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Results on Cadmium (Cd) and Nickel (Ni) Concentration in Wild Fish Squalis Cephalus &Barbus Barbus Tissues in Vardar River, North Macedonia

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Abstract

The concentrations of Cadmium(Cd) and Nickel(Ni) in wilde fish from the Vardar river have been investigated in order to assess safety for consumers and the level of heavy metal contamination. The selected tissues (muscle, liver and skin) of two fish species: Europian Chub (*Squalius cephalus*)and Common barbel (*Barbus barbus*)from Vardar river stream, Republic of North Macedonia. Samples are collected(hooked) in nine different points (Hot Spots) in total distance of 301km and approximate 33km between sampling sites. The effect environmental conditions and urban discharges on lead accumulation in muscles, liver and skin were investigated. The metal analyses were performed using Inductively coupled plasma mass spectrometry(ICPMS). The average of metal concentrations (micrograms per gram wet weight) in nine hot spots (HS) occurred in the following ranges:For cadmium(Cd)HS-1:muscles 0.035-liver 0.050-skin 0.040, HS-2:muscles 0.040-liver 0.025-skin 0.020HS- 3:muscles0.020-liver 0.020-skin0.010,HS-4:muscles 0.025-liver 0.030-skin 0.010,HS-5:muscles 0.090- liver 0.073-skin 0.000,HS-6:muscles 0.016-liver0.160-skin 0.000, HS-7:muscles 0.030-liver 0.050-skin 0.010,HS-8:muscles 0.041-liver 0.160-skin 0.010and HS-9:muscles 0.060.-liver 0.135-skin 0.010.For Nickel(Ni) HS-1:muscles 0.55-liver 0.65-skin 1.05, HS-2:muscles 0.50-liver 0.90-skin 0.55HS- 3:muscles0.40-liver 0.20-skin0.20,HS-4:muscles 0.40-liver 4.10-skin 0.10,HS-5:muscles 1.04-liver 0.54- skin 0.00,HS-6:muscles 0.50-liver0.20-skin 0.00, HS-7:muscles 0.80-liver 1.50-skin 0,00,HS-8:muscles 0.60-liver 1.94-skin 0.00and HS-9:muscles 0.60-liver 2.20-skin-0.00 The lowest levels of the were detected in the skin. The muscles and liver were found to accumulate the highest amounts of Cd and Ni in the case of organs, the highest levels were found, as follows: liver > muscles >skin.Further investigation of heavy metals is recommended, including a survey of fish consumption frequency among the local inhabitants.

Keywords:*heavy metals, cadmium,nickel, fish tissue, Republic of North Macedonia*

INTRODUCTION

Fish is an important part of the human diet, but also a good indicator of trace metal pollution in the aquatic ecosystem. Fish samplesare considered as one of the most indicativefactors, in fresh water systems, for the estimationof trace metals pollution potential (Rashed,2001). Pollution of water bodies is becoming a major cause of concern with respect to human health(Jarup, 2003).

Heavy metal from anthropogenic pollution source are released in to the aquasystems ,and then heavy metal become serious threat because of their toxicity, long persistence bioacumullation and biomagnifications in the food chain (Eisler, 1988). Metals in waters may be of natural origin from the rocks and soil or from human activities, including industry, domestic wastewater, agricultural discharge, mine runoff, solid waste disposal and atmospheric deposition.Metals generally enter the aquatic environment through atmospheric deposition, erosion of the geological matrix, or due to anthropogenic activities caused by industrial effluents, domestic sewage, and mining wastes.Increase in the human population has greatly contributed towards the conversion of these water bodies to impending contamination sinks (Tarvainen et al., 1997; Stephen et al., 2000).

Heavy metals are well known to be non- biodegradable and when present at high concentrations, they tend to bioaccumulate (DeForest et al, 2007).Being non-biodegradable, metals can be concentrated along the food chain, producing their toxic effects at points often far away from the source of the pollution (Fernandez et al., 2000). Heavy metals can cause a variety of ailments in humans depending on the degree of exposure. These vary from minor skin irritation to severe damages of the liver, kidney, skeleton,nerve,muscle tissues and circulatory system.Liver and muscle are usually used as a targeted tissues for the analysis of the heavy metal concentration,according to the studies carried out with the different fish species have shown that trace metals are accumulate mainly in metabolic organs such as the liver, where metal are stored for detoxication through the metalothioniens (Carpene and Vasak, 1989;Kargin and Erden 1991; Hogstrand and Howx,1991)

Cadmium(Cd) Cadmium is a naturally occurring nonessential trace element and its' tendency to bio accumulate in living organisms often in hazardous levels, raises environmental concern Sfakianakis DG, Renieri E,Kentouri M,Tsatsakis

AM (2015) Cadmium production, consumption and emissions to the environment have increased

dramatically during the 20th century, due to its industrial use (batteries, electroplating, plastic stabilizers, pigment), and consequently lead to contamination of aquatic habitats. Higher doses of cadmium caused visible external lesions such as discoloration and necrosis on livers of Cyprinidae Cavas T, Garanko NN, Arkhipchuk VV (2005).Fish exposed to cadmium revealed a negative effect on the growth rate, meat quality and blood physiology.Abbas HHH, Hammada MM, Miller JD (2007).

