LEVELS OF POPS PESTICIDES IN FRESHWATER FISH (CRUCIAN CARP) IN S. KOREA

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Introduction

Persistent organic pollutants (POPs) in freshwater fish from major river systems of S. Korea were determined. The objective of this investigation was to grasp concentrations and accumulation profiles of POPs pesticides and HCHs in crucian carp (*Carassius auratus*) in Korea. DDTs, chlordanes, drins, heptachlors, HCB, and HCH were determined, and 16 sampling stations were selected along the major river systems. The HCHs and drins (dieldrin, endrin, and aldrin) were never detected. HCB was detected only once, and the detection frequencies of heptachlors (trans- and cis-heptachlor expoxides, and heptachlor), chlordanes (trans-nonachlor, trans-chlordane, cis-chlordane, and oxychlordane), DDTs (DDT, DDE, and DDD) were 3, 9, and 6, respectively. Concentrations of heptachlors, chlordanes, and DDTs ranged 0.50-1.87, 0.10-2.21, and 0.4-4.2 ng/g wet weight, respectively. This investigation is a part of nationwide project to monitor levels of endocrine disruptors in freshwater fish started from the year 1999, and it ended in the year 2004 due to the low detection frequencies and very low concentrations.

Materials and Methods

A total of 20-30 crucian carps were collected at every 16 sampling location (Fig. 1) from the year 1999 to 2003. Whole fishes were filled, skinned and stored at below -20℃ prior to analysis. Pooled samples were prepared by mixing and homogenizing muscle part of several individuals from each sampling location. The internal standard was added into the homogenized fish sample, and homogenized this sample again by adding a 1:4 mixture of acetone:n-hexane followed by centrifuging it for 10 minutes at 3000 rpm. The proper extraction and separation procedures were performed one-by-one with hexane-in-water, anhydrous sodium sulfate, acetonitril saturated with n-hexane, 5% NaCl aqueous solution, and n-hexane. The pretreatment solution was concentrated to 5 ml by a rotary evaporator and then a Florisil column was applied for sample clean-up. The column was eluted in sequence with 40 ml of n-hexane, 100 ml of 4% diethylether/hexane and 200 ml of 15% diethylehter/hexane. The volume of the eluent was reduced by using a rotary evaporator and finally reduced to 1 ml by purging with an ultra pure nitrogen gas. The analyses were performed with a HP5-MS (5% phenylmethylsiloxane) column and

a Hewlett Packard 6890 GC system equipped with a mass selective detector. Detection limit (DL) of individual compound was determined by analyzing seven blank samples. The standard deviation (stdv) of the measured value for each compound was obtained and then detection limit was calculated by following equation[2] : DL = 1.943 × stdv. Median detection limits were 0.25 ng/g wet wt for HCHs, HCB and DDTs, 0.10 ng/g wet wt for HCB and heptachlors, and 0.07 ng/g wet wt for chlordanes.

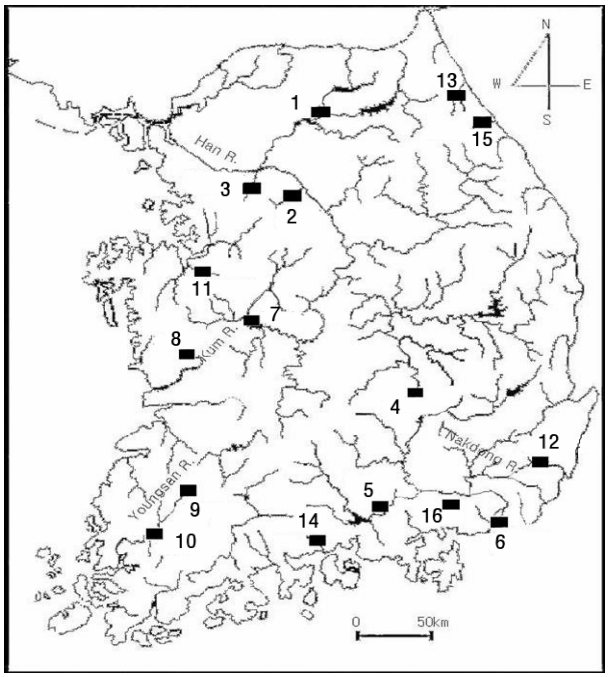

Fig. 1. Locations of sampling sites
(124.6º E ~ 129.6º E, 34.0º N ~ 38.5º N)

