13	ND	ND	0.13

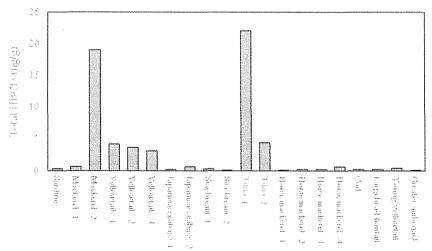


Fig. 2 Concentrations of HBCD in fish samples

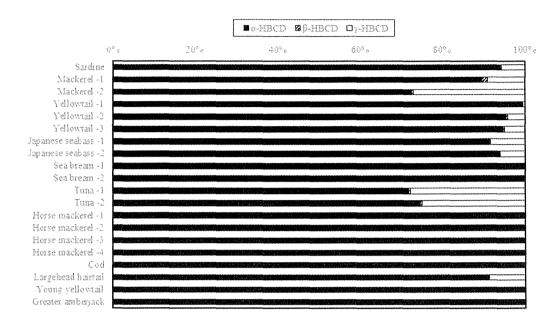


Fig.3 Ratio of HBCD isomers in fish samples

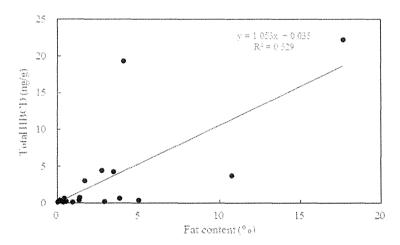


Fig.4 Correlation between HBCD and fat content (%) in fish samples

# 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<sup>1)</sup>. 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<sup>2)3)</sup>. 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<sup>4)</sup>. 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 <sup>13</sup>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<sup>4</sup>. 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<sup>4</sup>). The eluent was concentrated and fortified with <sup>13</sup>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  $\mu$ l 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.

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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<sup>5</sup>).

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<sup>1)</sup>. 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<sup>4)</sup>.

#### Acknowledgements

This work was supported in part by a Health and Labour Sciences Research Grant from the Ministry of Health, Labour and Welfare, Japan.

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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

Table 1 Fish samples used in the present study

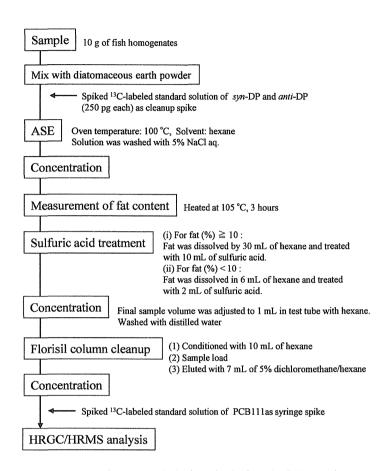


Fig. 1 Analytical method of DP in fish samples

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 ℃
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 ℃
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

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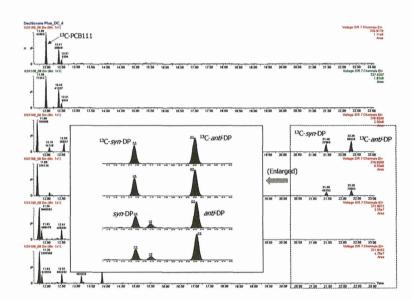


Fig. 2 HRGC/HRMS profiles of DP in an Amberjack-1

Table 3 Concentarions of DP isomers in fish samples

No.	Sample name	Fat	Conc (pg/g-wet)			<u> </u>
110.		(%)	syn-DP	anti-DP	Total DP	$f_{ m anti}$
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	1
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	-1,	-
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	1_1

ND: <1pg/g

#### DIETARY INTAKE OF DIOXINS IN JAPAN, FISCAL YEAR 1998-2013

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#### Introduction

Food is generally recognized as the main source of human intake of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs), which are known collectively as dioxins. It is therefore important to estimate dietary intakes of dioxins for risk assessments. A total diet study (TDS), also known as a market basket study, is a useful method of estimating the average dietary intake of contaminants. We have conducted a nationwide TDS of dioxins in Japan annually since fiscal year (FY) 1998. Here, we report the TDS results for FY 2013 and also discuss the time trend of dietary intake of dioxins from TDS results obtained over the last 16 years (FY 1998-2013). The TDS has already revealed that fish and shellfish are the main sources of intake of dioxins; therefore, since FY 1998 we have been surveying the dioxin concentrations in various kinds of food, focusing on fish and shellfish in Japanese markets. We also conducted a Monte Carlo simulation using our surveillance data to obtain information on the distribution of intake of dioxins from fish and shellfish in the general Japanese population.

