Monitoring of 7 indicator PCBs in shellfish, Korea

Jeounghwa Shin, Jijeong Ryu, Seunghee An, Haejoo Kim, Jungju Seo*

Seoul Center, Korea Basic Science Institute, South Korea

Introduction

Polychlorobiphenyls (PCBs) have been produced commercially for some five decades starting about 1920, by direct chlorination of biphenyl[1]. This chlorination occurs with one to ten chlorine atoms, resulting in 209 possible PCB congeners. Since most PCBs congeners are very lipophilic and persistent, PCBs tend to accumulate in soils, sediments and the food chain. PCB mixtures were used in a wide scale of applications, such as coatings, inks, flame retardants and paints[2-4]. Its major uses, however, were in electronic appliances, heat transfer systems, and hydraulic fluids. For the different applications many different technical mixtures were being used. The total world production is estimated at 1-2 million tonnes. Due to the persistent nature of PCBs in the environment it was decided by many countries some decades ago to ban the use of PCBs in open applications. PCBs may, however, still be in use in closed systems such as capacitors and transformers[1].

The chlorination pattern of the PCB is important for the toxicity of the substance. A number of PCB congeners show 'dioxin-like' toxicity. Mixtures of PCBs are generally assessed on the basis of a chemical analysis of the (sum of the) seven so-called 'indicator PCBs'. The indicator PCBs are known to be persistent in the environment and to bioaccumulate in the food chain, and are assumed to be 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.

The survey of the most recent (2013) on the occurrence of indicator-PCBs in shellfish in Korea. The data on occurrence collected during measurement on occurrence were combined with food consumption data to assess the dietary intake of the seven indicator-PCBs (polychlorinated biphenyls, congeners 28, 52, 101, 118, 138, 153 and 180).

Materials and methods

Samples of selected 41 shellfish species in 472 samples were collected to being distributed at multiple supermakets and traditional market for measurements of indicator-PCBs in 9 major Cities (Seoul, Daejeon, Gangneung, Daegu, Gunsan, Gwangju, Pohang, Daegu, Jeju) in 2013.

A representative population of each area of the city's multiple supermakets and traditional market were purchased and samples were mixed. Targeted that the actual intake of the sample areas were studied, keep dry ice to the laboratory under homogenization. The samples are stored at -20 ^{o}C.

Indicator PCBs isomer is selected for the analysis of the seven indicator-PCBs. Congers 28 and 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.

A Hewlett-Packard GC 7890A equipped with HP MSD 5975 and DB-1 capillary columns (length, 60 m; column i.d., 0.25 mm; film thickness, 0.25um) was used to analyze the PCB congeners. The MS was run in the single ion monitoring (SIM) mode The temperature programme consisted of an isothermal period (160°C, 2 min), a rise at 10°C/min to 200°C(2min), then at 5°C/min to 210°C(5min), a rise at 2°C/min to 300°C(10 min). The instrument was operated in electron ionisation (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. Selected ion monitoring was used, and the two most intense ions in the molecular ion cluster were measured for each ^{13}C-labelled indicator PCBs and native indicator PCBs homologue group.

Table 1. Information of sample

	Species	No		Species	No
1	Patinopecten yessoensis/Scallop	12	22	Venerupis philippinarum/Manila clam	18

2	Sepia officinalis L/Cuttlefish	16	23	Meretrix meretrix/Common orient clam	13
3	Urechis unicinctus/Spoon worm	9	24	Anthiocidaris crassipina/Sea urchin	7
4	Polinices didyma/Whelk(internalorgans)	10	25	Turbocornutus/Spinyturbanshell(internalorgans)	2
5	Polinices didyma/Whelk (flesh)	18	26	Turbo cornutus/Spiny turban shell (flesh)	10
6	Crassostrea gigas/Pacific oyster	13	27	Todarodespacificus/Squid(internalorgans)	11
7	Tegillarca granosa/Cockle	18	28	Todarodes pacificus/Squid (flesh)	18
8	Loligo beka Sasaki/Beka squid	9	29	Pomacea canaliculata/Apple snail	1
9	Portunustrituberculatus/Swimmingcrab(internalorgans)	10	30	Corbicula fluminea/Marsh clam	3
10	Portunustrituberculatus/Swimmingcrab(flesh)	18	31	Haliotisdiscus/Abalone(internalorgans)	12
11	Octopus minor/Longarm octopus (internal organs & ink)	4	32	Haliotis discus/Abalone (flesh)	18
12	Octopus minor/Longarm octopus (flesh)	17	33	Octopus ocellatus Gray/Webfoot octopus	18
13	Cipangopaludina chinensis malleata/Pond snail	9	34	Atrinapectinatajaponica/Combpenshell(internalorgans)	5
14	Chionoecetesopilio/Snowcrab(internalorgans)	2	35	Atrina pectinata japonica/Comb pen shell (flesh)	18
15	Chionoecetes opilio/Snow crab (flesh)	7	36	Penaeus monodon/Tiger Prawn	18
16	Fenneropenaeus chinensis/Fleshy prawn	9	37	Uroteuthis chinensis/Mitra squid	4
17	Meretrix lusoria/Calm	9	38	Holothuria sp/Sea cucumber	13
18	Halocynthia roretzi/Sea squirt	18	39	Rhopilema esculenta/Jellyfish	18
19	Paroctopus dofleini/Giant octopus	9	40	Mytilus coruscus goulc/Mussel	16
20	Styela clava Herdman/Warty sea squirt	18	41	Litopenaues vannamei/White shrimp	5
21	Homarus americanus/Lobster	9			
Total					472

