

# RESIDUES OF SOME ORGANOCHLORINE INSECTICIDES AND POLYCHLORINATEDBIPHENYLS IN THE FISH AND SEDIMENT FROM TWO CAGE CARP (*Cyprinus carpio*) FARMS

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## Abstract

Due to liposolubility and bioaccumulation, organochlorine insecticides (OCIs) and polychlorinated biphenyls (PCBs) are very harmful compounds and can be found in various parts of organisms, most commonly in the adipose fish tissue in very high concentrations which can even be one million times higher than those occurring in water. These compounds and other toxic matter in the sediment of an aquatic ecosystem such as cage farm, are often accumulated in sediment and fish as a consequence of the constant presence of the unused feed and fish feces. Qualitative identification and quantitative determination of OCIs and PCBs residues were carried out on a Hewlett Packard 5890, Series II gas chromatograph with a PAS-1701 ECD tested 1710 Siliconic (25 m x 0.32 mm x 0.25  $\mu$ m) capillary column and the electron-capture detector. Working parameters: injector temperature: 250°C; column temperature: 215°C; detector temperature: 300°C; gas carrier: nitrogen. Residues of  $\Sigma$ DDT, p,p-DDE and p,p-DDD were detected in all samples: fish (*Cyprinus carpio*), sediment and water in the Crvenka and Bac cage carp farms. Residues of  $\alpha$ -HCH,  $\beta$ -HCH,  $\delta$ -HCH, Lindan and p,p-DDT were detected in the samples of fish (*Cyprinus carpio*).

**Keywords:** Organochlorine insecticides (OCIs); polychlorinated biphenyls (PCBs); cage carp farms; fish (*Cyprinus carpio*); sediment.

## Introduction

To detect primary or secondary (direct or indirect) pollution source it is very useful to monitor the contamination of the polluted system which is under control. In that case cage fish farms represent the optimal biosystems for control, monitoring and evaluation of the various types of pollution.

The polluting matter, which in aquatic ecosystems is under influence of a number of physico-chemical parameters and biological processes, is concentrated in plant organisms and through them enter the food chain of the subsequent members. In this way, the contaminants from

water via microflora, zooplankton, and fish are bioaccumulated and biomagnified in human being. In the intensive fish rearing, the pollutants are accumulated in the fish of the given biotope, and also from the industrially produced fish feed, whose composition reflects the pollution degree of the environment in which the feed components were manufactured.

Continuing on our previous investigations (1-5) in the field of the determination of OCIs and PCBs in the different Vojvodina aquatic systems, in this paper we investigated the levels of OCIs and PCBs in the fish and water sediment in cage carp farms in Crvenka and Bač.

## **Methods**

Samples of fish, sediment, and water were taken in conventional way from the carp cage farms of the sugar factory "Crvenka" in Crvenka and the "Arma" fish farm in Bač, during 2002. The analyses encompassed the edible part of fish tissue (without guts, scales, gall bladder, and bigger bones), after its crumbling and homogenization. The homogenized sediment samples for the analysis of OCIs and PCBs were used in the native form.

The quantities of about 20 g of fish samples were taken for the analysis. Extraction of OCIs and PCBs was carried out with the methanol:chloroform:water (2:2:1) mixture. The water-methanol layer was removed and the chloroform solution was evaporated in the oven, then dissolved in n-hexane to digest the lipids and other co-extracts, and in sulphuric acid till the discolouration of the n-hexane layer. The final purification of the OCIs and PCBs extracts from fish tissue was carried out by column chromatography with florisil as adsorbent. Organohalogens were eluted with 4% solution of diethyl ether in n-hexane. The eluate was collected in a cuvette and the volume was reduced on a rotating evaporator, the content quantitatively transferred to an ampoule and evaporated to dryness. The purified extracts contained the OCIs and PCBs residues. Samples of raw sediments (about 50 g) were extracted with 50 cm<sup>3</sup> of the acetone-n-hexane (1:1) mixture, then filtered and washed with the same solvent mixture. Acetone was removed by washing with water. The hexane layer was purified with concentrated sulphuric acid till the discolouration of the acidic layer. Sulphuric acid was washed out with distilled water and then copper powder was added to the n-hexane extract, whereby sulphur, which interferes in the gas-chromatographic determination, was removed in the redox process. After filtration through the appropriate filtration paper the content was heated in an oven at 40<sup>0</sup>C, to reduce its volume. The purified extracts contained a mixture of OCIs and PCBs. Qualitative identification and quantitative determination of OCIs and PCBs residues were carried out on a Hewlett Packard 5890, Series II gas chromatograph with a PAS-1701 ECD tested 1710 Siliconic (25 m x 0.32 mm x 0.25 µm) capillary column and the electron-capture detector. Working parameters: injector temperature: 250<sup>0</sup>C; column temperature: 215<sup>0</sup>C; detector temperature: 300<sup>0</sup>C; gas carrier: nitrogen.

