RISK ASSESSMENT OF DIOXINS IN FOOD STUFF

Shin ES, Kim JC, Chang Y-S

School of Environmental Science &Engineering, Pohang University of Science and Technology (POSTECH), San 31,Hyojadong, Namgu, Pohang, Kyungbuk,790-784, Korea

Abstract

Fish samples (37 food, total 480 samples) collected in nine major cities have been analyzed for a range of dioxins (29 congeners; PCDD/Fs 17 congeners and dioxin-like PCBs 12 congeners) using the isotope dilution method in HRGC/HRMS. For the test method validation, certified reference materials were analyzed. Based on the measured dioxins levels, average daily dietary intake estimates of dioxins were calculated. The range of detected dioxins (the total sum of PCDD/Fs and DL-PCBs) levels were 0.0360 - 1.5930 pg WHO_{05}-TEQ/g weight. PCDFs, penta-PCBs and hexa-PCBs in congeners of dioxins in fishes were mainly detected when converted into TEQ (toxicity equivalents). In this study, we considered many components of uncertainty, and made 'cause and effect' fish bone model. Various components were considered, and the expanded uncertainty is obtained by multiplying the combined standard uncertainty by a coverage factor. The result is expressed as ±0.094 pg-TEQ/g wet weight with a level of confidence of approximately 95% and coverage factor 2.

Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are concerned compounds among 12 persistence organic pollutants of the Stockholm convention. These compounds can increase the risk of cancer and cause damage to immune system[1]. Because of the lipophilic property, they can be bioaccumulated and biomagnified in a food chain. Dioxin-like compounds can induce lipid peroxidation, DNA single-strand breaks, and modified base formation by DNA adduct[2].The number of 17 PCDD/Fs has TEF (toxic equivalence factor) for calculation of TEQ value. Among the total 209 PCBs, only 12 PCBs congeners which have dioxin-like toxicity are classified as DL-PCBs. Most of PCDD/Fs and DL-PCB is exposed to human through the food chain, especially fish. Fish consumption is a major route (80.4%) of exposure for dioxins in Korea owing to diet characteristic[3].

In this study, fish samples (37 food, total 480 samples) collected in nine major cities have been analyzed for a range of dioxins (29 congeners; PCDD/Fs 17 congeners and dioxin-like PCBs 12 congeners) using the isotope dilution method in HRGC/HRMS. The range of detected dioxins (the total sum of PCDD/Fs and DL-PCBs) levels were 0.0360 - 1.5930 pg WHO_{05}-TEQ/g weight. For risk assessment of dioxins, the data of daily intake from Korea National Health and Nutrition Examination Survey (2008~2010) are considered. Most contributed fish items were scomber japonicus, engraulis japonica and trichiurus lepturus. As a result of estimated daily intake and TEQ value, total amount of dioxins exposure to Korea general population was 0.211 pg-TEQ/kebw/day. On account of Korean TDI (tolerable daily intake) is 4 pg-TEQ/kebw/day,compared to TDI, daily intake of dioxins via fish ingestion was 5.27%. In order to take closer to the true value, we should know the uncertainty to prevent decline the confidence of measurement. In this study, we considered many components of uncertainty, and made a 'cause and effect' fish bone model. The result is expressed as 1.3644±0.094 pg-TEQ/g wet weight with a level of confidence of approximately 95% and coverage factor 2.

Materials and Methods

Sampling: Fish samples were obtained from 9 cities of South Korea: Seoul, Daejeon, Daegu, Busan, Gwangju, Gangneung, Gunsan, Pohang and Jeju. 480 samples of 37 species were brought from markets because most of consumers used to buy food stuff there. For the selection of foods, the report of the Korea National Health and Nutrition Examination Survey (KNHANES IV-2) 2008 was used. The sample lists were selected in order of the amount of intake. The samples were freeze-dried, transferred to a Teflon-lined capped glass botle, and frozen until analysis.

