INVESTIGATION INTO LEVELS OF 7 INDICATOR PCBs IN FISH, KOREA

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Introduction

PCBs and other halogenated organic compounds, such as dioxins and furans are ubiquitously present in the environment, and they are persistent and accumulate in the food chain and human diet.

PCBs consist of two benzene rings contain one to ten chlorines, for a total of 209 compounds or congeners.The chlorination pattern of the PCB is important for the toxicity of the substance. A number of PCB congeners show dioxin-like'toxicity. This group of non-ortho (PCBs 77, 81, 126, 169) and mono-ortho (PCBs 105, 114, 118, 123, 156, 157, 167, 189) PCBs are assumed to have essentially the same toxicity potential as the dioxins and furans, since they also bind to the Ah receptor.

Other PCBs (non-dioxin-like PCBs) do not exert their toxicological effects via binding to the Ah receptor but nonetheless are associated with a wide spectrum of toxic responses, including developmental effects, immuno- and neurotoxicity, endocrine disrupting effects and tumor promotion.

The so-called marker or indicator PCBs have been used as indicators of the total PCB content or body burden of environmental biota, food and human tissue. The most frequent approach is to use either the total level of six of the most commonly occurring PCBs (6 indicator PCBs, PCBs 28, 52, 101, 138, 153 and 180) or the total level of seven of these (7 indicator PCBs, PCBs 28, 52, 101, 118, 138, 153 and 180), including the dioxin-like PCB 118[1].

The indicator PCBs are known to be persistent in the environment and to bioaccumulate in the food chain, and are assumed a suitable representative for all PCBs. Since these are the predominant congeners in biotic and abiotic matrices, this group was chosen for the present dietary intake assessment[2]. In EU, the sum of the six marker or indicator PCBs (PCB 28, 52, 101, 138, 153 and 180) comprises about half of the amount of total NDL-PCB present in feed and food. That sum is considered as an appropriate marker for occurrence and human exposure to NDL-PCB and therefore should be set as a maximum level[3].

These monitoring provide current estimates of the exposure of human to PCBs and are a valuable tool to improve risk assessments and to develop the appropriate strategies to manage risks that may be associated with these contaminant.

In the present study, we analyzed indicator PCBs (PCB 28, 52, 101, 138, 153 and 180) in fish from 9 regions cities(Seoul, Daejeon, Gangneung, Daegu, Gunsan, Gwangju, Pohang, Daegu, andJeju) in Korea and estimated daily intake levels of PCBs. The data on occurrence collected during measurement on occurrence were combined with food consumption data to assess the dietary intake of the seven indicatorPCBs.

Materials and methods

Chemicals and Sampling

All PCBs standard solutions were purchased from Wellington Laboratories (ON, Canada). A mixed native PCBs standard solution (BP-MS) was prepared. A 13C-labeled internal standard solution (MBP-D7) contained 13C12-PCB 28, 53, 101, 118, 138, 153 and 180. An injection standard of 13C12-PCB-170(MBP-170) was used for this study.

Samples of selected 37 fish species in 480 samples were collected from multiple supermakets and local fish markets for measurements of indicatorPCBs in 9 major cities (Seoul, Daejeon, Gangneung, Daegu, Gunsan, Gwangju, Pohang, Daegu, Jeju) in 2012.

The samples were homogenized immediately after collection and stored at −20 °C until further treatment. In case of food items where wastage could be supposed, inedible parts such as bone, skin, etc. were removed prior to homogenization.

