ELEMENTS CONCENTRATION IN TISSUE OF CHUB (*SQUALUS CEPHALUS*) FROM RESERVOIRS OF NATIONAL PARK "TARA"

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KONCENTRACIJE ELEMENATA U TKIVIMA KLENA (*SQUALUS CEPHALUS*) IZ AKUMULACIJA NACIONALNOG PARKA „TARA"

Apstrakt

Planinsko područje Tare nalazi se na krajnjem zapadu Srbije. Sa severne i zapadne strane ograničeno je dolinom Drine, sa jugozapada dolinom Rzava, sa juga plitkom kremanskom udolinom koja ga odvaja od zlatiborske površi. Ceo prostor Nacionalnog parka obuhvata: planinu Taru, Crni vrh, Zvezdu, Stolac, kanjon Drine sa Perućcem i okolinu Bajine Bašte. Nacionalni park „Tara" i njegova uža zaštitna zona raspolaže rekama i potocima koji pripadaju uglavnom gornjim i delimično srednjim pastrmskim regionima. Najznačajnije reke su Rača, Derventa sa pritokama, Brusnički potok sa pritokama, Karaklijski Rzav i Baturski Rzav i reka Jarevac. U Nacionalnom parku „Tara" formirano je nekoliko veštačkih jezera različitog tipa. Akumulacija „Perućac" je veštačko jezero nastalo u rečnom koritu reke Drine, njenim pregrađivanjem betonskom branom. Na osnovu lokacije, pripada nizinskom tipu. Akumulacija „Zaovine" je po lokaciji visinskog tipa, a po načinu nastanka reverzibilna. Nastaje izbacivanjem vode iz akumulacije „Perućac" i sakupljanja vode od Karakliskog i Baturskog Rzava i drugih manjih pritoka. Akumulacija „Spajići" je visinska sabirna akumulacija koja nastaje od proceđene vode iz jezera „Zaovine", te reke Zmajevačke i Popovića potoka. Jezero „Kruščica" nastaje od Karaklijskog i Baturskog Rzava i koristi se kao pijaća voda (Hegediš, 2012).

Ribolovne vode NP „Tara" naseljava 28 vrsta riba iz sedam familija, a šaranske vrste (Ciprinidae) dominiraju po brojnosti sa 17 vrsta. Klen (Squalius cephalus) je ciprinidna vrsta ribe, široko rasprostranjena u Srbiji južno od Save i Dunava dok je u Vojvodini redak. U Srbiji je popularna sportsko-rekreativna ribolovna vrsta i lovi se različitim tehnikama ribolova. U akumulacijama Zaovine, Spaići i Kruščica klen je najzastupljenija vrsta, dok je i u akumulaciji Perućac prisutan u značajnom broju (Hegediš, 2012).

Tokom terenskih istraživanja 2014. godine ispitivan je nivo akumulacije 17 elemenata u tkivima (mišić, jetra, škrge) klena iz četiri akumulacije – Perućac, Zaovine, Spaići i Kruščica. Ribe se nalaze na vrhu lanaca ishrane u vodenoj sredini i često u organizmu akumuliraju velike količine pojedinih teških metala (Yilmaz et al., 2007). Takođe se smatraju i jednim od najosetljivijih akvatičnih organizama na prisustvo toksičnih materija u vodi (Alibabić i sar., 2007).

Ribe se često koriste kao bazični organizmi po pitanju pozicije u lancima ishrane, kao i u ishrani ljudi, zbog njihovog potencijala za bioakumulaciju toksičnih materija i njihove osetljivosti na čak i male koncentracije mutagena (Szefer et al., 1990; Višnjić-Jeftić et al., 2010). Jedinke klenova sa Perućca su se na osnovu analize glavnih komponenata (PCA – Principal Components Analysis) izdvajale po višim koncentracijama Cu i Zn u jetri, kao i B i Cu u mišićima; jedinke sa Zaovina se izdvajaju po koncentracijama Sr, Mo, Fe, Cr, Al, Hg u jetri višim nego u jedinkama sa drugih akumulacija, Mn, Sr, Hg, Mo i Cr u mišićima i Al, Sr, Li i Hg u škrgama; jedinke sa akumulacije Kruščica se izdvajaju po koncentracijama Pb, Mn i Ni u jetri, kao i, Mo, Mn, Fe, Pb i Cr u škrgama; jedinke sa akumulacije Spaići su bile grupisane između jedinki sa drugih analiziranih akumulacija, nisu se izdvajale po koncentracijama bilo kog analiziranog elementa u bilo kom tkivu, a najsličnije su bile jedinkama sa Perućca.

