DISTRIBUTION OF PCBs IN FISH AS BEING REPRESENTATIVE OF KOREA

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Introduction

Certain organic compounds such as PCBs, dioxins and pesticides are concern in many areas of world because of their toxicity, their widespread presence, high stability and resistance to degradation.[1-2] They may accumulate in the tissue of aquatic organisms posing a health threat to consumers. The primary focus of this study is PCBs, substances that are now considered to be ubiquitous environmental contaminant and are recognized to be more than 95% of human exposure to them occurs through intake of common foods.[3-5] To report on the rate of occurrence and levels of PCBs in food, marine-origin fishes were selected as food samples and 62 PCB congeners were chosen as target compounds among 209 PCB congeners as shown in Table 1.[6] In general, fish may be divided into two classes: one is dark-fleshed fish and the other is white-fleshed fish. The dark-fleshed fish samples selected were eel (*Anguilla japonica*), mackerel (*Scomber japonica*), Spanish mackerel (*Scomberomorus niphonius*), and pacific saury (*Cololabis saira*). The white-flesh fish samples chosen were Alaska pollack (*Theragra chalcogramma*), bastard halibut (*Paralichthys olivaceus*), flatfish (*Limanda yokohamae*), harvest fish (*Pampus argenteus*), hair tail (*Trichiurus lepturus*), jacopever (*Sebastes hubbsi*), pacific cod (*Gadus macrocephalus*), and yellow croaker (*Pseudosciaena polyactis*). These are the only individual ones which account for 1% or more of the whole fish, and together these account for 70% of all.[7] Fish samples were collected at the local markets in Seoul, Kangneung, Daejeon, Mokpo and Busan. For each sample, all individuals were filleted at the laboratory and composited for analysis.

Methods and Materials

The experimental conditions used for analyzing PCBs were described in detail elsewhere.[6,8-9] The alkali digestion in 1M ethanolic KOH at 80^{o}C for 1 hr, solvent extraction with n-hexane, defatting with conc. sulfuric acid and column chromatography on silica gel were carried out to prepare sample for HRGC/LRMS (Agilent GC6890/MSD5973) analysis. Ten ^{13}C-labeled compound standards (EC-4189, Cambridge Isotope Laboratory, USA) with known concentration added to the sample before extraction. The capillary column (Ultra-2, 50mx0.2mmidx0.33μm) was temperature programmed as follows: 130^{o}C initial, increased 2.5^{o}C per min to 180^{o}C, hold for 1 min, increased 1.8^{o}C per min to 220^{o}C, increased 10^{o}C per min to 300^{o}C, hold for 15 min. BP-MS

(Wellington Laboratories, Canada) was used for the calibration standard.