#### Materials and methods

TDS estimation of dietary intake of dioxins: TDS samples were prepared at 8 locations in 7 regions (Hokkaido, Tohoku, Kanto, Chubu, Kansai, Chugoku-Shikoku and Kyushu) across Japan from FY 2010 to FY 2013. From FY 1998 to FY 2009, TDS samples were prepared at 9 to 16 locations in 7 regions. More than 100 food items were collected from supermarkets at each location. The composition of TDS samples was designed based on official food classification and consumption data obtained by the National Health and Nutrition Survey in Japan. The collected food samples were cooked or prepared in typical ways for consumption. The samples were then blended to form 14 food group composites for TDS samples. Since FY 2002 we have prepared three TDS samples from each of food groups 10 (fish and shellfish), 11 (meat and eggs) and 12 (milk and dairy products). As far as possible, we chose different food items from these groups, such as different fish species and different edible parts of meat. This was because food items classified into these groups have a relatively wide range of dioxin concentrations. Therefore, the choice of food items has a strong influence on the estimated dioxin intake. For the remaining food groups (1 to 9, 13, and 14), each region was classified into five blocks, and composite food groups from each block were prepared by mixing regional samples according to regional consumption data. Dioxins in the TDS samples were analysed in accordance with a previously reported protocol by using highresolution gas chromatography coupled with high-resolution mass spectrometry<sup>1</sup>. The limits of detection (LODs) for PCDD/Fs were as follows: 0.01 to 0.05 pg/g in food groups 1 to 3 and 5 to 13; 0.05 to 0.2 pg/g in food group 4; and 0.1 to 0.5 pg/L in food group 14. The LODs for dl-PCBs were as follows: 0.1 to 1 pg/g in food groups 1 to 3 and 5 to 13; 0.5 to 5 pg/g in food group 4; and 1 to 10 pg/L in food group 14. The toxic equivalent (TEQ) concentrations were calculated by using WHO toxic equivalency factors (2005). The total TEQ concentration in a sample was calculated by assuming that all isomer concentrations lower than the LODs were equal to zero [not detected (ND) = 0] or half of the LODs (ND = LOD/2). Dioxin intakes were estimated by multiplying the food consumption data by the TEQ concentrations of dioxins in each food group.

Estimation of dioxin intakes from fish and shellfish by Monte Carlo simulation: We used a probabilistic approach with Monte Carlo simulation to estimate dioxin intakes in fish and shellfish. The distribution of food consumption data was calculated on the basis of the values obtained in Japanese Nutritional Surveys performed from FY 2003 to 2007. Dioxin concentrations in fish and shellfish were obtained from a nationwide survey of dioxins in foodstuffs; this survey was performed under a Health Sciences Research Grant from the Ministry of Health, Labor and Welfare of Japan during the period FY 1998 to FY 2010. Dioxin intakes were estimated as follows:

Step 1. Assumption of the distribution of consumption of fish and shellfish groups. Fish and shellfish were categorized into 13 groups in accordance with the Japanese Nutritional Survey. The distribution of consumption

could not be fitted to typical distributions such as a lognormal distribution, therefore, real distributions were used for the consumption data.

Step 2. Assumption of the distribution of dioxin concentrations in the fish and shellfish groups. Data on dioxin concentrations in fish and shellfish (approximately 730 samples) were categorized into the same 13 groups as the consumption data. A lognormal distribution was assumed for the dioxin concentrations in the 13 groups.

Step 3. Monte Carlo simulation. A random number "a" was generated from the real distribution of the consumption data in step 1 and was defined as the consumption of each of the 13 groups. A random number "b" was generated on the basis of the distribution determined in step 2 and was defined as the dioxin concentration in each of the 13 groups. "a × b" was defined as the dioxin intake from each fish and shellfish group. Total dioxin intakes from fish and shellfish were calculated as the sum of dioxin intakes in each fish and shellfish group. The simulation was run with 20,000 iterations using a software for Monte Carlo simulation (Crystal Ball, Decisioneering Inc., USA).

