Scientific Papers. Series D. Animal Science. Vol. LVI
ISSN 2285-5750; ISSN CD-ROM 2285-5769; ISSN-L 2285-5750

EXAMINATION OF CONTENT OF HEAVY METALS AND PESTICIDES IN FISH IN THE ACCUMULATION STREZEVO IN THE REPUBLIC OF MACEDONIA

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Abstract

In the period from 2007 to 2009th year, the heavy metal concentration (Pb, Cd,? s? Hg) in carp, barbell, catfish and silver carp's muscular tissue, bones and internal organs was examined on three locations in the accumulation Strezevo in the Republic of Macedonia
According to Rulebook of maximum allowed quantities of pesticides, metals and metalloid and other toxic substances in the Republic of Macedonia, in our examined samples the concentration of all examined toxic elements was under maximum allowed limits, except lead and cadmium in the following samples: (carp's bones, silver carp's internal organs) on location 3 in accumulation Strezevo in the Republic of Macedonia where lead concentration was 1.07 and 1.81.
Cadmium concentration was also increased on the same location in the samples of carp's, silver carp's and barbel's bone tissue as in silver carp's internal organs.
Also the concentration of examined insecticides in all samples were significantly under maximum allowed quantities.
The results from our examinations have shown that the above mentioned locations in accumulation Strezevo in the Republic of Macedonia are relatively unpolluted. However, for more realistic ecological picture the number of analised samples should be increased.

Key words: *accumulation, heavy metals, pesticides.*

INTRODUCTION

Environment's pollution with noxious materials is a consequence of industrial development, imple-mentation of certain agrotechnical mea-sures in agriculture, urbanization and so on.
The contents of heavy metals in natural waters (Bojcic, 1982) are generally very low, the rea-son for this being their very small presence in Earth's crust. However, due to the disharmony between the industrial development and the corresponding measures of environmental pro-tection it came, among else, to water pollution with heavy metals (lead, cadmium, arsenic and mercury), as well as with organochloric pes-ticides' residuums (chlorinated carbohydrates, organophosphates, carbamates etc.).
Fish are one of the best bioindicators of pollution with these elements (Baltic and Todorovic, 1997), therefore our investigations are oriented in that direction.
Different chemical forms of the same ecosystem may have multiple biological effect. When some po-tentially toxic substance is present in the water, many chemical processes may take place and much later the aquatic organisms to manifest their response. This substance, present in the water, can start interacting with other constituents of the water, so, in example, pH has impact on dissociation of acid and base, while humite acids form complexes with certain heavy metals. Cognition and determination of such processes is very important in understanding the inluence of toxic matters on hydrobionts. The amount of toxicants and their arrangement within the organism are closely related with the physiological processes such as: absorption through gills, bowels and skin, transport and distribtion through vascular system, metabolic transformation, accumulation in various tissues and organs, and excretion as well.
In their work Sorensen (1991) explained in details the emergence of interaction between different physiological processes which can occur if an organism is exposed to two or more toxic substances. Absorbed and accumulated chemicals bond with plasmatic proteins,

influence receptor sites so that the organisms give their response expressed through growth, behaviour, creation of offsprings and advent of death.

Rivers have important role in the transport of substances dissolved or associated with suspended solid particles and as recipients collect waste materials and metals before confluence into the lakes (Mason, 1981). Geologic substrate and erosion regime have the biggest impact on the chemical composition of rivers and the concentrations of heavy metals in them. However, in many areas the influence of atmos-pheric falls, industry and agrotechnical measures very often having prevalent effect on river water′s com-position, heavy metals including as well, prevails. From the aspect of anthropogenic pollution, the impact of big mining, industrial and urban centers is the most significant.

The total flora and fauna have central place in investigating and monitoring the heavy metals and other inorganic toxic substances within the ecosystem. Microorganisms, plants and animals play special role in determining the chemical form transport, also in the transfer to the storage locations of metals. The pos-sibility of potential toxic matters′ transfer through water or food to the people and the effects on people′s health causes great concerns. Heavy metal contamination in rivers and other water ecosystems depends on the type and the amount of waste materials arriving in them, on the vicinity of the confluence point into the recipient and its design and operational efficiency, and on the hydrology and the climate of the region (Harrison et all., 1991). The contaminants arrive into water ecosystems by washing the upper earth layers, filtrating surface waters, and sometimes in the form of vapors that reach water surface. Sewerage system′s waste water is the biggest source of heavy metals distributed in life environment, through effluents or faecal silt that usually contains larger concentrations of copper, lead, zinc, cadmium and silver (Forstner and Wittman, 1983). The inflow of melted snow from urban places often contains relatively high heavy metal concentrations.

Heavy metals in aquatic environment are present in three forms: as dissolved, colloidally dispersed and suspended. The form they appear in is of great importance to the behaviour, toxicity and bioavail-ability. They can also be classified based on the factors which primarily define their behaviour in fluvial environment:

- heavy metals in the largest portion controlled by biological processes – iron and manganese are good examples, whose forms of interaction directly depend on the aquatic system′s redox po-tential, and participate directly in the microbiological and photo-chemical reactions.
- heavy metals which in the largest portion are controlled by geochemical processes: absorption and complexing processes with suspended and colloidally dispersed materials (Cu, Pb, Zn and Cd).

In this paper four heavy metals were analyzed- the ones most often appearing in hydrobionts (Pb, Cd, As and Hg).

MATERIALS AND METHODS

During 2007-2009, the contents of heavy metals and residuums of organochloric pesticides in the muscle tissues, bones and internal organs of carp, tolstolobik, seathfish and babushka were being ex-amined, from five locations in Strezevo accumulation (26 carp samples, 7 barbell samples, 2 catfish samples and 20 silver carp samples).

