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Juridical Mass for Protection of Waters from Pollutants – Heavy Metals in Water of Lake Ohrid and in Fish Species – *leuciscus cephallus albus*

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Abstract— Metals occur in different forms: as ions dissolved in water, as vapours, or as salts or minerals in rock, sand and soil. They can also be bound in organic or inorganic molecules, or attached to particles in the air. Both natural anthropogenic processes and sources emit metals into air and water. The effects of metals in the environment depend to a large extent on whether they occur in forms that can be taken up by plants or animals. Uptake of metals in an animal involves metal ions crossing a cell membrane.

The aim of this paper was analysis and determination of heavy metals like Cu, Zn, Cd and Pb in water samples of different prophiles from Ohrid Lake. Studied water samples were taken in different locations and different depths (0m, 20m, 40m, 75m, 100m and 150m). The presence of toxic heavy metals in food chain was studied in fish species – Klein (Leuciscus Cephallus albus Bp Bonaparte).Determination of analysed heavy metals was done using Atomic Absorphion spectroscophy using a Perkin Elmer 370 A and 370 flames – aer acetylene and AAS Peyunicam 926 model.

Index Terms— Bones, heavy metals, gills, liver, muscular tissues.

1 Introduction

Metals occur naturally in the environment and are present in rocks, soil, plants, and animals.Often a ligand, or a carriers, executes this transport. Sometimes there are additional specific carriers within the cell. If an organism's uptake of metal is greater than its ability to get rid of it, the metal will accumulate.[2.4. 13]

Heavy metals tend to accumulate in storage compartments.For example, cadmium accumulates preferentially in the kidneys, and lean in the skeleton. The accumulation can continue throughout the organism's life and is the major cause of chronic toxicity. In contrast to organic pollutants, metals accumulate in protein tissues and bone rather than fat.[3,5]

2 Ohrid Lake

Lake Ohrid (Macedonian*:* transliterated: *Ohridsko Ezero*; *Albanian*: *Liqeni i Ohrit*). It is one of Europe's deepest and according to most experts the oldest lake in *Europe*, preserving a unique aquatic ecosystem with more than 200 endemic species that is of worldwide importance. The importance of the lake was further emphasized when it was declared a World Heritage site by *UNESCO* in 1979. [9.12]

However, human activity on the lake shores and in its catchment area is resulting in the ecosystem coming under stress. Lake Ohrid is situated in the Southeastern part of Europe, with Albania and FYR of Macedonia as the only two lakeshore states. It is peculiar for it's rich biodiversity, that derives of it's very old age. Ohri Lake is the biggest and the deepest from all the lakes of the group known as "Desaret". It is called a Museum of living fossils and it offers a living environment for too many organisms typical for mild waters, which, in the Balkans Peninsula and Central Europe are found only in the fossile form. [15].

Another typical peculiarity of this Lake is its the only flow - the river Drini i Zi, with an approximate flow of 22.4 m s, for most of the time.

3 Living Species

Ohrid Lake is well known for its 17 kinds of fish. They are all autochthonous species. Ten of them are commercially important. [7.8.11]

Another peculiar feature of this lake is its ability to self regeneration. Its water comes from different sources as well as from its water accumulating basin.

4 Socio-juridical aspects for protection of living environment

Protection of living environment is one of the most important fields of our time and, it is more than a logical thing that, the society should show special attention to this field in R. of Macedonia, as well.[1]

This is stated in act 8 of Constitution of R. of Macedonia where arrangement and space humanity and protection and

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advancement of living environmental and nature and respect of the norms of international Law, in general is accepted and is stated as one of the fundamental amount of Constitution of R. of Macedonia [6,10,14].

Clean Living Environment should be guaranteed to every citizen. Everyone is obliged to protect living environment and nature that means to protect the soil, the air and water.

Of course, regulation of living environment and nature protection, and it need to be arranged with other special laws that must have accordance with international norms and Constitution of R. of Macedonia. But in a state not always inside law's and International Convents are observed, like changing riverbed of river Sateska in 1962. Before this year this river was pour in River Drini i Zi and without a reason its riverbed diverted and now it pours in Lake Ohrid, even if a thing like this is disallowed with International Konvent and with protection law of Lake Ohrid, Prespa and Dojran (act 7) [1,6].

Along pouring this river brings with itself dangerous materials with which humans and other organisms are in dangerous. This materials can bring change's on water quality and world life, in physical-chemical, biological, radiological, microbiological aspects, etc.

Fig. 1. Images of a beautifull part of Lake Ohrid

Fig. 2. Images of dirty parts of Lake Ohrid

5 Experimental engagement material Gathering and working methods

In this output, the presence of heavy metals (Fe, Mn, Cu, Cd, Pb, Ni, Zn) in the water on its vertical profile was analyzed, beginning from levels (0m, 20m, 40m, 75m, 100m and 150m depth), as well as their impact in the nutrition chain. Three exemplars of fish known as Leuciscus Cephallus Albus, L1, L2 and L3 were examined. From each of them organs like gills, liver, muscular tissues and bones were dissected.

