

DIOXIN LIKE PCBs LEVELS IN FISH FROM THE HAN-RIVER

Micro Pollutant Analysis Team

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한강 어류 중 다이옥신 유사독성을 가진 폴리클로리네 이티드비페닐의 농도 조사 연구

미량물질분석팀

최용석 · 엄정훈 · 정종흡 · 엄석원 · 김민영

초 록

서울이 도시화 산업화가 되면서 오랜기간 동안 한강이 서서히 오염되었고, 환경중에서 잘 분해되지 않는 POPs(persistent organic pollutants)등이 하층 저질이나 물고기 등에 오염되었을 가능성이 있다. 최근 환경호르몬 중 하나인 다이옥신류와 PCBs가 논란의 대상이 되고 있고, 이들 오염물질은 한강 물고기등의 생체내에서 잔류할 수 있는 가능성이 큰 것으로 알려져 있다.

고분해능 질량분석기를 이용, 다이옥신 유사독성을 가진 PCBs를 조사 분석했다. 육식성인 어류조직에서의 PCBs 농도는 초식성 어류보다 높은 것으로 나타났다.

주요어 : 물고기, 다이옥신류, PCBs, 육식성 어류, 초식성 어류

Introduction

The Han river flows through in Seoul, Korea. They have been polluted by industrial and domestic waste water including heavy metals and organic contaminants, and by deposition including hydrophobic compounds such as dioxins and PCBs from the air for a long term. But the degree of pollution was not severe, and it is still important

to be used for agricultural, recreational, and domestic purpose as well as a source of potable water. There are many kinds of fishes in Han river. These fishes might be polluted and bioaccumulated by many kinds of pollutants and ultimately, it can inflict harm upon humans. In this study, the highest toxicity 12 species of PCBs among the 209 species of PCBs in fish were researched and discussed. We selected one of the

samples and then also analyzed PCBs level of spawn and liver of the sample and examined a degree of bioaccumulation of PCBs and possibility of handing down.

Material and methods

Sampling : The fish samples were collected from the Han river January to March in 2001. The kinds of samples are carp, crusian carp, *Erythroculter erythropterus* Basilewsky-Cyprinidae, ussurian bullhead, Korean bullhead - Bagridae and Far Eastern catfish-Siluridae. These fishes are carnivorous except carp and crusian carp.

Analytical Procedure : The fresh fish samples were skinned, filleted and stored frozen at -25°C until analysis. These samples were cut small, crushed with stomacher and homogenized. Each sample (40g) was spiked with ¹³C₁₂-labeled PCBs as internal standard, and then digested with 300ml of KOH-Ethanol by shaker during 12hr.

The solution was extracted by n-hexane and then the n-hexane layer was treated with conc. sulfuric acid (100ml) in a separate funnel until remaining color was removed completely, and then washed with distilled water (100ml) until pH of the hexane layer became neutral. This step was followed by a purification in a multi-layer silica column with n-hexane and alumina column with 4% dichloromethane/n-hexane. The purified extract was concentrated to final volume 20ml under nitrogen stream, and then spiked with ¹³C₁₂-labelled PCBs as recovery standard. The extract was analyzed by HRGC-HRMS on Micromass VG Autospec Ultima equipped with a CE 8000 series gas chromatograph, operating at 10,000 resolving power in the SIM mode, using a 60m DB-5ms fused silica capillary column (0.32mm id × 0.25mm film thickness).

Results and discussion

The PCBs level showed big differences according to species. The concentration of PCBs in herbivo-

Table 1. PCBs level in fish muscle (I-TEQ pg/g, wet weight)

Congeners	Carp	crusian Carp	Far Eastern catfish	Ussurian bullhead	Korean bullhead	Erythroculter euythropterus Basilewsky
PCB-77	0.01	0.00	0.01	0.02	0.01	0.01
PCB-81	0.00	0.00	0.00	0.01	0.00	0.00
PCB-105	0.02	0.04	0.13	0.54	0.05	0.13
PCB-114	0.01	0.02	0.06	0.25	0.02	0.06
PCB-118	0.07	0.11	0.37	1.47	0.13	0.42
PCB-123	0.01	0.02	0.04	0.17	0.02	0.06
PCB-126	1.14	0.47	2.01	7.07	0.9	2.46
PCB-156	0.04	0.08	0.25	1.06	0.09	0.37
PCB-157	0.01	0.01	0.05	0.19	0.02	0.07
PCB-167	0.00	0.00	0.00	0.01	0.00	0.00
PCB-169	0.00	0.00	0.00	0.04	0.00	0.03
PCB-189	0.00	0.00	0.00	0.02	0.00	0.01
Sum	1.31	0.75	2.92	10.85	1.24	3.62