For determination of the amount of toxic elements (Prpic-Majkic, 1985), the samples were prepared using ″wet combustion″ procedure (warming the sample with addition of $Mg(NO_3)_2$, concentrated nitric acid and hydrogen peroxide). After glowing at the temperature of 5.400°C, resulting ash was dissolved in 0.1 M hydrochloric acid and diluted with demineralized water to the suitable volume (25 ml).

The amounts of lead and cadmium were determined using the method of absorption spectrophoto-metry, on the instrument Varitan Spectar AA-10. For determining mercury (Mesaric, 1974) the technique of flameless (″Cold Vapor″) atomic absorption was used, whereas arsenic was determined spectrophoto-metrically. Organochloric insecticides′ residuums were determined using the method of gas chromato-graphy on VARIAN 3400 gas chromatograph, together with an EC detector with Sc ″3″ foil. Residuums′ extraction was done using n-hexane together with extract's purification using concentrated sulfate acid (Vojinovic-Miloradov & al., 1992).

RESULTS AND DISCUSSIONS

The contents of heavy metals in samples of muscle tissue, bones and internal organs of carp, barbell, catfish and silver carp were examined (Table 1).

According to the Regulations on the amounts of pesticides, metals, metaloids and other toxic sub-stances (Sl. list RM, 5/92), all the toxic elements' concentrations in our samples were below maximum allowed limits, except for lead and cadmium in the samples (carp bones, barbell internal organs) from location 5 where lead concentrations were 1.07 and 1.81 respectively.

On the same location cadmium concentration was also increased in the samples of carp, barbell and silver carp bone tissue, as well as in the internal organs of barbell (Table 1).

Table 1. Contents of toxic elements in examined fish samples

Samples examined	Pb (mg/kg)	Cd (mg/kg)	As (mg/kg)	Hg (mg/kg)
muscle tissue carp – location 1	0.223	< 0.01	< 0.050	< 0.03
muscle tissue carp – location 2	0.215	< 0.01	< 0.050	< 0.03
summary sample internal organs (1+2)	0.420	0.043	< 0.050	0.11
muscle tissue carp – location 3	0.090	< 0.01	< 0.050	< 0.03
internal organs carp – location 3	0.138	0.014	< 0.05	0.08
muscle tissue catfish – location 4	0.253	< 0.01	< 0.050	< 0.03
muscle tissue carp – location 5	0.23	< 0.01	< 0.01	< 0.05
Bones carp – location 5	1.07	0.39	< 0.01	< 0.05
internal organs carp – location 5	0.23	0.07	0.05	< 0.05
muscle tissue silver carp – location 5	0.59	< 0.01	< 0.01	< 0.05
Bones silver carp – location 5	0.45	0.37	< 0.01	< 0.05
internal organs siver carp – location 5	0.31	0.03	0.05	< 0.05
muscle tissue barbell – location 5	0.29	0.04	< 0.01	< 0.05
Bones barbell – location 5	0.39	0.30	< 0.01	< 0.05
internal organs barbell – location 5	1.81	0.14	0.08	< 0.05

Allowed amounts of metals, non-metals and some specific contaminents, expressed in mg/kg according to the Regulations on the amounts of pesticides, metals and metaloids (Sl. list RM 5/92).

Pb 1 mg/kg
Cd 0.1 mg/kg
As 2 mg/kg
Hg 0.5 mg/kg

Table 2. Contents of organochloric insecticides in examined fish samples*

Examined samples	**Aldrine and dialdrine (mg/kg)**	**DDT & deriva-tives (mg/kg)**	**Endrine (mg/kg)**	**Total HCH (mg/kg)**	**Lindane (mg/kg)**	**Hepta-chlorine (mg/kg)**
muscle tissue carp – location 1	n.a.	0.05	n.a.	0.001	0.001	n.a.
muscle tissue carp – location 2	〃	〃	〃	〃	〃	〃
summary sample carp internal organs (1+2)	〃	〃	〃	〃	〃	〃
muscle tissue carp – location 3	〃	〃	〃	〃	〃	〃
internal organs carp – location 3	〃	〃	〃	〃	〃	〃
muscle tissue catfish – location 4	〃	〃	〃	〃	〃	〃
muscle tissue carp – location 5	〃	〃	〃	〃	〃	〃
Bones carp – location 5	〃	〃	〃	〃	〃	〃
internal organs carp – location 5	〃	〃	〃	〃	〃	〃
muscle tissue silver carp – location 5	〃	〃	〃	〃	〃	〃
Bones silver carp – location 5	〃	〃	〃	〃	〃	〃
internal organs silver carp – location 5	〃	〃	〃	〃	〃	〃
muscle tissue barbell – location 5	〃	〃	〃	〃	〃	〃
Bones barbell – location 5	〃	〃	〃	〃	〃	〃
internal organs barbell – location 5	〃	〃	〃	〃	〃	〃

Maximum allowed concentrations of these organochloric insecticides expressed in mg/kg according to the Regulations on the amounts of pesticides, metals and metaloids (Sl. list RM 5/92) are such:

Aldrine and Dialdrine 0.2 mg/kg
DDT & derivatives 1.0 mg/kg
Endrine 0.1 mg/kg
HCH 0.1 mg/kg

CONCLUSIONS

The results obtained indicate that the examined fishing locations are relatively unpolluted, where in larger number of samples certainly should be analyzed so we could get a more realistic ecological picture. Nevertheless, the most important thing is that the muscle tissue of fish from these locations, from the aspect of examined contaminants′ contents, is a health-friendly high-value food of animal origin.

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