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RESULTS ON LEAD (Pb) CONCENTRATION IN WILD FISH SQUALIUS CEPHALUS & BARBUS BARBUS TISSUES IN VARDAR RIVER, NORTH MACEDONIA

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Abstract

The concentrations of Lead (Pb) in fish from the Vardar river have been investigated in order to assess safety for consumers and the level of contamination. The selected tissues muscle**,** liver and skin of two fish species: European Chub (*Squalius cephalus*) and Common barbel (*Barbus barbus*) from Vardar river stream, Republic of North Macedonia. Samples are collected in nine different points (Hot Spots) in total distance of 301km and approximate 33km distance between sampling sites. During the experiment it was investigated the effect of environmental conditions and urban discharges on lead accumulation in muscles, liver and skin. The metal analyses were performed using Inductively coupled plasma mass spectrometry (ICP-MS). The average of metal concentrations (microgram per gram wet weight) in nine hot spots (HS) occurred in the following ranges:HS-1:muscles 0.10-liver 0.47-skin 0.06, HS-2:muscles 0.30-liver 0.18-skin 0.06HS-3: muscles0.10liver 0.11-skin0.00,HS-4:muscles 0.10-liver 0.61-skin 0.01 HS-5:muscles 0.10-liver 0.27-skin 0.00HS-6:muscles,0.10-liver0.17-skin 0.00, HS-7:muscles 0.10-liver 0.38-skin 0.00,HS-8:muscles 0.30-liver 0.68-skin 0.00and HS-9:muscles 0.15-liver 0.47-skin 0.00.The lowest levels of the lead were detected in the skin. The muscles and liver were found to accumulate the highest amounts of Pb. In case of organs, the highest levels were identified 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, lead, fish tissue, Republic of North Macedonia*

1. Introduction

Fish is an important part of the human diet, but also a good indicator of trace metal pollution in the aquatic ecosystem. Fish samples are considered as one of the most indicative factors in fresh water systems, for the estimation of trace metals pollution potential (Rashed,2001). Organisms retain Pb through gastrointestinal system to liver into the soft tissue muscle to deposit at the end within the skeleton system. Pollution of water bodies is becoming a major cause of concern with respect to human health (Jarup, 2003). 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 bio accumulate (De Forest 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 diseases in humans depending on the degree of exposure. These vary from minor skin irritation to severe demages of the liver, kidney, skeleton, nerve tissues and circulatory system.

River Vardar is the longest river in the Republic of North 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 Macedonia. These tributaries and river Vardar are directly or indirectly connected with the mining areas and foundry for Lead (Pb) in the locations. The first reported information about ichthiofauna of river Vardar vas from (Steindachner, 1892) and then he describes 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.

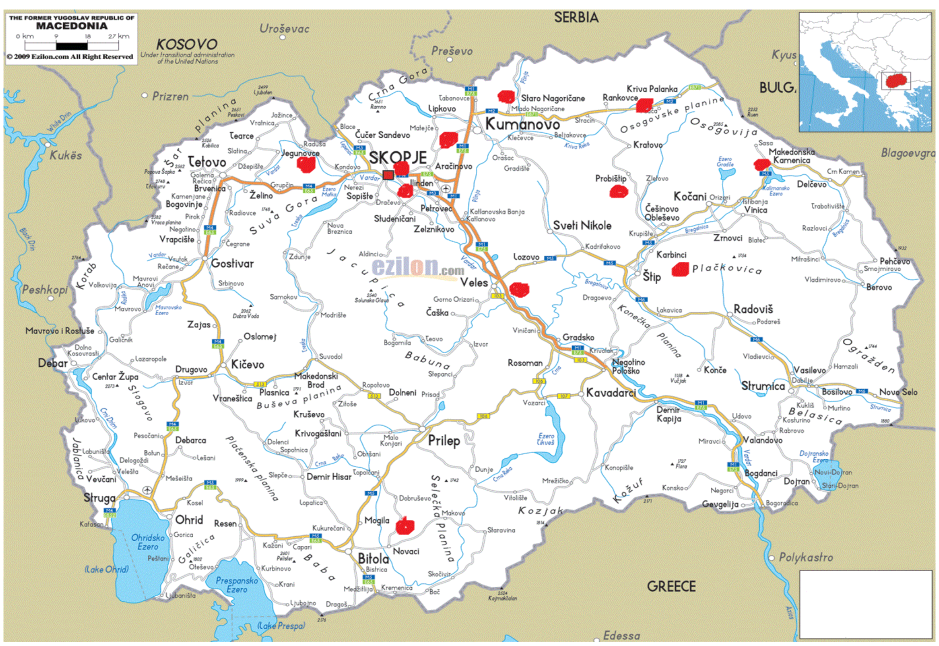

Figure.1 In the map of the Republic of North Macedonia, showing hot point spots

The aim of this study is to provide information and evaluate the level of Lead as a heavy metal in fish organs (muscle, liver and skin) from European Chub (*Squalius cephalus*) and Common barbell (*Barbus barbus*) fish species.

2. 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 the licensed fishermen for sport fishing in the North Macedonian fishing Federation.

Fish samples were transported with the plastic bags set in transport refrigerator in laboratory submitted for dissection of target organs were collected for study including skin, liver and muscle. Each sample of fish tissue has been measured with analytical scale then set in plastic bag, marked with number marking the catching location and tissue, then finally refrigerated below the -18ºC.Total numbers of samples were sixty (60) from European Chub and Common barbell.