Ključne reči: klen, teški metali, koncentracija, akumulacija, Nacionalni park „Tara"
Key words: Chub, Heavy metals, Concentrations, Reservoir, National park "Tara"

INTRODUCTION

Mountain Tara is located on the far west Serbia. Limited with the Drina valley, from the southwest with valley of River Rzav, from the south limited with valley Kremansko that separates it from Zlatibor surface. The teritory of the National Park includes the mountain Tara, Crni vrh, Zvezda, Stolac, canyon of River Drina with Perućac Lake and surrounding of Bajna Bašta. National Park "Tara" and its narrower protection zone has rivers and streams that belong mostly to the upper and middle part trout regions. The most important rivers are the Rača, Derventa and its tributaries, bilberry stream with its tributaries, Karaklijski Rzav and Baturski Rzav and the River Jarevac. The National Park "Tara" is composed of several artificial lakes of different types. Accumulation "Perućac" is an artificial lake created in the riverbed of the Drina River. Based on the location, it belongs to the lowland type. Accumulation "Zaovine" is reversible, upper-level type, created by removing water from the reservoir "Perućac" and collecting water from Karaklijski and Baturski Rzav and other smaller tributaries. Accumulation "Spajići" collects drained water from the lake "Zaovine" and Zmajevačka River and stream Popović. Lake "Kruščica" arises from Karaklijski and Baturski Rzav and it is used as source of drinking water. Fishing areas of the NP "Tara" are inhabited with 28 fish species (7 families), while Cyprinids are dominating with 17 species. The Chub (*Squalius cephalus*, Cyprinidae) is widely distributed south of Sava and Danube in Serbia, while in Vojvodina province it is rare. In Serbia, chub has considerable recreational-fishing importance and catches with various techniques of fishing. In reservoirs Zaovine, Spaići and Kruščica chub is the most common species, significantly presented in Perućac (Hegediš, 2012).

Fish, as situated at the top of the food chain, accumulate large amounts of metals and trace elements (Yilmaz et al., 2007). Also, fish are considered as one of the most sensitive aquatic organisms on the presence of the toxic elements in the water (Alibabić i sar., 2007).

Fish are often used as sentinel organisms due to their role in the food webs, human nutrition, their potential for bioaccumulation of toxic substances, and their sensitivity to even low concentrations of mutagens (Szefer et al., 1990; Višnjić-Jeftić et al., 2010).

The Chub, is ubiquitous fish species widely distributed all over Europe, which provides the possibility to explore a variety contexts of pollution (Durand et al., 1999). Monitoring of the concentrations of heavy metals in fish tissues has an important role as an early warning indicator of the problems related to the water and sediment quality, and it also enables detection of toxic chemicals in fish as a source of nutrition supply for the humans. Thus, such monitoring allows taking appropriate and timely measures to protect public health and environment (Lenhardt et al., 2012).

MATERIAL AND METHODS

The Chub specimens were collected between July and September 2014, from four reservoirs: Perućac (N 43°59"54', E 19°16"20'), Zaovine (N 43°52"03', E 19°24"13'), Kruščica (N 43°54"13', E 19°23"04') i Spajići (N 43°51"34', E 19°24"21') located at National park "Tara". Sampling was performed with benthic and pelagic gillnets (dimension 20-30m x 1-2m, 20-50mm mesh size). Gillnets were left over night. Total weight (g) and total body length (cm) of each fish were measured. The samples of gills, liver and dorsal muscles were removed, washed with distilled water and stored at -20 ºC prior to analysis.

Samples were dried by Freeze Dryers Rotational-Vacuum-Concentrator, GAMMA 1-16 LSC, Germany, and sample portions between 0.2 and 0.4 g dry weight were subsequently processed in a microwave digester (speedwave TM MWS-3þ; Bergof productsþInstruments GmbH, Eningem, Germany), using 6 ml of 65% HNO3 and 4 ml of 30% H2O2 (Merck suprapure) at a food temperature program (100–170 ºC). Potential presence of analyzed elements in chemicals used in digestion was resolved by using a number of blank samples. Following cooling to a room temperature, the digested samples were diluted with distilled water to a total volume of 25 ml. The analysis was performed by inductively-coupled plasma optical spectrometry (ICP-OES).