Sample analysis: About 10 g of food samples were measured and extracted using hexane:dichloromethane mixed solution (v/v=1:1) 300 mL for 24h. Before soxhlet extraction, 13C-labelled internal standards were added to

samples. For removal of lipid in samples, the concentrated extracts were treated by sulfuric acid. After this treatment, the extracts were eluted on multilayer silica gel column and alumina column. The analytes were eluted using hexane 150 mL and hexane:dichloromethane mixed solution (v/v=1:1), respectively. In alumina column clean-up, eluted solution was separated to two fractions. The first fraction using hexane 60 mL was discarded, and second fraction using hexane:dichloromethane mixed solution (v/v=1:1) was collected for determination. The cleaned extracts were injected and analyzed using an Agilent 6890 Gas Chromatograph equipped with a DB-5MS capillary column (60 m × 0.25 mm × 0.25 μm) and coupled to a Jeol 800D Mass Spectrometer with the electron impact (EI) mode.

Chemicals: Internal standard of PCDD/Fs and DL-PCBs were supplied by Wellington Laboratories Inc.(EPA 1613LCSand 68B-LCS, Wellington Laboratories, Canada) and were comprised of $^{13}C_{12}$-Labelled 17 and 12 congeners, respectively. For investigation of recovery, 1613-IS and 68B-IS were purchased from Wellington Laboratories Inc.and were used as recovery standard, respectively. The solvents and chromatographic materials were all of HPLC grade.

Results and Discussion

TEQ value and risk assessment of Dioxins in fish samples

TEQ values of PCDD/Fs and DL-PCBs in fish samples are given in Table 1. The TEQ values were calculated in all fish samples (n=480). The range of detected dioxins (the total sum of PCDD/Fs and DL-PCBs) levels were 0.0360 - 1.5930 pg WHO_{05}-TEQ/g weight. In this study, 2,3,4,7,8-Pentachlorodibenzofuran and 3,3',4,4',5-pentachlorobiphenyl (IUPAC congener #126) were mainly detected when converted into TEQ value of PCDD/Fs and DL-PCBs, respectively. Based on the TEQ value and estimated daily intake, risk assessment was considered. Although *Arctoscopus japonicas* has the highest TEQ value, the results of risk assessment show that dioxins are exposed though *Scomber japonicas* because of daily intake.(Fig.1)

In general, the non-ortho PCBs have the largest contribution to total TEQ for the foodstuffs of marine origin, PCDD/Fs and mono-ortho PCBs in that order[4].