Results and Discussion

The identification, quantitation and confirmation were accomplished with HRGC/LRMS. Detection limits varied depending on congener were 0.08 μg/kg for tetra- to hexa-PCB congeners, 0.10 μg/kg for hepta-PCB congeners and 0.25 μg/kg for the octa-PCB congeners. Under the experimental conditions, the recoveries were ranged from 73.7% to 119.8% and the correlation coefficients were 0.995~0.999. Thus the analytical method applied was very simple and effective for determining PCBs in fishes. As might be expected, contamination patterns and levels appear to differ among species. As shown in Fig. 1, tri-, tetra-, penta-, hexa- and hepta-PCB homologues dominate. However, the most commonly detected PCBs were the penta- and hexa-congeners. As not shown in data, the most contributing congers were IUPAC #138, #153 for hexa- and #118, #101 and #99 for penta-congeners among 62 selected PCB targets. Regarding 5 different sampling sites, a similar picture was found in most of fishes except hair tail and eel. A wide range of PCB levels was observed in eel and hair tail, whereas a wider spectrum of PCB homologues is observed in hair tail (from tri to octa). Although the living circumstances are quite different from individual country, the distribution of PCB homologues detected in fish samples of Korea is close to that of New Zealand.[4] Mean levels of PCBs determined are given in Table 2. The total level was in a wide range of 1.19 to 81.05 μg/kg wet weight. On a whole weight basis, all level was below 0.1 mg/kg. In other words, these levels are well below the allowable tolerances of USA, Japan and EU for PCBs in food. Usually the dark-fleshed fishes feed on other schooling fishes like anchovies and herrings, and on invertebrates and the white-fleshed fishes feed on a variety of animals, mostly mollusks, sea squirts, and other fishes. Moreover, the lipid contents of the dark-fleshed fishes are higher than those of most of the white-fleshed fishes. As results, these data are shown that PCB levels in the dark-fleshed fish are on the order of 3~4 times higher than those in the white-fleshed fish except hair tail. Especially, samples of hair tail gave a remarkably high contamination level of 183.81 μg/kg wet weight. Higher levels in hair tail might be due to the influences from high lipid content and habitat such as estuaries and open sea over mud. In addition, hair tail is voracious, feeding on almost any kind of fish. A similar picture is found in eel. As expected fatty fishes such as eel, mackerel, Spanish mackerel, pacific saury, hair tail and yellow croker show higher contamination level of PCBs than non-fatty fishes such as Alska pollack, bastard halibut, flatfish, jacopever and pacific cod. However, it is interesting that mean level of PCBs in harvest fish is 4.94 μg/kg wet weight even if the lipid content is 12%. In general, harvest fishes feed on jellyfishes, crustaceans, worms, and small fishes, but the juveniles are plankton feeders and often live among floating weeds or large jellyfishes. It is clear that the harvest fish samples are juvenile. It is beginning of the survey to determine the national distribution and levels of PCBs in fishes. Further studies need to be done to completely assess levels of PCBs in Korean food such as fishes, shellfishes, meats, milk and milk products.

Table 1. List of target compounds and ions for PCB analysis

No. of Cl	Targets (IUPAC No.)	Ion
Mono	1, 3	188, 190
Di	4, 8, 10, 15	222, 224
Tri	18, 19, 22, 28, 33, 37	256, 258
Tetra	44, 49, 52, 54, 70, 74, 77, 81	290, 292
Penta	87, 96, 99, 101, 104, 105, 110, 114, 118, 119, 123, 126	324, 326
Hexa	128, 138, 149, 151, 153, 155, 156, 157, 158, 167, 168, 169	360, 362
Hepta	170, 171, 177, 178, 180, 183, 187, 188, 189, 191	394, 396
Octa	194, 199, 201, 202, 205	428, 430
Nona	206, 208	462, 464
Deca	209	498, 500

Table 2. Levels of PCBs in fishes

Food Item		Total PCB Levels (min~max)	(μg/kg ww)	Lipid (%)	Daily Intake (g/day)
Dark-fleshed fish	Eel	3.08~40.47	14.56±15.2	12	0.8
	Mackerel	11.47~20.55	17.67±3.61	14	6.1
	Spanish mackerel	9.56~24.76	18.49±5.53	13	1.0
	Pacific saury	6.40~18.68	13.94±4.66	14	0.8
White-fleshed fish	Alaska pollack	N.D~ 2.27	1.26±0.86	2	6.5
	Bastard halibut	1.85~ 6.16	4.11±1.73	3	1.5
	Flatfish	0.79~18.48	6.99±7.51	2	1.2
	Harvest fish	2.62~ 8.65	4.94±2.53	12	0.5
	Hail tail	12.96~183.81	81.05±71.3	12	2.6
	Jacopever	6.07~11.35	8.50±2.42	5	0.7
	Pacific cod	0.52~ 2.06	1.19±0.61	1	0.5
	Yellow croker	13.94~19.78	16.37±2.76	13	4.3