1: Uiam-Dam, 2: Bokha-stream, 3: Gyungan-stream, 4: Goomi, 5: Nam-River, 6: Nakdong-estuary, 7:Daecheong-Dam, 8:Booyeo, 9: Damyang-Dam, 10: Najoo, 11: Oncheon-stream, 12: Myungchon, 13: Yangyang, 14: Hadong, 15: Gangnung, 16: Junam

Results and Discussion

Table 1 shows the detection limits and concentrations of POPs pesticides in crucian carp collected from 16 locations along the major river systems. No POPs were detected over the detection limit during the period of this investigation at half of the sampling locations as shown in Fig. 2. There were 64 determinations for each POPs pesticide from 16 sampling sites for 4 years. Drins and HCH were never detected above the detection limit. HCB was detected (0.19 ng/g wet wt) only once at Goomi located along the Nakdong River in the year 2000. Trans-heptachlor epoxide was detected once at Bokha-stream in 2002, and twice at Bokha-stream and Booyeo in 2003. The detected concentrations of trans-heptachlor epoxide ranged from 0.50 to 1.87 ng/g wet wt. The detection frequency of DDTs was 6 and that of chlordanes was 9, and their concentrations ranged from 0.4 to 4.2 ng/g wet wt and from 0.10 to 2.21 ng/g wet wt. respectively. There was neither systematic distribution pattern nor increase in concentration at the same location after detected. This resulted from the fact that the use of these POPs was banned more than 20 years ago from the investigation time. The major POPs pesticide groups in crucian carp

were DDTs and chlordanes, and the proportions of these were 59% and 28% of total POPs concentrations, respectively. Table 2 shows the consumption volume[3], period of service[3], $logK_{ow}$, total detected concentration and mean values of each pesticide. Although the consumption volume of DDTs was around half level of HCHs during the same period of service, the detection frequency and concentration were much higher than those of HCHs. This is believed to be due to the higher persistency of DDTs ($logK_{ow}$ = 6.02-6.91) than that of HCHs ($logK_{ow}$ = 3.72-4.14). The proportion of p,p'-DDE, the metabolite of p,p'-DDT, was 87.6% of the sum DDTs, followed by 9.7% of p,p'-DDT and 2.8% of p,p'-DDD. The highest concentration of DDTs, however, was 4.2 ng/g wet wt, and this value is much lower than the guideline of 14.4 ng/g wet wt set by U.S. EPA[4]. The main component of chlordanes was trans-nonachlor (57.3%) followed by trans-chlordane (29.9%) and cis-chlordane (12.8%). This trend is the same as determined in lake fish from the Sir Dam Lake, Turkey.[5] Among heptachlors, only trans-heptachlor epoxide was detected, and the detection frequency was extremely low. Both concentration and detection rate were much lower than those observed in fish species from Qiantang River in east China.[6]

Table 1. Detection limits and concentrations of POPs pesticides in crucian carp, ng/g wet weight.