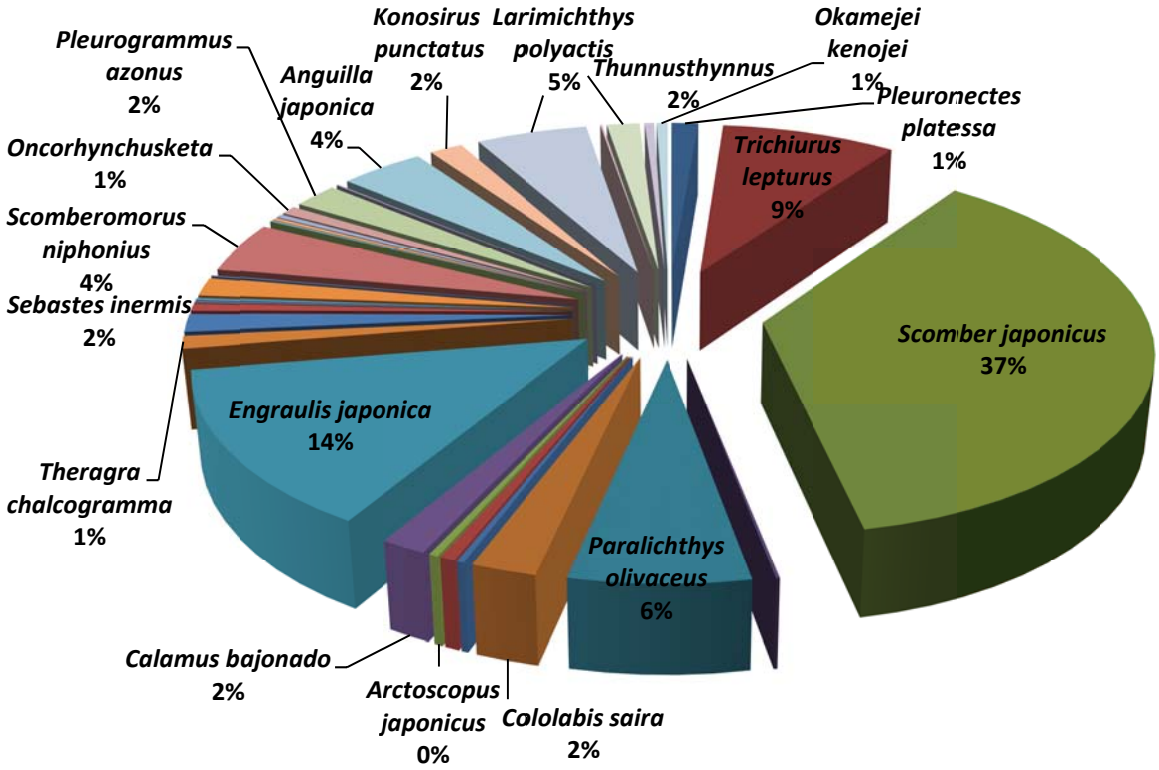

Fig. 1. Daily intake contribution of PCDD/Fs and DL-PCBs

Table 1. TEQ values (pg-TEQ/g wet weight) of PCDD/Fs and DL-PCBs in fish

	Species	(Korean)	Mean	Min	Max	SD	Median
1	*Pleuronectesplatessa*	가자미	0.3675	0.0014	1.7181	0.4381	0.3012
2	*Trichiuruslepturus*	갈치	0.8506	0.0072	2.4483	0.7904	0.5824
3	*Scomberjaponicus*	고등어	1.1159	0.3201	3.0471	0.7299	0.8990
4	*cetacea*	고래	0.9797	0.8909	1.2085	0.1245	0.9250
5	*Paralichthysolivaceus*	광어	0.5979	0.0457	1.5690	0.4836	0.5469
6	*Cololabissaira*	꽁치	0.2263	0.0058	1.5085	0.3791	0.1335
7	*Gadusmacrocephalus*	대구	0.0789	0.0013	0.1765	0.0544	0.0805
8	*Pleuronichthyscornutus*	도다리	0.8689	0.0534	1.9539	0.6993	0.7710
9	*Arctoscopusjaponicus*	도루묵	1.4749	0.6501	2.5959	0.5298	1.3500
10	*Calamusbajonado*	돔	0.4140	0.0146	1.5278	0.4096	0.2142
11	*Theragrachalcogramma*	동태	0.0336	0.0052	0.1076	0.0338	0.0307
12	*Engraulis japonica*	멸치	0.6978	0.0000	1.3316	0.2883	0.6646
13	*Theragrachalcogramma*	명태	0.0446	0.0005	0.1676	0.0436	0.0335
14	*Misgurnusanguillicaudatus*	미꾸리	0.2206	0.0780	0.3341	0.0778	0.2320
15	*Silurusasotus*	민물메기	0.3137	0.0539	0.5135	0.1445	0.3479
16	*Miichthysmiiuy*	민어	0.0735	0.0133	0.1329	0.0416	0.0725
17	*Pampusargenteus*	병어	0.3603	0.1707	0.6932	0.1548	0.2866
18	*ostracionsolorensis*	복어	0.0851	0.0077	0.3172	0.0878	0.0488
19	*Sebastesinermis*	볼락	0.2646	0.0030	0.7012	0.2181	0.3370
20	*Carassiuscarassius*	붕어	0.3756	0.1163	0.5566	0.1994	0.4515
21	*Scomberomorusniphonius*	삼치	1.0128	0.0066	2.1168	0.6657	1.0072
22	*Selachimorpha*	상어	0.0628	0.0000	0.2245	0.0741	0.0336
23	*Cynoglossusjoyneri*	서대	0.0412	0.0003	0.2222	0.0660	0.0209
24	*Oncorhynchusmasou*	송어	0.2606	0.1403	0.4785	0.1258	0.2084