#### Results and discussion

Table 1 shows the national average dietary intakes of dioxins from the 7 regions in FY 2013. The average dietary intake calculated at ND = 0 was 28.9 pg TEQ/day, corresponding to 0.58 pg TEQ/kg bw/day for an adult weighing 50 kg. The intake was about one-seventh of the tolerable daily intake (TDI) of 4 pg TEQ/kg bw/day set by the Japanese government in 1999<sup>2</sup>. The dietary intakes in the 7 regions ranged from 0.18 to 0.97 pg TEQ/kg bw/day (data not shown). The maximum intake was still about one-fourth of the TDI. The dietary intakes calculated at ND = LOD/2 are also given in Table 1 for reference. The average dietary intake was 80.8 pg-TEQ/day (1.62 pg TEQ/kg bw/day), which is about twice the average intake calculated at ND = 0. The dioxin intakes were highest from fish and shellfish (group 10) followed by meat and eggs (group 11) at ND = 0, and were highest from fish and shellfish (group 10) followed by beverages (group 9), and rice and rice products (group 1) at ND = LOD/2. The TEQ contributions of the fish and shellfish group were noticeable in the total TEQs (about 91% at ND = 0 and 33% at ND = LOD/2). Compared with the other groups, much greater differences in intake were observed between the estimates obtained at ND = 0 and ND = LOD/2 for beverages and for rice and rice products, because these food groups contained high percentages of ND data and had high daily rates of consumption.

Figure 1 shows the dioxin intakes obtained from our TDS results between FY 1998 and 2013. The national average intakes were within the range of 0.58 to 1.92 pg TEQ/kg bw/day at ND=0, which is below the Japanese TDI. Additionally, except FY 1999, the maximum dioxin intakes observed during the same period were below the TDI, although some maximum intakes were close to the TDI. The latest average intake was the lowest for the last 16 years and was about one-third of the average intake in FY 1998. Overall, the average intakes appeared to be decreasing slowly, although the TDS samples yielded a wide range of dioxin intakes. The Law Concerning Special Measures against Dioxins was enacted in Japan in 1999; this might have contributed to the decreasing trend.

We also estimated the distribution of dioxin intake in the general Japanese population by using a Monte Carlo simulation. The distribution of dioxin intakes at ND = 0 in the general population from fish and shellfish is shown in Figure 2. The estimated average dioxin intake was 1.3 pg TEQ/kg bw/day. The average dioxin intake was well below the Japanese TDI but about twice the intake estimated by the TDS in FY 2013. This is probably because we used surveillance data for the period FY 1998 to FY 2010 for the simulation. In fact, the average intake according to the TDS during the same period (FY 1998 to FY 2010) was 1.2 pg TEQ/kg bw/day at ND = 0, and it was almost identical to the intake estimated by the simulation. The estimated median, 90th percentile, and 95th percentile values of the intake distribution were 0.36, 2.9, and 4.9 pg TEQ/kg bw/day, respectively. The estimated 95th percentile intake was slightly over the Japanese TDI. However, the 90th and 95th percentile intakes are less reliable, because fitting of the distribution to the dioxin concentrations in some fish and shellfish groups was not completely achieved especially in the high concentration area of the distribution curve. Fish groups, including horse mackerel, sardine, tuna, yellowtail, and fishery products (salted and dried fish etc.), are the main sources of dioxin intake from fish and shellfish in the Japanese population (Figure 3).

Thus, dietary dioxin intake in Japan has been decreasing gradually, and the current intake as estimated by TDS was well below the Japanese TDI. However, overconsumption of fish and shellfish would lead to an increase in our intake of dioxins from food, and a balanced diet is recommended

#### Acknowledgements

This work was supported by a Health Sciences Research Grant from the Ministry of Health, Labor, and Welfare of Japan.