The principal component analysis (PCA) was applied to assess the differentiation among the analyzed fish from four reservoirs, based on elemental concentrations. The untreated data for elemental concentrations in each tissue were used as input variables.

RESULTS AND DISCUSSION

During this study 10 individuals of chub from each reservoir have been analyzed. Mean body weight of individuals from Perućac reservoir was 223.1 g (range 120 – 392 g), total body length 27.4 cm (range 23 - 34 cm); from Zaovine reservoir mean body weight was 250.4 g (range 130.9 – 414.5 g), total body length 28.3 cm (range 23 - 33 cm); from Kruščica reservoir mean body weight was 212.1 g (range 140.7 – 330.4 g), total body length 26 cm (range 22.4 – 31.2 cm); from Spaići reservoir mean body weight was 279.1 g (range 221.7 – 388.7 g), total body length 28.3 cm (range 25 – 31 cm).

A total of 17 elements of heavy metals and trace elements (Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Sr and Zn) were analyzed in three tissues of chub. Mean values and standard deviation are shown in Tables 1, 2 and 3.

At the locality Perućac elements that were not detected are: As, Cd, Co Li, Mo and Ni; at the locality Zaovine elements that were not detected are: As, Ba, Cd and Co; at the locality Spajići elements that were not detected are: As, Cd, Co and Li; on the accumulation Kruščica in all three tissues were not detected: As, Cd and Co.

In the muscle of the chub, in samples taken on the locations Zaovine and Perućac, largest number of heavy metals and trace elements had the highest concentrations. On the locality Zaovine the highest concentrations had Al, Cr, Hg, Mo and Sr. On the locality Perućac highest concentrations had B, Cu, Fe, Pb and Zn. Locality Kruščica was distinguished by the highest concentrations of Ba and Mn (Table 1).

Table 1. The mean value of element concentrations in the muscle of chub (*S. cephalus*) from reservoirs NP „Tara"

Elements	Perućac	Zaovine	Spajići	Kruščica
Al	3.69	11.14	6.53	8.99
B	0.94	nd	nd	nd
Ba	0.50	nd	0.17	0.61
Cr	0.25	3.01	2.19	2.82
Cu	1.33	0.50	0.84	0.40
Fe	21.75	16.63	19.49	13.67
Hg	0.15	0.70	0.23	0.25
Mn	0.87	0.85	0.67	1.01
Mo	nd	2.74	2.54	2.16
Pb	0.18	nd	nd	nd
Sr	1.19	4.48	1.14	1.60
Zn	49.20	30.06	28.57	20.74

* (As, Cd, Co, Li and Ni – not detected in all specimens)

Liver had the highest concentrations of the most analyzed elements at the locality Zaovine (Al, Cr, Fe, Hg, Mo and Sr). On the locality Perućac B, Cu and Zn had the highest concentrations and on the locality Kruščica the elements with the highest concentrations were Mn, Ni and Pb. On the locality Spajići no heavy metal and trace element had the highest concentration (Table 2).

Table 2. The mean value of element concentrations in the liver of chub (*S. cephalus*) from reservoirs NP „Tara"

Elements	Perućac	Zaovine	Spajići	Kruščica
Al	4.34	17.83	7.86	7.87
B	2.37	2.17	0.46	0.77
Cr	0.26	7.25	3.89	4.56
Cu	28.46	21.33	27.99	7.95
Fe	265.33	761.92	431.92	652.50
Hg	0.24	0.56	0.26	0.31
Mn	3.79	3.77	5.24	14.40
Mo	nd	5.78	2.85	2.81
Ni	nd	nd	nd	0.56
Pb	0.5	nd	1.83	1.90
Sr	0.37	0.73	0.49	0.61
Zn	125.65	104.6	125.14	65.89

* (As, Cd, Co. Ba and Li – not detected in all specimens)

In the gills at the locality Spajići, most of the elements had the highest concentrations (Cr, Fe, Mn, Mo, Ni, Pb). Locality Zaovine had four elements with highest concentrations (Al, Hg, Li, Sr). Perućac and Spajići, each, had two heavy metals and trace elements (B and Ba; Cu and Zn) (Table 3).