Extraction, clean-up procedure and instrumental analysis

A 10-g aliquot of homogenized fish sample was spiked with the 13C-labeled compounds. The sample was mixed with anhydrous sodium sulfate, dried for a minimum of 30 minutes, and extracted for 24 hours in a Soxhletextractor. The extraction solvent was a mixture of hexane/dichloromethane 50:50 (v/v). The extract was evaporated to dryness, and the lipid content was determined. Tissue extracts are first cleaned up using an

anthropogenic isolation column (anhydrous sodium sulfate 1g, silica 2 g, acid silica 8 g, silica 2g, basic silica 4 g, silica 2 g and anhydrous sodium sulfate 1 g) and all extracts are cleaned up using back-extraction with sulfuric acid, and gel permeation, silica gel, as required. After addition of external standards for the recovery calculation (13C12-PCBs #170 for the PCBs), the final sample extract was evaporated under a nitrogen stream to dryness and reconstituted by addition of nonane.
Indicator PCBs isomer is selected for the analysis of 28, 52, 101, 118, 138, 153 and 180. PCB 28 and PCB 118 are dioxin-like PCBs. Analytical material is detected in GC/MSD by the isotope dilution method and internal standard substance is commercially available for accurate quantification.
Indicator PCBs were analyzed by gas chromatography – mass spectrometry (GC-MS). These measurements were performed on Hewlett Packard 6890 Plus GC system and Agilent 7890A mass spectrometer.
The gas chromatography was fitted with a 60m x 0.25mm i.d.0.25mm DB-1 fused silica capillary column and operated in constant flow 1mL/min helium mode. Indicator PCBs were monitored in a using a GC oven temperature program : 160℃(2 min), a rise at 10℃/min to 200℃(2min), a rise at 5℃/min to 210℃(5 min), a rise at 2℃/min to 300℃ (10 min), a rise at 10℃/min. The instrument was operated in electron ionization (EI) mode at a mass spectrometer. Selected ion monitoring (SIM) was used to record the two most intense ions in the molecular ion cluster for each homologue.

Quality control

480 fish samples collected from nine major cities were analyzed of the occurrence of indicator PCBs (7 congeners). For the test method validation, extraction efficiency, cleanup patterns of multi-column for various food samples have been tested.
The method detection limits, which were acquired by 3 times standard deviation of seven repetitions of test method and recoveries of 13C-labeled internal standard of all samples, were listed in table 1. For the validation of proposed test method, Standard Reference Material 1947 (NIST: Lake Michigan Fish Tissue) was analyzed by this method and all measured values were within SRM permitted values.

Table 1 Method detection limits (MDLs) of indicator PCBs and recoveries of 13C-labeled internal standard

Congener	*MDL (ng/g)*	*Recoveries (%)*
PCB-28	0.025	82 ± 20
PCB-52	0.010	82 ± 17
PCB-101	0.022	99 ± 11
PCB-118	0.033	106 ± 10
PCB-138	0.016	105 ± 9
PCB-153	0.019	102 ± 9
PCB-180	0.023	106 ± 11

Results and discussion:

A food market basket, representative for the general Korean population, containing various fish was assembled and analyzed by gas chromatography-mass spectrometer for its seven indicator PCBs (congeners 28, 52, 101, 118, 138, 153, 180) content. There was no difference in indicator PCBs concentrations between the foods from the different supermarkets and cities, therefore average was derived using all analyses regardless of the origin.
Table 2 displays summary statistics by fish type for lower bound levels below the limit of detection of total indicator PCBs measured in Korea fish.

Table 2 Levels of indicator PCBs based wet weight in the fish (ng/g). N is sample number.

	Species	*N*	*Min*	*Max*	*Mean*	*Median*	*SD*
1	Flat fish	17	ND	2.242	0.648	0.971	0.662