Nickel (Ni) Nickel belongs to essential elements and it is emitted into the environment from natural and man-made sources. Nickel is released during nickel mining and by industries that convert scrap or new nickel into alloys or nickel compounds or by industries that use nickel and its compounds. These industries may also discharge nickel in wastewater. Nickel is also released by oil-burning power plants, coal-burning power plants and trash incinerators.Al-Attar AM (2007).While nickel is an essential element at low con-

centrations for many organisms, it is toxic at higher concentrationsMagyarosy A, Laidlaw RD, Kilaas R, Echer C, Clark DS, et al. (2002).Nickel can cause respiratory problems and is carcinogenic ATSDR (Agency for Toxic Substances and Disease Registry) (2004).The toxicity of nickel may be due to nickel being in contact with the skin (body surface), penetrating the epidermis and combining with body proteinNielson, F.H. (1977) Nickel toxicity.Ghosh et al. (2018) studied Ni toxicity on common carp (Cyprinuscarpio) and suggested that Ni does not precipitate in water as fast as other heavy metals and therefore making it more heavily bioavailable to aquatic organisms. Ghosh et al. revealed that Ni primarily accumultes in the gills of Cyprinidae and transportation of Ni from gill to liver, kidney, and muscle tissues is too little to detect within 96 hours of exposure and the Ni amount evaluated in the gut was negligible. Ghosh et al. concluded that Ni toxicity mainly occurs gill- mediated in Cyprinidae Ghosh, A., Kaviraj, A., Saha, S. 2018.

River Vardar is the longest river in the Republic of Macedonia and Republic of Greece with distance of over 388 km, with his source in the location Vrutok and stream at the Aegean sea.

The Vardar river, with its tributaries, makes up a great part of the total water resource of North Macedonia. These tributaries and river Vardar are directly or indirectly connected with the mining areas and foundry for metal in the locations.The firs reported informacion about ichthyo fauna of river Vardar vas from Steindachner(1892) and then he describe the Leucos macedonicus from the Vardar river.Some fish species in the river Vardar (Squalius cephalus,Barbus Barbus, Vimba vimba) are good examination samples for pollution because they are in the all stream of river.The ichthiofauna of the Vardar river is important part of the aquatic food chain for their omnivorus way of feeding.The river is widely used for fisheries (wild fish and fish farming), sports and recreation. Very little recent information is available regarding the contamination with metals in the Vardar river fish species. The river Vardar passes near and across the biggest cities including Gostivar, Tetovo, Skopje, Veles, Negotino, Demir Kapija and Gevgelija with possibility of environmental contamination from domestic and industrial sewage Hot point spots in Fig.1.

Fig.1 In the map of the Republic of North Macedonia, showing hot point spots

The aim of this study is to provide information and evaluate the level of Cadmium (Cd) and (Ni) Nickel as a heavy metal in fish organs (muscle, liver and skin)from Europian Chub (Squalius cephalus) and Common barbel (Barbus barbus) fish species.

MATERIAL AND METHODS

Samples were collected in nine(9) places with distance between them in around 33km along the river Vardar.From each place fishes were collected from both species with support from fishermen's licenced for sport fishing in the North Macedonian fishing Federation.

Fish samples were transported with the plastic bags set in transport refrigirator in laboratory submitted for dissection of target organs were collected for study including skin,-liver and muscle.Each sample of fish tissue has been measurement with analytical scale then set in plastic bag, marked with number which show the catching location and tissue then finally refrigerated below the -18ºC. Total numbers of samples were sixty (60) from Europian Chub and Common barbell. Next step was the sample to set in the porcelain pots then the sample was heated in microwave in 105°C for 24h to drain.

The next day the samples were taken out from microwave and they passed to the stove for 24h in 550°C where they were burned. After 24h the burned samples are prepare for digestion with HNO3 65%.Prepared sample after digestion are ready for reading and analyze by Inductivly coupled plasma mass spectrometry with the ICP- MS type Agilent 7500 series. All data are presented in the unit mg/kg wet weight of a sample tissue.