Table 3. The mean value of element concentrations in the gills of chub (*S. cephalus*) from reservoirs NP „Tara"

Elements	Perućac	Zaovine	Spajići	Kruščica
Al	9.51	27.49	7.76	9.26
B	1.06	0.61	0.17	0.23
Ba	13.09	nd	8.93	10.44
Cr	0.69	2.80	2.38	3.27
Cu	1.12	1.17	1.36	1.28
Fe	87.70	126.49	129.24	153.75
Hg	nd	0.25	0.11	0.15
Li	nd	5.14	nd	1.93
Mn	13.43	12.86	10.55	26.07
Mo	nd	3.07	2.86	7.36
Ni	nd	0.04	0.33	0.72
Pb	nd	1.80	1.66	3.27
Sr	41.36	121.83	47.94	63.62
Zn	294.54	293.81	463.34	228.39

* (As, Cd and Co – not detected in the all specimens)

Results of the PCA analysis showed that the grouping can be performed based on the concentrations of heavy metals and trace elements in the muscle, liver and the gills of the chub (Figure 1).

In the liver of the chub there is a separation on all four localities. Perućac stands out based on the concentrations of the Cu and Zn; Zaovine based on the concentrations of Sr, Mo, Fe, Cr, Al, Hg; and Kruščica based on the concentrations of Pb, Mn and Ni (Figure 1a). According to the results of PCA analysis for chub muscle, separation can be observed: for locality Perućac based on the concentrations of B and Cu; for locality Zaovine based on the concentrations of Mn, Sr, Hg, Mo and Cr; both locations Kruščica and Spajići stand out based on the concentrations of Al and Ba (Figure 1b). In the case of the results of PCA analysis for chub gills, separation can be observed for the locality Kruščica based on the concentrations of Ni, Mo, Mn, Fe, Pb and Cr; for the locality Zaovine based on the concentrations of Al, Sr, Li and Hg (Figure 1c).

Monitoring of the concentrations of metals and trace elements in fish tissues has an important role as an early warning indicator of the problems related to the water and sediment quality and it also enables detection of toxic chemicals in fish as a source of nutrition supply for the humans. Thus, such monitoring allows taking appropriate and timely measures to protect public health and the environment (Lenhardt et al., 2012). Current status of metal and trace element concentrations in tissues of one of the common fish species in the waters of National park ‘’Tara’’ was analyzed. In Serbia chub has considerable recreational-fishing importance and thus it is commonly used in the human diet. Using fish tissues as a bioindicator of water quality is good method for screening waterways for the presence of heavy metals. The results can be used for the environmental managers and policy makers to improve management measures of the observed reservoirs which are currently under the status of the protected area of the National park ‘’Tara’’.

Basic hypothesis of the research from which we started was to analyze represented fish species from the reservoirs of National park ‘’Tara’’, as a source of cleaner water without obvious pollutants and to compare results of fish tissue contamination with other lowland water bodies, expecting that ‘’Tara’’ can be used as a reference locality. The significant differences between two types of the reservoirs (mountain-Tara vs. lowland-Medjuvršje reservoir, Skorić & Djikanović, 2013) were not found after one sampling.