Next step was the sample to set in the porcelain pots, heated in microwave in 105°C for 24h to drain. The next day samples were taken out from microwave and they passed to the stove for 24h in 550°C where they were burned. After 24h burning, samples were ready for digestion with HNO3 65%. Prepared samples after digestion are ready for reading and analyze by Inductively 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.

3. 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 Lead was different in the analyzed organs and differently in the sampling locations. The average of concentration of the Lead in the organs (muscle, liver and skin) and the locations (nine locations) is showed in Table 1.

Sampling point	Muscle	Liver	Skin
HS-1	0.10	0.70	0.06
HS-2	0.30	0.18	0.06
HS-3	0.10	0.11	0.00
HS-4	0.10	0.61	0.01
HS-5	0.10	0.27	0.00
HS-6	0.10	0.17	0.00
HS-7	0.10	0.38	0.00
HS-8	0.30	0.68	0.00
HS-9	0.15	0.47	0.00

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

Higher Pb concentrations 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 (Nefail, Jani.2014).

There are guidelines on acceptable levels of Pb in the edible parts of fish suggested in North Macedonia is according to international standards 0.30-1.00mg/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 Pb content in their muscle and were safe within the limits for human consumption.

From results we can see that we have a different Lead concentration, and the highest level is in the HS-8 sampling site, which is the location where the river Bregalnica is connected to the river Vardar, waste water and atmospheric water from the capitol city of Skopje are loaded to the river Vardar at the upper part between city of Veles and Skopje, so it is expected to have registered Lead presence to the fish from downstream of the river Vardar. In the most studies of similar analyzed samples, bones accumulate the highest concentration of Lead, in our study this is shown in the samples of liver collected at sites from HS-4 until the HS-9, this shows that fishes in the part of river Vardar from Skopje till the border with Republic of Greece have accumulated higher concentration of Lead. In previous study, increased concentrations of these hazardous substances, especially Pb and Cd in water and sediment from the lower part of the Vardar River, influenced higher accumulations of metals in liver, gills and gonads of Gobio gobio L. (Nastova et al. 2017), concentration of Pb in muscle is not reported.

In our country the river pollution with heavy metal contaminations it is a concern because of potential thrived waste from domestic and industrial sewage, non-secured industrial landfill and mining fields. The Pb is calculated as potential hazards that can endanger both animal and human health. Knowledge of its concentration 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, fish is the most interested for humans, in particular for sport activities, it also presents source of food mainly for fisherman families. Fishes are considered as indicators of the presence of the heavy metal contaminations in river ecosystem with light level risk as a potential for human food consumption, because they (fish) are at the top of aquatic food chain, this makes them easy transmitters of heavy metal accumulation to humans.

4. Conclusion

Our preliminary results provide information for the levels of Pb in 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 Lead is close to the higher border with the range of international standards 0.30-1.00 mg/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 metals. In this study metal 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.

References

[1]. Amundsen P.A., Staldvik F.J., Lukin A., Kashulin N., Popova O., Reshetnikov Y. Heavy metals contamination in freshwater fish from the border region between Norway and Russia. *Sci Total Environ* 1997; 201:211 –24.

[2]. De Forest D.K., Brix K.V. and Adams WJ., 2007. Assessing metal bioaccumulation in aquatic environments: The inverse relationship between bioaccumulation factors, trophic transfer factors and exposure concentration. *Aquatic Toxicology*, 84(2), 236–246.

[3]. Fernandez, M., Cuesta, S., Jimene, O., Garcia, M.A., Hernandez, L.M., Marina, M.L. and Gonzalez, M.J. 2000. Organochlorine and heavy metal residues in the water/sediment system of the Southeast Regional Park in Madrid, *Spain. Chemosphere* 41:801-812.

[4]. Jarup L., 2003. Hazards of heavy metal contamination. British Medical Bulletin, 68: 167-182.

[5]. Khallaf, E.A., Galal, M. and Authman, M. 1998. Assessment of heavy metals pollution and their effects on *Oreochromisniloticus*in aquatic drainage canals. J. Egypt. Ger. Soc. Zool. 26: 39-74.

[6]. Nastova R., V. Kostov, I. Ushlinovska. 2017. Heavy metals in organs of gudgeon (Gobiogobio L.) from Vardar River, R. Macedonia. *Agricultural Science and Technology*, Vol. 9, No. 4, pp 340 – 346.

[7]. Nefail B, Jani M, 2014 *Veterinary Toxicology*

[8]. Rashed M.N. Monitoring of environmental heavy metals in fish from Nasser lake. *Environ Int* 2001; 27:27–33.

[9]. Steindachner F, 1892. Ubereinigenene und seltene Fischartnaus der ichthyologischensammlung des Natur Historischen Hofmusenms. Dendschr. *Der Akad. der Wisserschaft*, Wien, Bd. LIX.

[10]. Stephen, C., Jewett, A. and Sathy Naidu, A. 2000. Assessment of heavy metals in red king crabs following offshore placer gold mining. *Mar. Pollut. Bull.* 40: 478-490.

[11]. Tarvainen,T., Lahermo, P. and Mannio, J. 1997. Source of trace metals in streams and headwater lakes in Finland. *Water, Air, Soil Pollut*. 94: 1-32.