2	Hairtail	15	ND	2.922	1.232	1.114	0.916
3	Mackerel	15	0.218	4.191	1.505	1.136	1.146
4	Whale	5	3.031	8.764	4.751	3.586	2.34
5	Halibut	15	ND	2.245	1.066	0.960	0.806
6	Pacific saury	14	0.0240	2.586	0.835	0.658	0.702
7	Pacific cod	17	ND	2.065	0.596	0.915	0.604
8	Finespotted flounder	11	ND	2.082	1.076	1.193	0.820
9	Sailfin sandfish	13	ND	3.935	1.953	2.077	1.163
10	Snapper	17	ND	1.995	0.455	0.148	0.580
11	Frozen pollack	8	ND	0.059	0.008	ND	0.021
12	Anchovy	16	0.179	6.553	2.372	1.981	1.685
13	Pollack	16	ND	2.101	0.639	0.474	0.735
14	Loach	16	0.012	1.243	0.557	0.454	0.494
15	Fresh water catfish	10	0.102	2.446	0.713	0.500	0.738
16	Kingfish	10	ND	1.090	0.426	0.080	0.517
17	Silver pomfret	14	ND	2.238	0.735	0.473	0.676
18	Swellfish	13	ND	1.317	0.634	0.916	0.510
19	Crucian carp	5	1.096	3.366	2.215	2.324	1.069
20	Spanish mackerel	15	0.480	4.734	1.843	1.470	1.137
21	Shark	8	ND	1.960	0.756	0.956	0.703
22	Tongue sole	10	ND	1.012	0.764	0.942	0.404
23	Trout	10	ND	1.511	1.094	1.420	0.591
24	Flathead mullet	12	ND	2.259	0.940	1.022	0.665
25	Blackmouth angler	14	ND	1.058	0.435	0.075	0.501
26	Conger eel	16	0.073	2.607	0.886	0.824	0.675
27	Salmon	14	0.069	3.556	1.872	1.503	1.492
28	Armorclad rockfish	15	ND	1.564	0.538	0.279	0.582
29	Atka mackerel	16	0.027	2.458	1.042	1.092	0.646
30	Common carp	6	0.991	2.206	1.525	1.464	0.561
31	Eel	10	0.108	2.095	0.896	0.897	0.700
32	Gizzard shad	12	0.471	17.312	3.787	2.075	4.466
33	Croaker	16	ND	2.261	0.854	1.035	0.714
34	Thread-sail filefish	12	ND	1.140	0.531	0.652	0.486
35	Tuna	16	ND	2.869	0.856	0.965	0.948
36	Pacific herring	12	0.841	4.031	2.597	2.637	1.114
37	Skate ray	16	ND	2.178	0.668	0.507	0.767

The measured concentrations of the sum of the seven indicator PCBs in fish range from ND to 4.7505ng/g wet weight. The highest mean level of indicator PCBs was whale 4.751 ng/g wet weight because PCBs was bio-accumulated and whale was the top of the food chain. The measured concentrations of the sum of the seven indicator PCBs in whale ranged from 3.031 to 8.764 ng/g wet weight

The detected indicator PCBs levels were 0.6479 in flat fish, 1.232 in hairtail, 1.505 in chub mackerel, 1.0657 in Halibut, 0.835 in Pacific saury, 0.596 in Pacific cod, 1.076 in finespotted flounder, 1.953 in sailfin sandfish, 0.455 in snapper, ND in frozen pollack, 2.372 in anchovy, 0.639 in pollack, 0.557 in loach, 0.713 in fresh water catfish, 0.426 in kingfish, 0.735 in silver pomfret, 0.634 in puffer, 2.215 in crucian carp, 1.843 in spanish mackerel, 0.756 in shark, 0.764 in tongue sole, 1.094 in trout, 0.940 in flathead mullet, 0.4347 in blackmouth angler, 0.886 in conger eel, 1.872 in salmon, 0.538 in armorclad rockfish, 1.042 in atka mackerel, 1.525 in

common carp, 0.896 in eel, 3.787 in gizzard shad, 0.854 in croaker, 0.531 in thread-sail filefish, 0.856 in tuna, 2.597 in Pacific herring, 0.668 in skate ray ng/g wet weight, respectively..
The contribution of indicator PCBs levels were 11% in whale, 9% in gizzard shad, 6% in Pacific herring, 5% in crucian carp and 5% in anchovy. The intake calculations were based on a theoretical estimate of the average daily food consumption. The contribution of daily intake ratio base on fishery products was occupied by 23% in chub mackerel, 21% in anchovy, 7% in croaker, 5% in pollack, 5% in hairtail and 5% in halibut. In case of fish products, all congeners of indicator PCBs were detected.