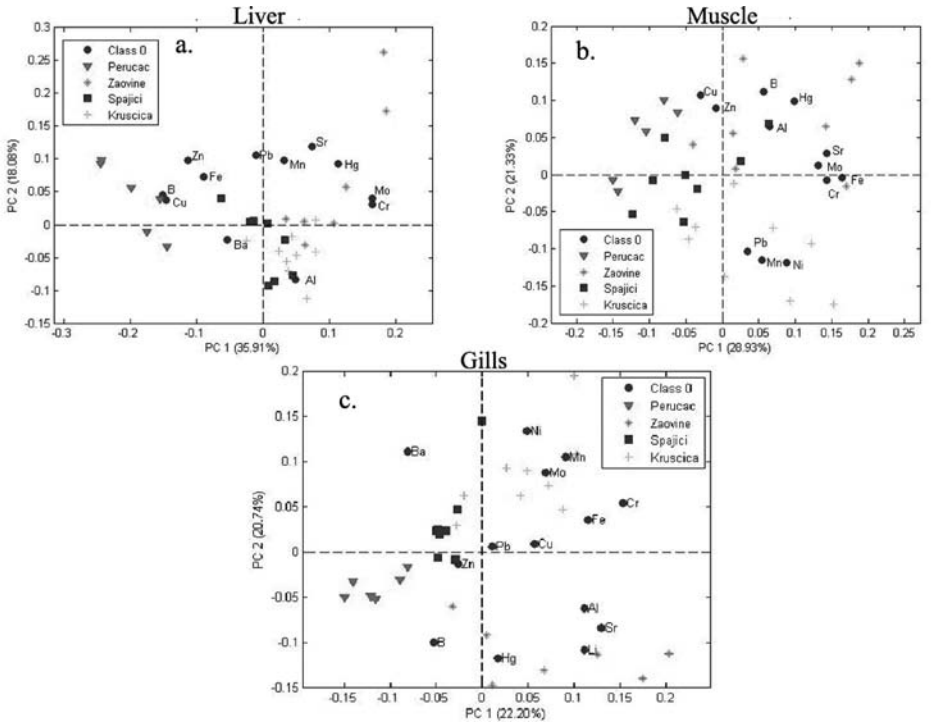

Figure 1. PCA analysis results for the chub liver (a), muscle (b) and gills (c) based on the heavy metals and trace elements from all four localities

Although, the differences between concentrations of some elements in analyzed tissues from different localities can be observed, all concentrations remained bellow MAC (maximum allowed concentrations, Službeni glasnik RS 25/2011, 28/2011).

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REFERENCES

Alibabić, V., Vlahčić, N., Bajramović, M. (2007): Bioaccumulation of metals in fish of Salmonidae family and the impact on fish meat quality. Environmental Monitoring and Assessment 131: 349-364.

Durand, J.D., Persat, H., Bouvet, Y. (1999): Phylogeography andpostglacial dispersion of the chub (*Leuciscus cephalus*) inEurope. Mol. Ecol. 8: 989–997.

Hegediš, A. (2013): Srednjoročni program upravljanja ribarskim područjem u Nacionalnom parku "Tara" za period 2013 – 2022.

Lenhardt, M., Jaric, I., Visnjic-Jeftic, Z., Skoric, S., Gacic, Z., Pucar, M., Hegedis, A. (2012): Concentrations of 17 elements in muscle, gills, liver and gonads of five economi-

cally important fish species from the Danube River. Knowledge and management of aquatic ecosystem 407: 02p1-02p10.

Službeni glasnik RS 25/2011, 28/2011 (2011): Pravilnik o količini pesticida, metala i metaloida i drugih otrovnih supstancija, hemioterapeutika, anabolika i dr. supstancija koje se mogu nalaziti u namirnicama.

Skorić, S. and Djikanović, V. (2013): Koncentracija 16 metala u tkivima odabranih vrsta riba iz akumulacije Medjuvršje. Beležnik Ovčarsko-kablarske klisure 4: 46-52.

Storelli, M.M., Barone, G., Storelli, A., Marcotrigiano, G.O. (2006): Trace metals in tissues of Mugilids (*Mugil auratus*, *Mugil capito*, and *Mugil labrosus*) from the Mediterranean Sea. Bulletin of Environmental Contamination and Toxicology 77: 43-50.

Szefer, P., Szefer, K., Skwarzec, B. (1990): Distribution of trace metals in some representative fauna of the Southern Baltic.Mar. Pollut. Bull. 21 (2): 60–62.

Visnjic-Jeftic, Z., Jaric, I., Jovanovic, L., Skoric, S., Smederevac-Lalic, M., Nikcevic, M., Lenhardt, M., (2010): Heavymetal and trace element accumulation in muscle, liver and gills of the Pontic shad (*Alosa immaculata* Bennet 1835) from the Danube River (Serbia). Microchem. J. 95 (2): 341–344.

Yilmaz, F., Özdemir, N., Demirak, A., Tuna, A.L. (2007): Heavy metal levels in two fish species *Leuscius cephalus* and *Lepomis gibbosus*. Food Chemistry 100: 830-835.