## **Results**

On the basis of the results presented in Table 1. and 2. it is evident that the variety and abundance of pesticides is greater for the Crvenka fish farm than for those in Bač.

Table 1. Residues of OCl<sub>s</sub> and PCBs in the fish, sediment, and water ( $\mu\text{g}/\text{kg}$ ) in the Bač cage carp farms

Pollutant Sample	$\alpha$ -HCH	$\beta$ -HCH	$\delta$ -HCH	Lindan	p,p-DDE	p,p-DDD	p,p-DDT	$\Sigma$ DDT	PCB
Carp - 1 <sup>-</sup> mass 0.300 kg	2.038	1.006	0.459	0.439	1.653	1.500	1.130	4.283	4.283
Carp - 1 <sup>+</sup> mass 0.325kg	BDL	BDL	BDL	BDL	0.151	0.246	0.141	0.538	BDL
Carp - 2 <sup>+</sup> mass 1.150 kg	BDL	BDL	BDL	0.166	0.974	1.319	0.411	2.704	BDL
Carp - 2 <sup>+</sup> mass 1.210 kg	BDL	BDL	BDL	0.151	0.519	0.890	0.344	1.753	BDL
Sediment	BDL	BDL	BDL	BDL	0.035	0.121	0.027	0.183	BDL

\*BDL - Below Detection Limit

Table 2. Residues of OCl<sub>s</sub> and PCBs in the fish, sediment, and water ( $\mu\text{g}/\text{kg}$ ) in the Crvenka cage carp farms

Pollutant Sample	$\alpha$ -HCH	$\beta$ -HCH	$\delta$ -HCH	Lindan	p,p-DDE	p,p-DDD	p,p-DDT	$\Sigma$ DDT	PCB
Carp - 1 <sup>+</sup> mass 0.288 kg	0.015	0.106	0.135	0.029	7.358	26.158	0.353	33.869	BDL
Carp - 1 <sup>+</sup> mass 0.475 kg	0.030	0.189	0.134	0.065	11.873	36.959	0.547	49.378	BDL
Carp - 2 <sup>+</sup> mass 1.390 kg	0.155	0.494	0.469	0.170	9.694	31.222	0.414	41.331	BDL
Carp - 2 <sup>+</sup> mass 0.840 kg	0.040	0.179	0.184	0.065	8.718	27.295	0.427	36.440	BDL
Carp - 5 <sup>+</sup> mass 6.170kg	0.037	0.237	0.307	0.042	5.005	18.623	0.297	23.925	BDL
Sediment	BDL	BDL	BDL	BDL	0.0064	0.0095	BDL	0.0115	BDL
Water	BDL	BDL	BDL	0.00018	0.000082	0.0002	BDL	0.00046	BDL

\*BDL - Below Detection Limit

## Discussion

The significant difference in the DDT content between the one-summer carp of the Bač fish farm can be ascribed to the possibility that the individual fish had been exposed to extreme contamination, which can also be seen from the total PCB amount registered. The presence of HCH in two-year old carp from Bac was not registered, whereas  $\Sigma$ DDT was significantly lower in the two-year than in the one-year old fish. The irregularities observed in the presence and content of OCl<sub>s</sub> and PCBs for the one-year fish in the Bac fish farm, as well as the significantly lower OCl<sub>s</sub> concentrations for the two-year compared to one-year old fish can be

explained by the different origin of young fish, so that it is probable that the two-year fish represents better the real state of the fish farm.

