Journal of Multidisciplinary Engineering Science and Technology (JMEST)
ISSN: 2458-9403
Vol. 6 Issue 9, September - 2019

Concentration of the Cobalt (Co) in Wild Fish *Squalius Cephalus* and *Barbus Barbus* Tissues in Vardar River of North Macedonia

Lulzim SHAQIRI[1], Jani MAVROMATI[2]*
[1]PhD student, Department of Veterinary Public Health, Faculty of Veterinary Medicine, Agricultural University of Tirana, Albania
[2]Department of Veterinary Public Health, Faculty of Veterinary Medicine, Agricultural University of Tirana, Albania
*Corresponding author: jmavromati@ubt.edu.al

***Abstract*—The concentrations of Cobalt (Co) 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 301 km and approximate 33 km distance between sampling sites. During the experiment it was investigated the effect of environmental conditions and urban discharges on Cobaltd 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 0.15-skin 0.15, HS-2: muscles 0.10 -liver 0.15-skin 0.10, HS-3: muscles 0.00 liver 0.10-skin 0.00, HS-4: muscles 0.10-liver 0.60-skin 0.00, HS-5:muscles 0.20-liver 0.10-skin 0.00, HS-6: muscles 0.07-liver 0.10-skin 0.00, HS-7: muscles 0.10-liver 0.30-skin 0.10, HS-8: muscles 0.07-liver 0.34-skin 0.00 and HS-9: muscles 0.10-liver 0.35-skin 0.00. The lowest levels of the Cobalt were detected in the skin. The muscles and liver were found to accumulate the highest amounts of Co. 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, Cobalt, fish tissue, Republic of North Macedonia**

1. Introduction

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 Cobalt (Co) through gastrointestinal system to liver into the soft tissue muscle and skin. Pollution of water bodies is becoming a major cause of concern with respect to human health (Jarup, 2003). The metals accumulated in the water by the 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. In generally the metals enter in 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 damages of the liver, kidney, skeleton, nerve tissues and circulatory system.

Cobalt belongs to the essential metal according to this in the lower concentrations is necessary for the living organisms like animals and some plants since it is required in vitamin B, formation (Lehninger, 1972).

Vardar River is the longest river in the Republic of North Macedonia with a distance of over 388 km and it is 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 heavy metal in the locations. The first reported information about ichthiofauna of river Vardar was 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 in the upper part), 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 Hot point spots in the map of the Republic of North Macedonia.

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

2. Material and methods

Samples were collected in nine (9) places with distance between them in around 33 km 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 barbel.

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 in the tissue samples were in descending order of liver > muscles > skin. In the study, we found that the concentration of Cobalt was different in the analyzed organs and differently in the sampling locations. The average of concentration of the Cobalt 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	0.15	0.15
HS-2	0.10	0.15	0.10
HS-3	0.00	0.10	0.00
HS-4	0.10	0.60	0.00
HS-5	0.20	0.10	0.00
HS-6	0.07	0.10	0.10
HS-7	0.10	0.30	0.10
HS-8	0.07	0.34	0.00
HS-9	0.10	0.35	0.00

Table 1. Concentration of Cobalt (Co) (mg/kg wet weight) in Fish muscle, liver and skin

Higher Cobalt concentrations were found in liver tissue, while the lowest were detected in skin tissues. According to our results, there is metal contamination, but it is lower than the guidelines, in the edible part of the examined fish. The examined fish were not associated with enhanced Cobalt content in their muscle and were safe within the limits for human consumption.

From results we can see that we have a different Cobalt concentration, and the highest level is in the HS-9 sampling site, which is the location at the end near the border where the river Bregalnica is connected to the river Vardar. Waste water and atmospheric water from the capital 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 higher Cobalt presence to the fish from downstream of the river Vardar. In the most studies of similar analyzed samples, muscle accumulate the highest concentration of Cobalt, 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 Cobalt. 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 Cobalt 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 Co 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 results provide information for the levels of Cobalt 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 Cobalt is lower on accumulation on the muscles tissue, 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. Rashed M.N. Monitoring of environmental heavy metals in fish from Nasser lake. Environ Int 2001;27:27–33.
8. Steindachner F, 1892. Ubereinigenene und selteneFischartnaus der ichthyologischensammlung des NaturHistorischenHofmusenms. Dendschr. derAkad. der Wisserschaft, Wien, Bd. LIX
9. 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.
10. 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.
11. Lehninger, 1972.Biochemistry - The Molecular Basis of Cell Structure and Function