Results and discussion:

A food market-basket, representative for the general Korean population, containing various shellfish was assembled and analyzed by gas chromatography-mass spectrometer for its 7 Indicator PCBs (congeners 28, 52, 101, 118, 138, 153, 180) content. We could not observe any differences in Indicator PCBs concentrations between the foods from the different supermarkets and cities, therefore averages were calculated using all analyses regardless of the origin**.**

The results of the analytical chemical analysis are summarized in Table 2. The measured concentrations of the sum of the seven indicator PCBs in shellfish range from ND to 9.6191ng/g wet weight. The highest mean level of indicator PCBs was Konosirus punctatus/Gizzard shad 9.6191 ng/g wet weight.

Figure 1 showed the contribution of Indicator PCBs levels. the dominated congener of indicator PCBs were 21% in Tri-PCBs(PCB 28), 18% in hexa-PCBs(PCB 153) and17% in hexa-PCBs (PCB 138) .

The dietary intake through shellfish was determined as Spiny turban shell (internal organs) 11% , Common orient clam 9%. It was estimated that PCBs was safe and could not have adverse effect in health in Korea yet.

Table 2. Levels of Indicator PCBs based wet weight in the shellfish

(ng/g)

	Species	**Mean**	**SD**	**Min**	**SD**	**Median**
1	Patinopecten yessoensis/Scallop	0.9899	1.5987	N.D	4.5248	N.D
2	Sepia officinalis L/Cuttlefish	1.6472	1.7990	N.D	4.8000	1.4054
3	Urechis unicinctus/Spoon worm	1.9842	1.7406	N.D	3.9707	2.3439

4	Polinicesdidyma/Whelk(internalorgans)	9.6191	5.5714	N.D	16.2462	10.1083
5	Polinices didyma/Whelk (flesh)	1.2398	1.7094	N.D	4.0051	N.D
6	Crassostrea gigas/Pacific oyster	1.8164	2.3505	N.D	7.2285	N.D
7	Tegillarca granosa/Cockle	0.7843	1.5324	N.D	4.2178	N.D
8	Loligo beka Sasaki/Beka squid	2.9385	1.8186	N.D	4.5513	3.5140
9	Portunustrituberculatus/Swimmingcrab(internalorgans)	5.2219	5.0006	N.D	15.4178	4.5364
10	Portunustrituberculatus/Swimmingcrab(flesh)	1.5636	1.6266	N.D	3.6408	1.0144
11	Octopus minor/Longarm octopus (internal organs & ink)	2.9414	2.0266	N.D	4.6391	3.5633
12	Octopus minor/Longarm octopus (flesh)	1.6096	1.8293	N.D	4.0900	N.D
13	Cipangopaludina chinensis malleata/Pond snail	0.0177	0.0496	N.D	0.1498	N.D
14	Chionoecetesopilio/Snowcrab(internalorgans)	6.8122	0.6697	6.3386	7.2857	6.8122
15	Chionoecetes opilio/Snow crab (flesh)	2.1214	2.6756	N.D	5.6348	N.D
16	Fenneropenaeus chinensis/Fleshy prawn	1.6246	1.9412	N.D	4.0850	N.D
17	Meretrix lusoria/Calm	1.7342	1.8370	N.D	4.7869	1.9366
18	Halocynthia roretzi/Sea squirt	1.1693	1.7461	N.D	4.3800	N.D
19	Paroctopus dofleini/Giant octopus	2.2448	1.7396	N.D	3.7725	3.1929
20	Styela clava Herdman/Warty sea squirt	1.1895	1.6756	N.D	4.3590	N.D
21	Homarus americanus/Lobster	0.0000	0.0000	N.D	0.0000	N.D
22	Venerupis philippinarum/Manila clam	1.1227	1.7183	N.D	4.5347	N.D
23	Meretrix meretrix/Common orient clam	1.4699	1.6879	N.D	4.1592	0.5853
24	Anthiocidaris crassipina/Sea urchin	1.3704	1.8403	N.D	4.4931	N.D
25	Turbocornutus/Spinyturbanshell(internalorgans)	7.7420	6.9447	2.8314	12.6527	7.7420
26	Turbo cornutus/Spiny turban shell (flesh)	2.5311	1.7857	N.D	4.2608	3.3086
27	Todarodespacificus/Squid(internalorgans)	8.0889	4.8066	N.D	13.2400	10.2098
28	Todarodes pacificus/Squid (flesh)	1.0505	1.7036	N.D	4.3149	N.D
29	Pomacea canaliculata/Apple snail	N.D	-	-	-	-
30	Corbicula fluminea/Marsh clam	0.0071	0.0123	N.D	0.0213	N.D
31	Haliotisdiscus/Abalone(internalorgans)	2.1552	1.4175	N.D	4.1585	2.5261
32	Haliotis discus/Abalone (flesh)	1.1412	1.5652	N.D	3.6032	N.D
33	Octopus ocellatus Gray/Webfoot octopus	1.2315	1.8534	N.D	4.4296	N.D
34	Atrinapectinatajaponica/Combpenshell(internalorgans)	2.6483	0.1654	2.4298	2.8681	2.6504
35	Atrina pectinata japonica/Comb pen shell (flesh)	1.4471	1.7505	N.D	4.2633	0.3783
36	Penaeus monodon/Tiger Prawn	1.1922	1.9528	N.D	6.0309	N.D
37	Uroteuthis chinensis/Mitra squid	1.5200	1.7636	N.D	3.2514	1.4144
38	Holothuria sp/Sea cucumber	1.4393	1.4809	N.D	3.4781	1.4788
39	Rhopilema esculenta/Jellyfish	2.1289	2.0367	N.D	4.9937	2.6171
40	Mytilus coruscus goulc/Mussel	1.4069	1.8284	N.D	4.9226	N.D
41	Litopenaues vannamei/White shrimp	N.D	N.D	N.D	N.D	N.D