After the dissection, the determination of the concentration of the heavy metals, such as: Zn, Cu, Cd and Pb in each of the organs was done.

To achieve this, SAA – Spectroscopy of Atomic Absorption – the flame technique was used. The measurements were done by Spectrophotometer of the atomic absorption of the type PERKIN – ELMER 370 A and 370. Flame – Air – Acetylene and SAA PEYUNICAM 926. (4)

Fig. 3. Leuciscus cephallus albus

6 Experimental results

Achieved results are presented in charts / graphics as follows: Charts 1-5 to represent the achieved results of the concentration of the heavy metals on the studied samples through experimental work.

TABLE 1
DETERMINATION OF HEAVY METALS IN THE WATER ON THE VERTICAL PROFILE OF THE LAKE BY SAA- MG/L

Sample	L1	L2	L3
Zn	25.1	10.3	19.9
Cu	14.8	14.6	27.3
Cd	0.38	2.69	0.69
Pb	-	-	-

Sample	L1	L2	L3
length cm	28	13	13.7
weight g	283.1	20.168	22.151
gills g	2.956	0.135	0.353
liver g	1.765	0.125	0.145
Muscular tissues g	34.115	3.112	0.575
Bones g	0.415	0.072	0.075

TABLE 2
PARAMETERS OF ANALYSED FISH

Sample	L1	L2	L3
Zn	0.91	2.64	2.69
Cu	3.41	15.3	11.2	0.217
Cd	0.14	0.49	1.1
Pb	0.09	-	-

TABLE 3
DETERMINATION OF HEAVY METALS ON GILLS OF FISH WITH SAA – µG/L

Sample	L1	L2	L3
Zn	2.71	186.8	3.33
Cu	10.2	227.8	77.4
Cd	0.14	1.18	0.46
Pb	3.29	-	4.01

TABLE 4
DETERMINATION OF HEAVY METALS ON LIVER OF FISH WITH SAA – µ µg/l

Sample	L1	L2	L3
Zn	7.85	11.5	7.73
Cu	46.4	266.9	412.8
Cd	0.34	3.52	2.4
Pb	0.91	2.64	2.69

TABLE 5
DETERMINATION OF HEAVY METALS ON THE FISH MUSCULAR TISSUE WITH SAA – µ µg/l

0m	20m	Sample	40m	75m	100m	150m
0.8	1.0	Fe	0.9	1.2	1.0	1.91
0.15	0.1	Mn	0.14	0.21	0.24	0.25
0.33	0.41	Zn	0.37	0.29	0.45	0.4
0.05	0.06	Cu	0.06	0.07	0.07	0.06
-	-	Cd	-	-	-	-
0.26	0.38	Ni	0.3	0.27	0.18	0.85
-	-	Pb	-	-	-	-

TABLE 6
DETERMINATION OF HEAVY METALS ON FISH BONES WITH SAA – µ µg/l

Graphic charts from A to E represent the same results – the results from the previous charts 1-5, added is only a better visual representation of them.

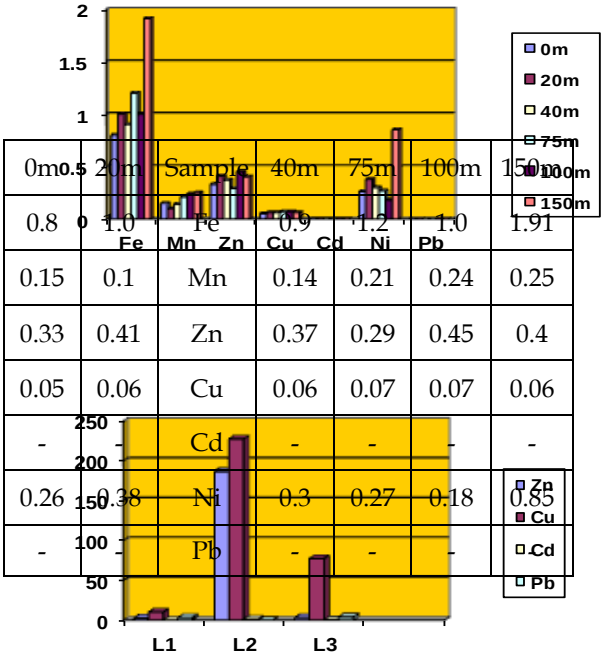

Fig. 4. Chart A - Concentration of Fe, Mn, Zn, Cu, Cd, Ni and Pb in water on the vertical profile of the lake, determined with SAA (mg/l).