rous carp and crusian carp muscle comparatively indicated less than that of carnivorous fishes. The PCBs levels in carp and crusian carp muscle were 1.31pg-TEQ/g and 0.75pg-TEQ /g, respectively. In carnivorous fishes, the PCBs level of *Erythroculter erythropterus* Basilewsky was 3.62pg-TEQ/g, ussurian bullhead 10.85pg-TEQ/g, Korean bullhead 1.24pg-TEQ/g and Far Eastern catfish 2.92pg-TEQ/g. The PCBs levels of fishes muscle are shown in Table 1.

The total concentration of PCBs ranged from 1304pg/g to 26391pg/g. The PCBs level of carnivorous ussrian bullhead had the highest value and that of herbivorous carp the lowest. Regardless of the big difference of fish species and the concentration of PCBs, the relative abundance of each isomer showed almost the same pattern. It is possible to say the bioaccumulation and biodegradation in vivo, which have almost same metabolism. The percentage of PCB-118 in whole PCBs concentration ranged from 51.1% to 56.7% and the average was 55%, and that of PCB-105 ranged from 17.0% to 20.4% and the average was 19.0%. The proportion of the two congeners in total concentration reached to 74%(Fig.1)

The ratio of PCB-118 in total concentration was the highest of the other isomers but the PCB-118 affected the TEQ value inconsiderably. The ratio of PCB-126 in total concentration was 0.4% only, regardless, it has the most influence on TEQ value. The occupation percentage of the isomer in TEQ value was 70% and that of PCB-118 was 11% merely.

We researched the PCBs level of Far Eastern catfish in three kind of tissue. They were muscle, liver and spawn. The PCBs of three kinds of tissue almost shows the same pattern(Fig. 2) The PCBs level of spawn is the highest of the three kind of tissue. The PCBs level(TEQ value) of liver and spawn in Far Eastern catfish was about

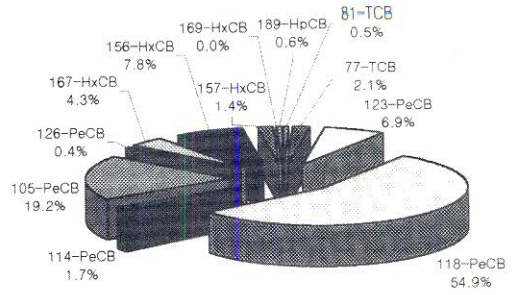


Fig. 1. The mean of relative abundance in fish muscle

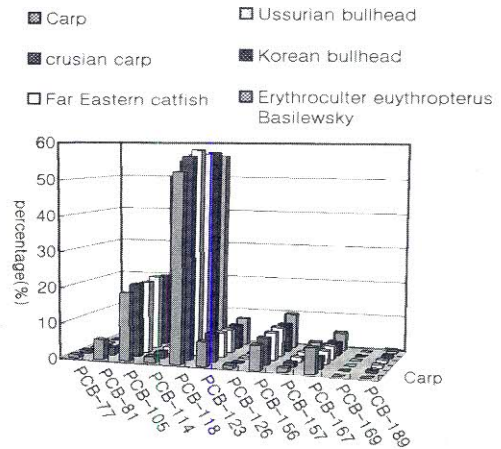


Fig. 2. The relative abundance of PCBs in fish

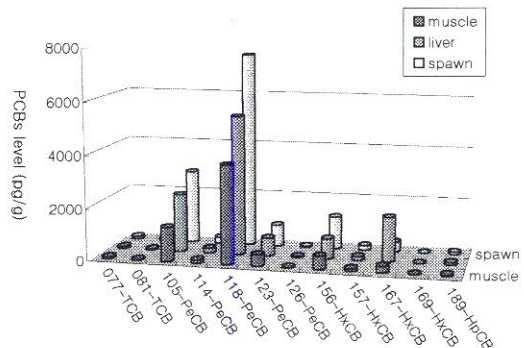


Fig. 3. PCBs congeners in far eastern catfish

1.5times and 1.9times as much as that of muscle respectively(Fig. 3). It says that a lot of PCBs in

the body would hand over next generation.

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