RESULTS AND DISCUSSION

Results of this study showed that the metal concentrations accumulated in the tissue samples were in descending order of liver > muscles >skin.In the study, we found that the concentration of Cadmium (Cd) and (Ni) Nickel were different in the analyzed organs and differently in the samp-

ling locations. The average of concentration of the Cadmium (Cd) and (Ni) Nickel in the organs (muscle ,liver and skin) andthe locations (nine locations) is showed inTable 1.

Sampling point	NICKEL (Ni)			CADMIUM (Cd)		
	Muscle	Liver	Skin	Muscle	Liver	Skin
HS-1	0.55	0.65	1.05	0.035	0.050	0.040
HS-2	0.50	0.90	0.55	0.040	0.025	0.020
HS-3	0.40	0.20	0.20	0.020	0.020	0.010
HS-4	0.40	4.10	0.10	0.025	0.030	0.010
HS-5	1.04	0.54	0.00	0.090	0.073	0.000
HS-6	0.50	0.20	0.00	0.016	0.160	0.000
HS-7	0.80	1.50	0.00	0.030	0.050	0.010
HS-8	0.60	1.94	0.00	0.041	0.160	0.010
HS-9	0.60	2.20	0.00	0.060	0.135	0.010

Table 1. Mean Heavy Metal Content (mg/kg wet weight) in Fish muscle,liver and skin

Higher concentrations of Cadmium (Cd)and (Ni) Nickel were found in liver tissue,while the lowest were detected in skin tissues. This finding is in agreement with those of other studies regarding the differences between heavy-metal accumulation in fish tissues (Biba,Mavromati.2014).

There guidelines on acceptable levels of in Cadmium (Cd) and (Ni) Nickel the edible parts of fish suggested in North Macedonia is according to international standards WHO/FAO which are for Cd-0.2mg/kg and for Ni-0.5mg/kg. According to our results, there is metal contamination, but it is higher than the guidelines, in the edible part of the examined fish. The examined fish were not associated with enhanced Cadmium (Cd) and (Ni) Nickel content in their muscle and were safe within the limits for human consumption.

From results we can see that we have a different Cadmium (Cd) and (Ni) Nickelconcentration, and as we can see that highest level is in the HS-4 and HS-5 sampling site, which is the point where the river Lepenci is connected to the river Vardar,waste water and atmosphric water from capitol city Skopje is load to the river Vardar,the uper part between city of Veles and Skopje, so it is expected to have registered Cadmium (Cd) and (Ni) Nickel pollution. In the most studies of similar analyzed samples,the liver accumulate the highest concentration of Cadmium (Cd) and (Ni) Nickel in our study is shown also that is the samples of liver in sampling sites HS -4 and till the HS-9, showed that fishes in the part of river Vardar from Skopje till the border with Republic of Greece accumulated higher concentration of Cadmium (Cd) and (Ni) Nickel.In previous study, increased concentrations of these hazardous substances also, especially Pb , in water and sediment from the lower part of the Vardar River, influenced higher accumulations of metals in liver, gills and gonads of Gobiogobio L. (Nastova et al. 2017), concentration of Cadmium (Cd) and (Ni) Nickel in skin is not reported. Metal contaminations are in the concern because off potential thrived waste from domestic and industrial sewage, non-secured industrial landfill and mining fields. The Cadmium (Cd) and (Ni) Nickel are regarded as potential hazards that can endanger both animal and human health. Knowledge of their concentrations in fish is therefore important both with respect to nature management and human consumption of fish as suggested in Amundsen et al., (1997).

In Vardar river, among all river aquatic organisms the fish are the most interested for humans for sport activities in particular, source of food mainly for fisherman's and their families as well. Fishes are considered as indicators in river ecosystem for heavy metal contaminations with light level risk as a potential for human food consumption, because fish are in the top of aquatic food chain, heavy metal accumulation and possibly for the transfer heavy metals on the humans.

CONCLUSION

Our preliminary results provide information for the levels of Cadmium (Cd) and (Ni) Nickel in In our country the river pollution with heavy common fish species of the Vardar river. Results will contribute to the effective monitoring of both environmental quality and the health of the organisms inhabiting the river ecosystem. According to the fish sample analyses the range of concentration with Cadmium (Cd) and (Ni) Nickel is in the higher border with the range of international standards Cd-0.2mg/kg and for Ni-0.5mg/kg wet weight, and it shows that the fishes from investigated Vardar river are safe for human consumption.

Aquatic organisms have been widely used in biological monitoring and assessment of safe environmental levels of heavy metalsIn this study metals concentrations in the muscle of both fish species were used to investigate possible transfer of metals to human populations via fish consumption. Since accumulation of metals in the biological system is dangerous to human beings in our country, there is a need for regular or continuous monitoring of heavy metals concentrations in the aquatic environments.

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