Fig. 5. Chart.B – Concentrtion of Zn in the organs of fish, determined with SAA (µg/g)

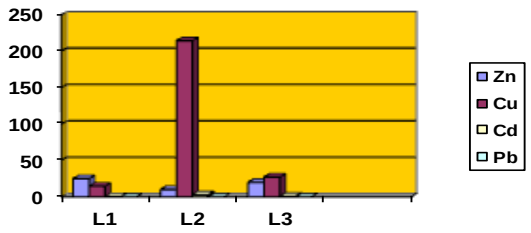

Fig. 6. Chart C – Concentration of Cu in the organs of fish, determined SAA (µg/g)

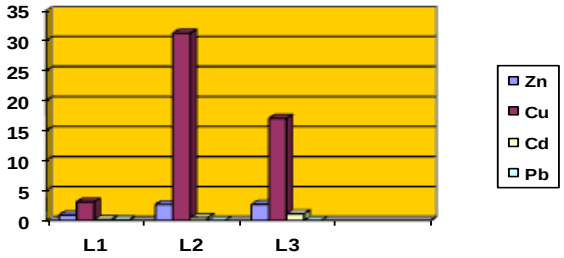

Fig. 7. Chart D – Concentration of Pb in the organs of fish, determined SAA (µg/g)

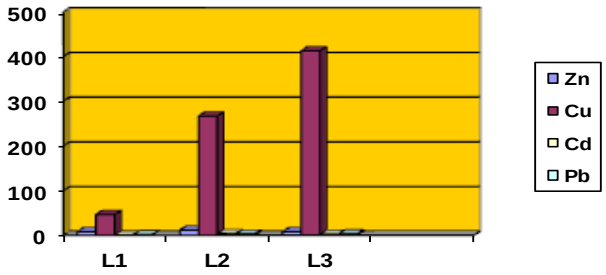

Fig. 8. Chart E – Concentration of cadmium in the organs of fish, determined SAA (µg/g)

7 DISSCUSION OF THE RESUTLS

After having thrown an analytic view on the results given above through the charts, both numeric and graphic ones, one can notice very clearly that on the vertical profile of the lake waters, the concentration of the metals were traced, as follows:

Concentration of Mn goes from 0.10 mg/l in 20 m to 1.91 mg/l in 150 m deepness (Tab.1,Chart A).

Iron - Fe was represented in concentrations 1.0 mg/l in 20 m up to 1.91 mg/ in 150 m deepness. (Tab.1,Chart A)

Zinc was registered on minimal values from 0.41 mg/l in 20 m, up to 0.45 mg/l in 100 m deepness. (Tab.1,Chart A) Copper was registered from 0.07 mg/l in 20 m to 0.07 mg/l in 100 m deepness. (Tab.1,Chart A)

Nickel gave these results: 0.38 mg/l in 20 m up to 0-85 mg/l in 150 m deepness. (Tab.1,Chart A). From the analyses done on the studied water samples, about the concentration of the above mentioned metals, one can easily understand that, with some exceptions, their concentration on the lake waters is not of a high level. That's why, we can say that the waters on the vertical profile of the Ohrid Lake belong to the waters of the first or second class.

In order to have a realistic view about what was stated above, during the determination of the presence of the heavy metals in the organs of fish, our results have shown the values given below:

In order to have a realistic view about what was stated above, during the determination of the presence of the heavy metals in the organs of fish, our results have shown the values given below:

Minimal amount of Zinc was accumulated in the muscles 0.91µg/g L1 (Tab 4, Chart B), up to 186.8 µg/g in the gills L2 (Tab 2, Chart B).

Copper did give these results: 3.1 µg/g - L1 in muscles (Tab 4, Chart C) up to 412 µg/g L3 in the bones (Tab 5, Chart C).

The amount of the concentrated Lead goes from 0.09 µg/g in muscles – L1 (Tab 4, Chart D), up to 4.01 µg/g in gills – L1 (Tab 2, Chart D).

Results of the Cadmium have shown that the gill of L3 possesses a concentration of 0.14 µg/g in muscules - L1 (Tab 4, Chart E), up to 3.52 µg/g in the bones of L2 (Tab 5, Chart E).

4 CONCLUSION

Presence of the heavy metals in the leaving creatures is done by their penetration through the cell membrane. This process is frequently done through some conductors specific for the cells.

Metals get accumulated in the organism in cases when the conductivity of a given metal is bigger than the capacity of the organism to get rid of it.

It is typical for the heavy metals to get themselves accumulated in the accumulative organs. This way, cadmium initially is accumulated in the kidney, copper in liver and Lead in skeleton.

This process goes on during the whole lifetime of the organism and occasionally it brings it to the level of chronic poisoning. From the above results, one can notice that the fish belbica does accumulate a higher amount of heavy metals and this amount get bigger together with the weight of the fish.

From what was stated above, one can conclude that the accumulation of heavy metals by the leaving creatures that do live within water ecosystems, is an ongoing process that is not preferred because it represents a sort of threat for their mere existence as well as for the nutrition chain to come.

Using of chemicals (pesticides) must be controlled in agriculture especially along watershed of the river wich are pure in the Lake Ohrid.

It is necessary bringing and application of rigorous juridical dispositives with international and national character.
Prevention measure's to delay river's and lakes pollution, which pour in Lake Ohrid.

International co-operation and in local degree between Macedonia and Albania.

Growth of the degree of cooperation between governmental organizations and nongovernmental organizates.

Cooperation of organs of central government (ministry) with organs of local government (sector for living environment protection) and co-operation of units of local self-government (Commune) between them.

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