#### References:

- 1. Tsutsumi T, Amakura Y, Yanagi T, Kono Y, Nakamura M, Nomura T, Sasaki K, Maitani T, Matsuda R. (2008); Organohalogen Comp. 70: 2313–2316.
- 2. Government of Japan, The Law Concerning Special Measures against Dioxins, 1999.

Table 1. Daily dietary intakes of dioxins in FY 2013 (national averages)

	Food group	Dioxin intake (pg TEQ/day)				
No.		ND	= 0	ND=	ND = LOD/2	
		Average	Ratio (%)	Average	Ratio (%)	
1 .	Rice and rice products	< 0.01	< 0.1	10	12.6	
2	Cereals, seeds and potatoes	0.019	< 0.1	5.7	7.1	
3	Sugar and confectionaries	0.026	< 0.1	1.0	1.2	
4	Fats and oils	0.015	< 0.1	1.2	1.5	
5	Pulses	< 0.01	< 0.1	1.4	1.7	
6	Fruits	< 0.01	< 0.1	2.7	3.4	
7	Green vegetables	0.042	0.1	2.3	2.9	
8	Other vegetables, mushrooms and seaweed	0.069	0.2	4.8	5.9	
9	Beverages	< 0.01	< 0.1	15	18.2	
10	Fish and shellfish	26	91.1	27	33.4	
11	Meat and eggs	2.3	7.9	4.5	5.6	
12	Milk and dairy products	0.034	0.1	2.9	3.5	
13	Other foods (seasoning)	0.080	0.3	2.4	3.0	
14	Drinking water	< 0.01	< 0.1	0.065	< 0.1	
	Total	28.9	100.0	80.8	100.0	

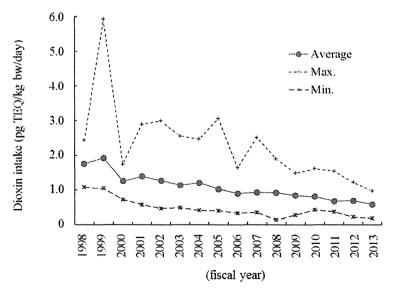


Figure 1. Time trend of dietary intake of dioxins in Japan (ND = 0)

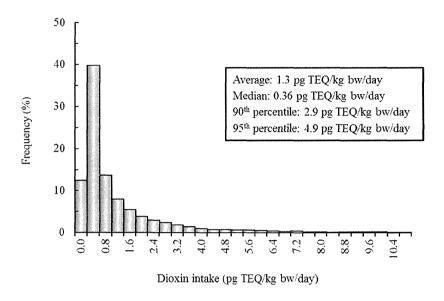


Figure 2. Distribution of dioxin intakes in the general population in Japan, as estimated by Monte Carlo simulation

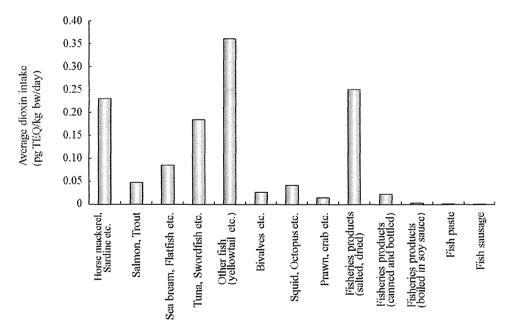


Figure 3. Average dioxin intakes in Japan from components of the fish and shellfish group, as estimated by Monte Carlo simulation

# 食品中化学物質のリスクについて

# Risk assessment of chemicals in food

Food consists of many chemical components which properties are known or unknown. FAO and WHO have developed food safety risk analysis to ensure food safety for public health and food safety authorities of many countries including Japan have adopted it. Risk analysis plays key role for our food safety system. Here I will provide a brief description focusing around food additives.



