CONTROL OF TOXIC ELEMENTS POLLUTION IN INTENSIVE PRODUCTION OF GRASS CARP (*Ctenopharyngodon idella*)

Pavlović A, Kevrešan Ž, Kelemen-Mašić Đ, Mandić A
Faculty of Technology, Department of Meat Technology, University of Novi Sad, Bul. cara Lazara 1, 21 000 Novi Sad, Yugoslavia

Background

Heavy metals have long been recognized as one of the most important pollutants, because of their toxicity and capacity to accumulate in living organisms. They are present in the soil, water and air, and only small quantities originate from natural sources. A heavy metal natural cycle, in the first phase, includes the implementation into ecosystems through fuel and industrial products, and in the second phase, through agrochemical products, waste water, industrial wastes and exhausted gases. In this way, plants, animals and humans are either directly contaminated or indirectly through accumulated components in soil, which, in the second phase contaminate plants, and, through them, animals and humans (Nriagy, 1984; Hecht, 1988). Fish is a valuable source of microelements. Lesser part of microelements belongs to the group of toxic substances, and their excessive intake into organism may cause serious deseases (Belinsky et al., 1996; Pennington, 1990; Mikavica et al., 2000; Mihaljev et al., 2000). Copper is an essential element in maintaining body functions. It is regulated in the body via absorption, excretion, and a combination of processes. However, copper overdose could be toxic (Chen et al., 1999). Zinc has been considered as an essential component of food since 1934. It is a part of over 100 different enzymes, and a part of insulin molecule. Zinc is involved in the metabolism of carbohydrates and is necessary for synthesis of DNA and RNA (Grujić, 2000). In some biochemical reactions, cadmium can push out zinc and create problems for functioning of organism. The Zn/Cd ration in the body is very important. Zn protects tissues from damages caused by cadmium. If there is not enough Zn in organism, the accumulation of Cd and poisoning risk is more often. Ions of lead affect normal brain and nervous system functioning. In the functioning of organs, lead is competing with Ca, Fe, Cu and Zn, enters the red corpuscles and enzymatic systems are influences the elimination of Ca from bones (Mikavica et al., 2000). Arsenic has wide spread uses in wood preservatives, pesticides, glass, nonferrous alloys, electronics, animal feed additives, and farmaceuticals. The toxicity of As ranges from very low to extremely high, depending on the chemical state. Elemental As and aresenious sulfide have low toxicities, whereas arsine is extremely toxic (Hepp, 1999). Mercury, long recognized as being toxic to humans, is also a prevalent environmental contaminant from both man-made sources, such as industrial wastes, incinerator emmisions, pesticides and fungicides, and natural sources, such as mineral deposits (Hepp et al., 2001). Lead is considered important as a contaminant in aquatic ecosystems with different toxic effects on various organisms (Merian, 1991).

According to the chemical content and energy value, fish meat does not lack behind the other sorts of meat. Moreover, due to higher contents of vitamins dissoluble in lipids, some mineral matters (iodine, zinc and selenium) and better digestion, meat of some species of fish has even higher biological value than meat of warm-blooded animals (Mikavica et al., 2000). That led to faster development of fishery in the world and in our country, as well as the increased level of fish consuption, especially from fishponds.

The grass carp (*Ctenopharyngodon idella*), macrophytovorous, is one of the Chinese carp, that has been introduced nearly worldwide, and is extensively cultured in channales and fishponds.

Objectives

Contents of Pb, Cd, As, Hg, Cu, Zn, Fe and Mn were determined in meat, skin, gills and liver of 3, 4 and 5 years old grass carps, as well as in the water and mud, in order to investigate the heavy metals pollution of fishpond "Futog", which receives the water from the Danube. Obtained results are an usefull indicator of environmental contamination, as well as a good paramether of fish meat quality control.

Methods

Area od study: Samples of fishes, water and mud were collected from the fishpond "Futog", which is located next to the village Futog, near to Novi Sad, Yugoslavia. The fishpond receives the water from Dunavac, the small backwater of the Danube.

Sample collections: Collected grass carps were divided into 3 groups (5 fishes per group) by age categories: 3, 4 and 5 years old fishes. Each fish was characterised by its length (standard and total), weight, gender and age. Content of heavy metals was determined in meat, skin, gills and liver, in triplicate, of average sample prepared for each group. Water samples were collected from the sites of 50, 100 and 150 cm depth. Precleaned polyethilene bottles were rinsed with water from each site, and used to collect water, with the bottle opening pointing 10 cm under the water surface. The water was filtered through a disposable 0,45 µm filter into a second bottle and acidified with 70 % nitric acid, to pH=2. After water sampling, from the same sites, mud was collected into polyethilene bags.