Sediment (Table 1), which is a continuous source of OCIs in an aquatic ecosystem, especially of a static one, has low  $\Sigma$ DDT concentrations, much lower than those observed for the fish. Since the registered OCIs residues in the bioorganisms do not exceed those prescribed by the corresponding regulations it can be concluded that the biotope is unpolluted. In the Crvenka fish samples, no regularity in the  $\Sigma$ DDT content was observed. A regularity was observed for the HCH content, which increases with the fish age. A comparison of the two aquatic ecosystems shows that the  $\Sigma$ DDT contents for the Crvenka fish farm are higher, so that its contamination is also higher.

In view of a relatively small number of the investigated samples involved, the results obtained do not give a full picture of the ecological state of these aquatic systems, especially because of the existence of differences between the individual fish of the same age and from the same fish farm. The repeated experiments involving a larger number of fish samples could be more representative for the given biotope, and thus give more reliable information about its pollution.

## **Conclusions**

The results of reported study show that the variety and abundance of OCIs and PCBs is greater for the Crvenka fish farm than for those in Bac. The significant difference in the DDT content between the one-summer carp of the Bac fish farm can be ascribed to the possibility that the individual fish had been exposed to extreme contamination, which can also be seen from the total PCB amount registered. The presence of HCH in two-year old carp from Bac was not registered, whereas  $\Sigma$ DDT was significantly lower in the two-year than in the one-year old fish.

The sediment, which is a continuous source of OCIs in an aquatic ecosystem, especially of a static one, has low  $\Sigma$ DDT concentrations, much lower than those observed for the fish. Since the registered OCIs residues in the bioorganisms do not exceed those prescribed by the corresponding regulations it can be concluded that the biotope is unpolluted. In the Crvenka fish samples, no regularity in the  $\Sigma$ DDT content was observed. A regularity was observed for the HCH content, which increases with the fish age. Comparing our previous results on residues of OCIs and PCBs in static aquatic system of fishpond Ecka to results from fish cage farm Crvenka and Bac, we can conclude that the content of residues is lower in fish cage farms. It implies that fish cage farms (artificial aquatic ecosystems), have better possibilities to control and management, and can provide the adequate conditions for increase of the fish population.

## Acknowledgments

This work was financially supported by the Ministry of Science, Technology and Development of the Republic of Serbia (Project: "Development of New and Improvement of Existing Analytical Methods and Techniques for Monitoring Quality of the Environment", No. 1622)

## References

1. F. Gaál, I. Bikit, D. Buzarov, Lj. Conkic, B. Francuski, M. Slavic, Z. Mihaljev, A. Ivanc, Contents of some organochlorine insecticides, polychlorinated biphenyls, toxic elements, and radionuclides in the fish and sediment from two cage carp (*Cyprinus carpio*) farms, Proceedings of the 6<sup>th</sup> Symposium on Analytical and Environmental Problems, Szeged, Hungary, pp 31-36, (30. September 1999).
2. D. Buzarov, M. Vojinovic-Miloradov, S. Pavkov, A. Ivanc, F. Gaál, Content of organochlorine insecticides and polychlorinated biphenyls in some aquatic systems in Vojvodina, Proceedings of the 4<sup>th</sup> Symposium on Analytical and Environmental Problems, Szeged, Hungary, pp 80-84, (29. October 1998).
3. M. Vojinovic-Miloradov, S. Pavkov, D. Buzarov, Residues of persistent organochlorine compounds in selected aquatic ecosystems of Vojvodina (Yugoslavia). *Water Science and Technology*, **22**, 5, 107-111. (1990).
4. M. Vojinovic-Miloradov, P. Marjanovic, D. Buzarov, S. Pavkov, Lj. Dimitrijevic, M. Miloradov, Bioaccumulation of polychlorinated biphenyls and organochlorine pesticides in selected fish species as an indicator of the pollution of aquatic resources in Vojvodina, Yugoslavia. *Water Science and Technology*, **26**, No 9-10 pp 2361-2364. (1992).
5. M. Vojinovic-Miloradov, D. Buzarov, J. Adamov, S. Simic, E. Popovic, Determination of polychlorinated biphenyls and polyaromatic hydrocarbons in frog liver. *Water Science and Technology*, **34**, No 7-8 pp 153-156. (1996).