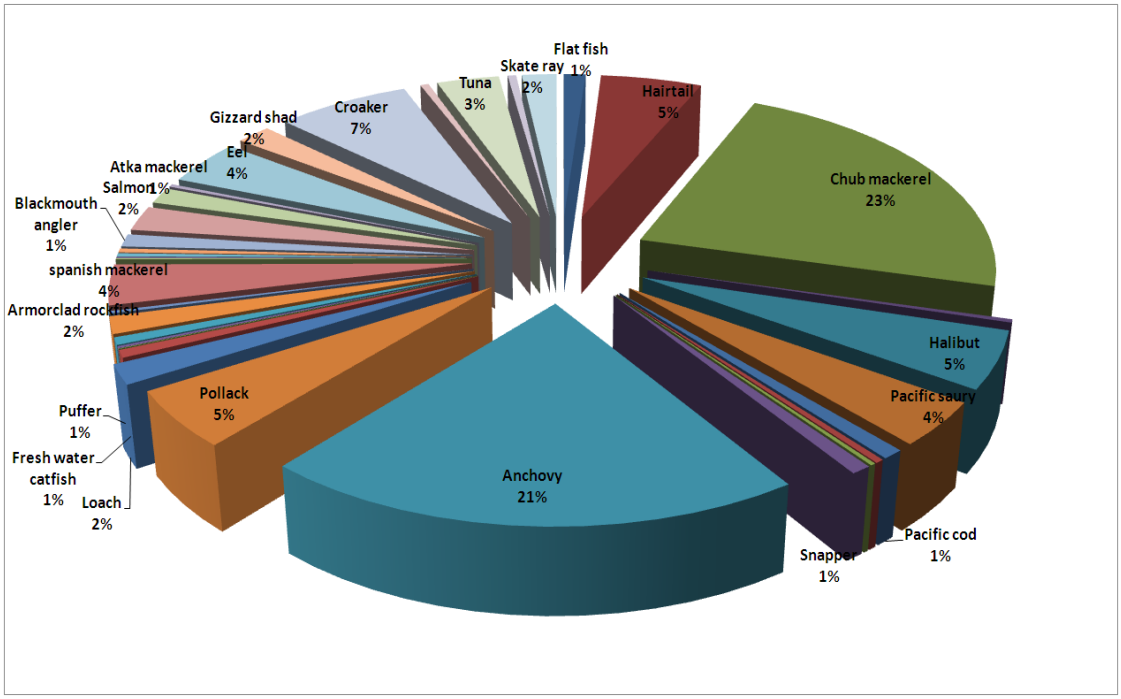

Fig 1.The contribution of PCBs daily intake in fish.

The dominated congener of indicator PCBs was hexa-PCBs (PCB 138, PCB 153). The dietary intake through fish was determined as 4.6% compared with TDI (10 ng/kg bw/day) of France. It was estimated that PCBs was safe and could not have adverse effect in health in Korea yet.

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References
1. ChristinaTlustos, Brendan McHugh, Iona Pratt, Linda Tyrrell and Evin McGovern, Investigation into levels of dioxins, furans, polychlorinated biphenyls and brominated flame retardants in fishery produce in IrelandMarine Environment and Health Series, No.26, 2006
2. M.I. Bakker, A.J. Baars, R.A. Baumann, P.E. Boon and R. Hoogerbrugge, Indicator PCBs in foodsruffs:occurrence and dietary intake in The netherland at the end of the 20th centry, RIVM report 639102025/2003, RIKILT report 2003.014
3. Official Journal of the European Union L320/18, 2011, COMMISSION REGULATION (EU) No 1259/2011.
4. Arnold Schectera, Linda Birnbaumb, John J. Ryanc, John D. (2006); Environmental Research 101 : 419–428