Sample preparation: For each group (3, 4, and 5 years old fishes) average samples of skin, meat, gills and liver were prepared. After chopping, and homogenisation, weighed portions of 1-2 g, measured with accuracy of 0,0001 g were prepared. Acidified water samples were either injected to aparatus directly, or concentrated by evaporation, depending on the metal to be analysed. After percent moisture determination, conducted gravimetrically, a 1-2 g portions of dried mud samples were measured with accuracy of 0,0001 g. All analyses were performed in triplicate. Samples were digested by two different procedures depending on the metal of interest. For the determination of Pb, Cd, Zn, Fe, Cu, As and Mn fish and mud samples were subjected to dry ashing procedure at 450 °C (Hepp, 1999). Ashed residue was subjected to treatment with 30 % H_2O_2 or/and nitric acid (1:2) if it further contained unoxidized organic matter. Ashing procedure at 450 °C was repeated, until oxidation of organic matter was completed. For the determination of Hg in fish and mud samples, wet digestion with sulphuric acid and potassium permanganate was performed (Mihaljev et al., 2000). The contents of Pb, Cd, Zn, Fe, Cu and Mn were determined using the Atomic Absorption Spectrophotometer VARIAN SpectrAA-10, with background correction (D_2-lamp). The content of As was determined using AAS - "hydride generation" technique, and Hg by AAS - "cold vapor" technique on the same apparatus equiped with VGA-76 Vapour Generation Accessory (Brodie et al., 1983).

Results and discussion

Metal concentrations in the water and mud of the fishpond "Futog" are summarized in Table 1. The presented results indicate that metal concentrations in water differed only marginally, among the examined spots. The signs of heavy metal pollution in water were not found, since Pb, Cd, As, Cu and Zn were under the detection limits of the used methods. On the other hand, metal concentrations were much higher in the mud than in water. Our results indicate that there is no consistent pattern in metal accumulation within the fishpond, regarding to the sampling points. Despite the fact that metal concentrations in the mud were elevated, except Cd which was not detected (Cd<0.005 mg/kg), they are much lower than those reported by other authors (Wong et al., 2001).

The contents of heavy metals in grass carp tissues are presented in Table 2. In general, metal concentration differed slightly among the investigated fish groups, but different fish tissues showed different capacities for accumulating heavy metals. The highest metal

concentrations were found in liver and gills. Edible tissues, such as muscle and skin, tended to accumulate less metal. The site of accumulation also appeared to vary among metals. Significantly higher concentrations of Fe were found in liver, than in gills, and the lowest were in meat. Cu concentrations were higher in liver than in other tissues, while the highest concentrations of Zn were found in skin. Content of Mn in liver and gills was higher than in meat and skin. Concentrations of Hg, As, Pb and Cd were under the detection limits of our methods, in all investigated tissues. Generally speaking, concentrations were: Pb<0.25 mg/kg; Hg<0.5 mg/kg; As<0.25 mg/kg; Cd<0.05 mg/kg. According to the regulations of SRJ (1992) obtained results for Pb, Cd, Hg, and As are under the permitted levels.Also, it is important to notice that content of heavy metals in grass carp has not varied between two years (2000-2001).

Conclusions

Regarding all the results, grass carp, water as well as mud from the fishpond "Futog" present low level of contamination caused by heavy metals. But, since fish can potentially accumulate heavy metals by absorption through gills or by consumption of contaminated food and sediments, we consider these and similar investigations are necessary to be carried out, from the aspect of environmental protection and healthy food production.