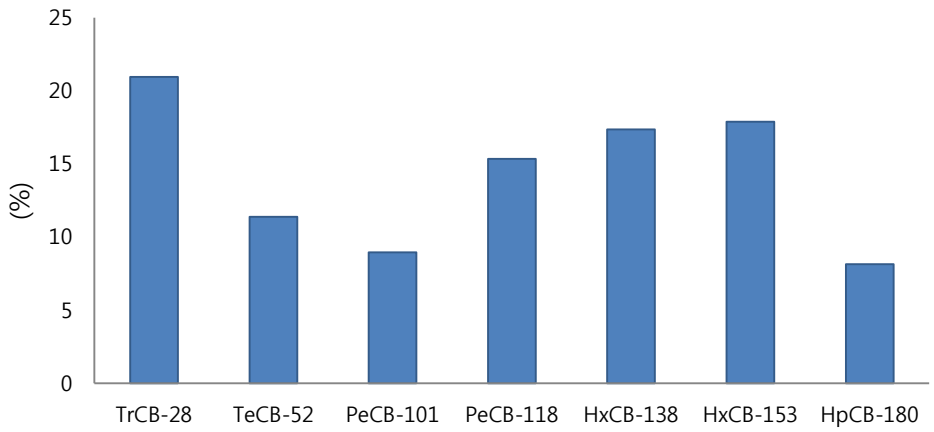

Fig 1. Contribution of indicator PCBs congeners

The contribution of Indicator PCBs levels were 11% in Polinices didyma/Whelk (internal organs), 9% in Turbo cornutus/Spiny turban shell (internal organs), 9% in Todarodes pacificus/Squid (internal organs), 8% in Chionoecetes opilio/Snow crab (internal organs), 6% in Portunus trituberculatus/Swimming crab, 3% Loligo beka Sasaki/Beka squid, 3% in Octopus minor/Longarm octopus (internal organs & inks), 3% in Paroctopus dofleini/Giant octopus, 3% in Turbo cornutus/Spiny turban shell and 3% in Atrina pectinata japonica/Comb pen shell.

The contribution of daily intake ratio base on shellfish products was occupied by 23% in Todarodes pacificus/Squid, 13% in Portunus trituberculatus/Swimming crab, 12% in Octopus minor/Longarm octopus, 12% in Crassostrea gigas/Pacific oyster, 9% in Venerupis philippinarum/Manila clam and 9% in Fenneropenaeus chinensis/Fleshy prawn. In case of shellfish products, most congeners of indicator PCBs were detected in food.

For exposure assessment of indicator PCBs, the dietary intake was estimated at 2.7% compared to TDI (10 ng/kg bw/day) set by France and the average Korean body weight of 60 kg. Consequently, indicator PCBs detected were not considered to cause adverse health effects on Koreans.

Acknowledgements:

This work was supported by outstanding researchers program of National Institute of Food Drug Safety Evaluation.

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