25	*Mugilcephalus*	숭어	0.2902	0.1189	0.6417	0.1602	0.2509
26	*Lophiomussetigerus*	아귀	0.0558	0.0000	0.1823	0.0544	0.0435
27	*Astrocongermyriaster*	아나고	0.5851	0.0198	1.3865	0.4534	0.3678
28	*Oncorhynchusketa*	연어	0.2719	0.0997	0.6024	0.1582	0.2385
29	*Pleurogrammusazonus*	임연수어	0.6773	0.1082	2.4921	0.6774	0.4031
30	*Cyprinuscarpio*	잉어	0.2689	0.0034	0.6163	0.2675	0.2289
31	*Anguilla japonica*	장어	0.1098	0.0283	0.2192	0.0521	0.1125
32	*Konosiruspunctatus*	전어	1.4684	0.2240	6.2368	2.0060	0.4215
33	*Larimichthyspolyactis*	조기	0.2951	0.0003	0.8855	0.3049	0.2225
34	*Stephanolepiscirrhifer*	쥐치	0.0538	0.0044	0.2837	0.0786	0.0300
35	*Thunnusthynnus*	참치	0.1696	0.0081	1.1177	0.3276	0.0306
36	*Clupeapallasii*	청어	1.1986	0.6450	2.2085	0.5246	1.0715
37	*Okamejeikenojei*	홍어	0.0824	0.0004	0.7750	0.1870	0.0294

Uncertainty

The uncertainty of measurement is defined as 'parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measure and' by ISO GUM[5]. All measurements have the uncertainty, and it is derived from various components. In order to be closer to the true value, we should know the uncertainty to prevent decline the confidence of measurement.

In this study, we considered many components of uncertainty, and made the 'cause and effect' fish bone model (Fig. 2). Various components exist, for example, accuracy of balance, deviation of syringe volume, expanded uncertainty of standard solution's concentration, and peak assignment. First, we classified the components to type A and type B uncertainty. Standard uncertainty of each component is calculated for each formula, and then it is combined. Individual standard uncertainties calculated by type A or type B evaluations can be combined validly by root sum of the squares. All the uncertainties must be expressed as one standard uncertainty and in the same units. Expanded uncertainty is obtained by multiplying the combined standard uncertainty by a coverage factor. The result is expressed as ±0.094 pg-TEQ/g wet weight with a level of confidence of approximately 95% and coverage factor 2.

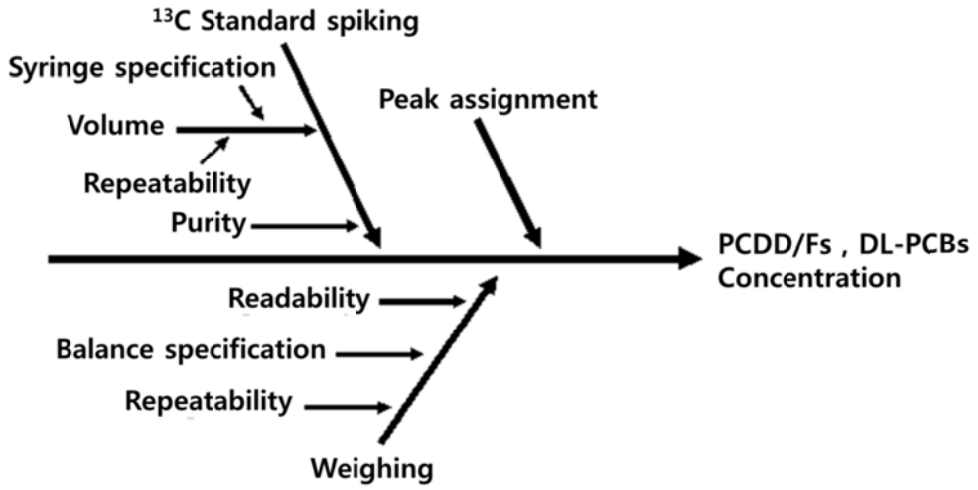

Fig. 2. Cause and effect fishbone diagram for PCDD/Fs and DL-PCBs analysis uncertainty

Acknowledgements
This work was supported by a grant (12162KFDA015) from Korea Food and Drug Administration (KFDA) and the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2011-0028723).

References

1. WHO (World Health Organization) 2010. Dioxins and their effects on human health (Fact Sheet No. 225)
2. MacDonald, C. J.; Cheng, R. Y.; Roberts, D. D.;Wink, D. A.; Yeh, G. C.,*J. Biol. Chem.* ,2009, 284(33): 22099-22107
3. Korea Centers for Disease Control and Prevention, Korea Health Statistics 2010 : Korea National Health and Nutrition Examination Survey (KNHANES V-1)」 2010
4. Georg Becher,Line SmåstuenHaug, Cathrine Thomsen,*Talanta*, 2004, 63 ,1115–1122
5. JCGM(Joint Committee for Guides in Metrology), 2008, Evaluation of measurement data-Guide to the expression of uncertainty in measurement