Pertinent literature

Belinsky D.L., Kuhlein H.V., Yeboah F., Penn A.F., Chan H.M., (1996): Composition of fish consumed by the James Bay Cree. *Journal of Food Composition and Analysis, 9*, 148-162; **Brodie K.**, Frary B., Sturman B., Voth L., (1983): An automated vapor generation accesory for atomic absorption analysis. *Varian, Atomic Absorption,* Number AA-38, March 1983, 1-8; **Chen S.S.**, Chen C.M., Cheng C.C., Chou S.S., (1999): Determination of copper in edible oils by direct graphite furnace atomic absorption spectrometry. *Journal of food and drug analysis, 7(3),* 207-214; **Grujić R.**, (2000): *Nauka o ishrani čovjeka.* Tehnološki fakultet, Banja Luka; **Hecht H.**, (1988): *Fleishwirtschaft, 68(7),* 877. Hepp N.M., (1999): Arsenic determination in certifiable color additives by dry ashing followed by hydride generation atomic absorption spectrometry. *Journal of AOAC International, 82(2),* 327-330; **Hepp N.M.**, Cargill A.M., Shields W.B., (2001): Automated microwave digestion of certifiable color additives for determination of mercury by cold vapor atomic absorption spectrometry. *Journal of AOAC International, 84(1),* 117-122; **Merian E.**, (1991): *Metals and Their Compounds in the Environment. Occurence, Analysis and Biological Relevance.* Verlag Chemie, New York; **Mihaljev Ž.**, Kelemen-Mašić Đ., Živkov-Baloš M., Kevrešan Ž., (2000): Investigation of toxic element content in meat products. *Tehnologija Mesa, 41*, 4-6, 191-194; **Mikavica D.**, Grujić S., Mandić S., Vučić G., Đurica R., (2000): Detrmination of selenium, lead, zinc and cadmium contents in meat of different fish species. *Tehnologija Mesa, 41*, 4-6, 155-161; **Nriagy J.O.**, (1984): *Changing Metal Cycles and Human Health.* Springer-Verlag, Berlin, Heidelberg, New York, Tokio; **Pennington J.A.**, (1990): Iron, zinc, copper, manganese, selenium and iodine in foods from the United States total diet study. *Journal of Food Composition and Analysis, 9,* 166-184; **Regulation of SRJ** (1992): Pravilnik o količini pesticida, metala i metaloida i drugih otrovnih supstancija, hemioterapeutika, anabolika i drugih supstancija koje se mogu nalaziti u namirnicama. Sl List SRJ 5/92 i 11/92; **Wong C.K.**, Wong P.P.K., Chu L.M., (2001): Heavy metal concentrations in marine fishes collected from fish culture sites in Hong Kong. *Archives of Environmental Contamination and Toxicology, 40,* 60-69.

Table 1. The contents of heavy metals in water and mud from the fishpond

Sampling point (depth)		Concentration of metal (mg/l for water and mg/kg for mud)							
		Fe	Zn	Cu	Mn	Pb	Hg	As	Cd
water	50 cm	0.13±0.02	< 0.01	<0.03	0.093±0.001	<0.03	<0.005	<0.005	<0.007
	100 cm	0.17±0.02	< 0.01	<0.03	0.093±0.001	<0.03	<0.005	<0.005	<0.007
	150 cm	0.11±0.01	< 0.01	<0.03	0.093±0.001	<0.03	<0.005	<0.005	<0.007
mud	50 cm	1371.8±128.2	113.5±6.3	2.75±0.08	259.5±32.4	6.53±0.23	0.384±0.028	0.023±0.001	<0.005
	100 cm	314.7±26.9	39.4±3.6	0.17±0.07	59.4±2.3	1.93±0.11	0.000	0.007±0.000	<0.005
	150 cm	1916.1±157.1	87.6±5.2	2.44±0.09	211.3±16.8	12.11±0.91	0.440±0.021	0.050±0.001	<0.005

Table 2. The contents of heavy metals in the grass carp tissues

Sample	Fish group	Concentration of metal (mg/kg)			
		Fe	Zn	Cu	Mn
meat	I – 2000	6.35±0.54	2.83±0.22	0.353±0.029	0.161±0.011
	I – 2001	7.97±0.41	4.39±0.42	0.544±0.038	0.232±0.019
	II – 2001	8.48±0.87	5.42±0.52	0.379±0.019	0.222±0.020
	III - 2001	6.17±0.56	4.32±0.41	0.307±0.030	0.204±0.020
skin	I – 2000	12.68±0.59	29.80±1.19	0.542±0.025	0.116±0.008
	I – 2001	8.36±0.76	59.34±2.91	0.279±0.021	0.196±0.018
	II – 2001	15.24±0.99	51.33±3.02	0.249±0.024	0.285±0.021
	III - 2001	15.52±0.97	24.16±1.73	0.396±0.031	0.354±0.003
gills	I – 2000	28.90±0.37	10.67±0.82	0.504±0.023	1.095±0.008
	I – 2001	29.42±0.49	10.24±0.79	0.389±0.029	1.090±0.030
	II – 2001	43.20±0.35	11.09±1.04	0.695±0.059	1.527±0.004
	III - 2001	53.78±5.27	16.27±0.38	0.898±0.078	2.316±0.097
liver	I – 2001	145.11±8.66	36.96±1.10	7.171±0.192	1.097±0.072
	II – 2001	303.31±9.98	22.09±0.17	9.531±0.288	1.748±0.024
	III - 2001	215.93±2.99	30.21±1.76	16.637±0.143	0.917±0.067

I – 2000: 5 years old grass carp analyzed in 2000; I – 2001: 5 years old grass carp analyzed in 2001; II – 2001: 4 years old grass carp analyzed in 2001; III – 2001: 3 years old grass carp analysed in 2001.