	DL (ng/g)	2000	2001	2002	2003
HCH(α, β, γ, δ)	0.25	<DL	<DL	<DL	not determined
HCB	0.10	0.19 (Goomi)	<DL	<DL	<DL
Heptachlors (heptachlors, trans- & cis-heptachlor expoxide)	0.10	<DL	<DL	1.87 (trans-Heptachlor epoxide, Bokha-stream)	trans-Heptachlor expoxide 0.50 (Bokha-stream), 0.80 (Booyeo)
Drins (aldrin, dieldrin, endrin)	0.25	<DL	<DL	<DL	not determined
Chlordanes(oxy-, cis-, & trans-chlordane; cis- & trans-Nonachlor)	0.07	0.35(trans-, Nam-River)	<DL	2.21(transNonachlor, Booyeo) 0.56(cis, Booyeo) 0.96 (trans, Oncheon-st)	transNonachlor 0.20 (Booyeo,) 0.10 (Bokha-stream, Damyang-dam, Gangnung), 2.2 (Yangyang)
DDTs(DDT, DDE, DDE)	0.25	4.2(p,p'-DDE, Nam-River)	<DL	1.40 (p,p'-DDT, Bokha-stream) 0.40 (p,p'-DDD, Bokha-stream)	all p,p'-DDE (3.2 Najoo, 2.4 Damyang-dam, 2.9 Gangnung)

Table 2. Total concentrations and description of POPs pesticides

Compound	Consumption volume, ton	Period of service	Log K_{ow}	Total concentration detected, ng/g wet wt (range)	Mean, ng/g wet wt (<DL was estimated as the half level of the DL)
HCHs	1,946	1949-1971	3.72- 4.14	<DL	0.12
HCB	No data		5.73	0.19 (<DL00.19)	0.05
Heptachlors	597	1962-1979	5.4- 6.1	3.17 (<DL-1.87)	0.10
Drins	147	1962-1972	5.2-6.5	<DL	0.12
Chlordanes	No data		4.76- 6.16	6.78 (<DL -2.21)	0.14
DDTs	1,062	1949-1971	6.02- 6.91	14.50 (<DL -4.2)	0.34

POPs pesticides applied to the agricultural land can be transported to the river due to the run off of the surface water. Organic materials in the soil containing POPs may be digested by fish, resulted in bioaccumulation of POPs in the lipid part of their bodies. These POPs may be transferred to the human beings through food chains.

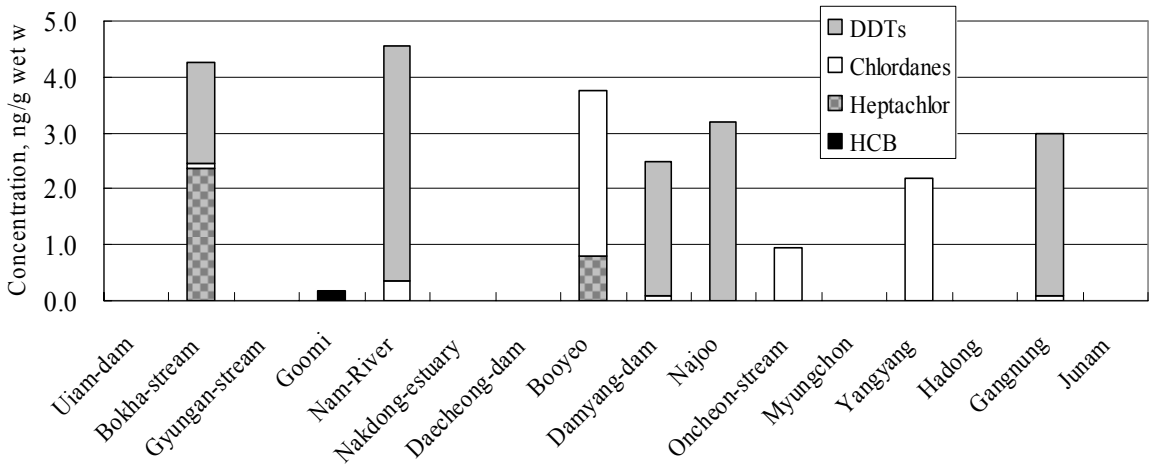

Fig. 2. Site specific POPs concentrations in crucian carp along the major river systems, Korea

Acknowledgements

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