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#### はじめに

食品の安全性確保は、日本を含め世界中の政府や 食品関連業者にとって重要な責務の一つである。し かしながら、食品の安全性を科学的に評価する、と いう考え方やその実践は、それほど古いものではな い。かつてはなんらかの健康被害が出た、事故が あった危険な可能性があるという警告が発せられた 場合に対応したり、規制を行うことが多かった。

日本においては、2002年ころから中国産冷凍野菜の残留農薬問題や国内でのウシ海綿状脳症(BSE)の発生などが社会問題になったことを契機に、内閣府に食品安全委員会が設立され、そこで「リスク分析」を基本にした食品の科学的な安全性評価が食品安全行政の中心に据えられることになった。

本稿では、食品安全リスク分析とはどういうものかについて、食品添加物を中心に簡単な解説を行う。なおここでは主に食品中に含まれる化学物質によるヒト健康への影響についての話題を扱う。環境への影響や、食品衛生において最も重要な微生物による食中毒などについては扱わない。

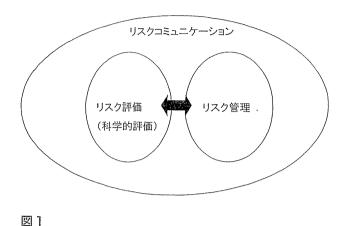
## リスクとは

ある物質がヒトや環境などに何らかの危害を及ぼすとき、その危害そのもののことを「ハザード」という。毒キノコやフグを食べると死亡することもある、というような記述がハザードについての記述である。そのハザードがどれだけの確率で起こるのか、ということも含めたものが「リスク」である。

たとえ猛毒のキノコであっても、食べるチャンスや量が極めて少なければリスクは小さい、と言えるし、ハザードが小さくみえても、毎日継続するなら大きなリスクになる。通常ハザードそのものは物質に固有で、ヒトが変えられるようなものではなく、食品の安全管理は、通常は暴露量を一定以下にすること、である。

## リスク分析とは

リスク分析 (risk analysis)とは、ヒトの健康と安全に対するリスクを推定し、リスクを管理するための適切な措置を特定して実施し、さらにリスクやリスク管理のための措置について、関係者とコミュニ



ハザードの同定

ハザードキャラクタリゼーション

リスクキャラクタリゼーション

図2

ケーションをとるために用いられるアプローチのことである"。

食品に関連するハザードは多様で膨大であり,国際貿易が活発になるに従って,特定地域に限定的だったハザードが,急速に世界中に拡散する可能性が出てきた。また例えば,日本人にとって昆布は日常的に食べられていて,特にリスクのある食品とは思われていないが,ヨウ素欠乏気味の世界の多くの地域においては,ヨウ素を大量に含むハイリスク食品となってしまう,などのように背景となる食習慣の違う地域においてはリスクが高い場合もある。

さらに、特に先進国においては、食品の安全性への要求水準が高くなっていることもあり、既存のシステムでは対応が難しくなってきた。そこで科学的根拠に基づいた総合的アプローチとして開発されてきたのがリスク分析である。

## リスク分析の主要3要素

リスク分析は、主にリスク管理・リスク評価・リスクコミュニケーションの3つの要素からなる。一般的に図1のように描かれることが多いが、それぞれ完全に独立した項目ではない。これらの主要3要素は、コーデックスの定義によれば以下のようになる。

#### ・リスク評価:

1) ハザード同定, 2) ハザードキャラクタリゼーション, 3) 暴露評価, 4) リスクキャラクタリゼーション,

から成り立つ科学的なプロセス(図2)。

#### ・リスク管理:

リスク評価とは、明確に区別できる、リスク評価の 結果や消費者の健康保護、公正な貿易推進などの各 種要因をふまえて、全ての利害関係者と協議しなが ら、リスク低減のための政策・措置の選択肢を評価 し、必要に応じ適切な予防管理手段を選択する。

#### ・リスクコミュニケーション:

リスク分析の全過程において,リスク評価者,リスク管理者,消費者,生産者,研究者,その他利害関係のある団体などの間で,リスク評価結果の説明やリスク管理に関する決定についての説明など,リスクやリスク関連要因,リスク認識などについて情報や意見を交換する。

現在の日本の食品安全行政においては、リスク評価は主に食品安全委員会が行い、その評価を受けて厚生労働省や農林水産省、消費者庁などの担当行政機関が、リスク管理方法を決定し実行するという役割分担になっている。リスクコミュニケーションについては、生産者から消費者まで、全ての関係者が何らかの形で関与する場面がある。

## リスク評価について

リスク分析において、最も科学の寄与が大きい プロセスがリスク評価である。リスク評価は、特定 の期間におけるハザードへの暴露に起因する、生