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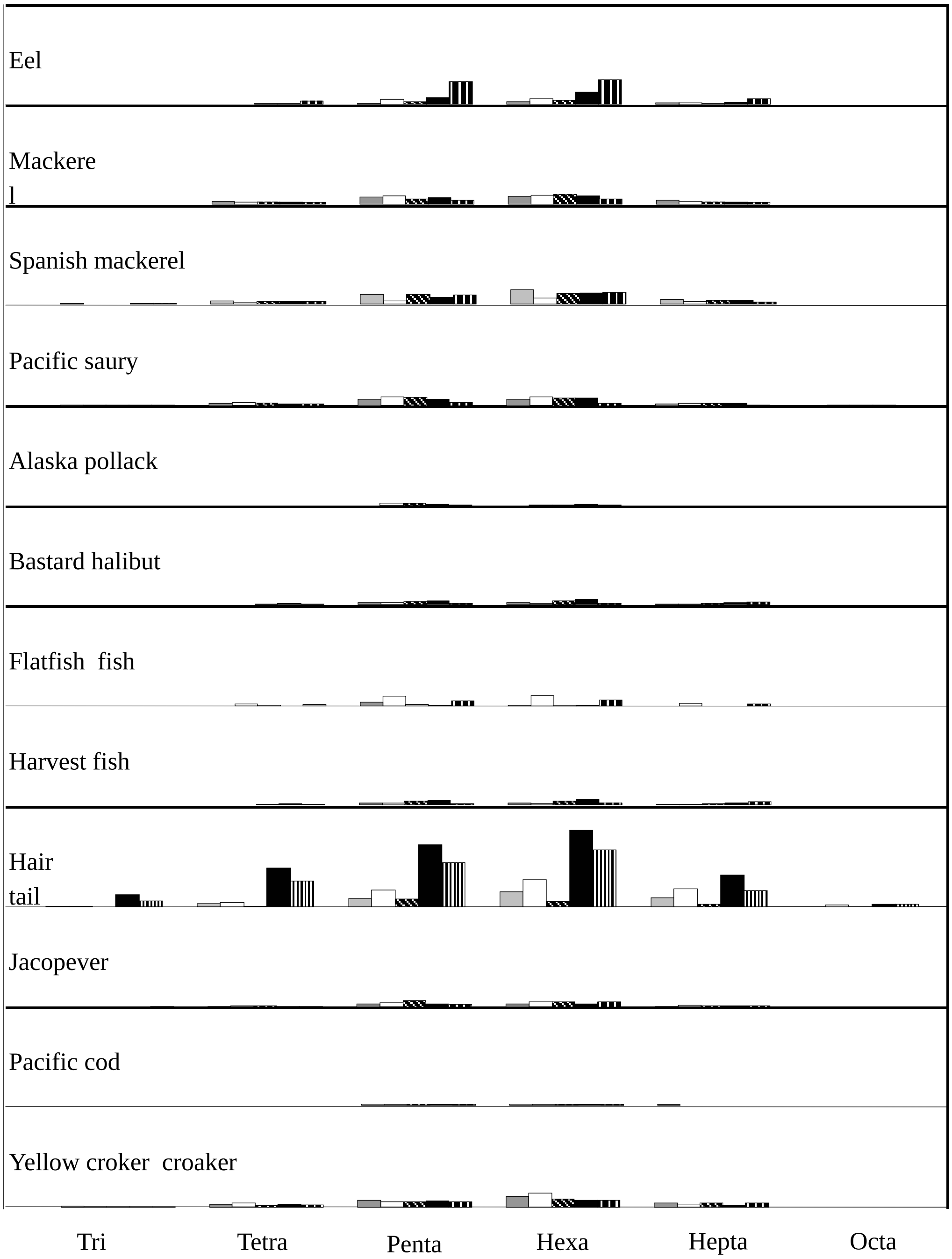

Fig. 1 Distribution of PCBs in fish sampled at 5 different cities in Korea.