Assessment of Heavy Metals Pollution of Snagov Lake, Romania

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Distribution of heavy metals and trace elements from anthropogenic origin in water, sediments, aquatic plants and different tissues of fish from Snagov Lake, Romania. has been investigated. The concentration of Cu, Zn, Cd, Ti, V, Cr, Mo, Co and Ni, was collected from three sites of the lake, during spring time from water, sediments, Ceratophyllum demersum, Phragmites australis reed, and Scardinius Erytrophtalmus fish. The fish samples were taken from gills, muscles, scales and bones. The ecological risk index has been assesed and bio-concentration factor, (BCF), of metals in anatomical tissues of studied fishes to be used as a diagnostic tool for lake pollution Experiments have shown that Ti and Zn had the highest concentration in water, sediments, aquatic plants and fish samples. Also, the metals bio-concentration is increased in branchiae and scales, compared with muscles and bones.

Keywords: metals ions, ecological risk, bio-concentration factor, Snagov Lake

Heavy metals are toxic environmental pollutants, that accumulate in water bodies influenced both the aquatic life and the quality of drinking water. The heavy metals (HM) in natural water bodies, either coming from atmospheric depositions, weathering of rocks, erosions, runoff, untreated sewage, agricultures activities, industries and mining, represent a stressors for living organisms and a pollution sources for drinking water [1-3]. In bodies water the HM will be distributed between liquid and solid phases, and will be find in dissolved phase(less than 0.1%), colloids, suspended mater and sediments (more than 99.9%), and in biota [4].

The distribution of Cu, Zn, Cd, Ti, V, Cr, Mo, Co and Ni in water, sediments, aquatic plants and different morpho-anatomical regions of fish sampled from Snagov Lake, Romania was studied in this paper. The lake pollution level has been assesed using the ecological risk index and bio-concentration factor, (*BCF*), of metals in anatomical tissues of studied fishes.

Experimental part

Material and methods

Snagov lake is situated about 25–30 km north of Bucharest, Romania, it has a surface of only 5.75 km², but due to its elongated shape it stretches for about 12 km, northeast to southwest, the average depth 5 meters and retention time is of 27 days, [5]. The pollution sources of lake are domestic wastewaters, agricultural and industrial effluents, leachate from synthetic and natural fertilizers and septic tanks, runoff and infiltration from animal feedlots, irrigations etc.

In this study the sampling was done on 05/25/2013. Samples duplicates were collected from water, sediments, algal, reed, and fish from three sampling sites: Antena Tâncãbe°ti, Complex Pacea, Santu Floresti. Figure 1 shows the details of sampling sites [6].

Fig. 1. Sampling points locations in Snagov Lake [6]

Water sampl*es*

The water samples were collected from the water column using a Ruttner sampler. The water samples were filtered, preserved and packed according to SR ISO 5667/2-1998, In table 1 are presented the standard methods and apparatuses used for analyzing different parameters used for general lake water quality characterization. For metals content analysis in laboratory the samples were acidulated to *p*H=2 using HNO_3 and HCl according to US EPA 3015-1994 – *Microwave assisted acid digestion of aqueous samples and extracts*.

Sediment samples

Sediment samples were collected in duplicate according to SR ISO 5567/4-2000 – Water Quality. Sampling. Part 4: Guide for water sampling from natural and artificial lakes using Ekman grab instrument. In laboratory the samples were firstly weighed at room temperature, milled and sieved by means of the sieving system CISA 08 (model RP 08). The samples were weighted and digested with an aqua regia mixture into Teflon tubes for heavy metals analysis. The digester apparatus used was ETHOS D Milestone from UK.

Plant samples

Two types of plants were sampled: *Ceratophyllum demersum* (Phylum Tracheophyta, Class Magnoliopsida,

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Nr. crt.	Parameter	Standard method	Analysis method	Apparatus
1	pH	SR ISO 10523-2012	Electrochemical	pH, conductivity-multiparameter WTW Inolab 740
2	Suspended solids	SR EN 872-2005	Gravimetric	Filtering system with vacuum pump / pressure Millipore; borosilicate glass fiber filters (GF6)
3	Secchi Transparence	No standard Methods	Visual	Secchi disk, 20 cm diameter, black and white design.
4	Turbidity	8237 HACH method - turbidity	Molecular absorption spectrometry	HACH Drell 2000 (molecular absorption spectrometer)
5	Dissolved oxygen	SR EN 25813-2000	Volumetric	Winkler methods
7	Total Nitrogen (TN)	SR EN 12260-2004	Catalytic combustion	Analytik Jena- Total nitrogen analyzer Multi N/C 3100 method
8	Total Phosphorus (TP)	SR EN ISO 6878-2005	Molecular absorption spectrometry	UV-VIS SPECOR 200 from Analytik Jena
9	Chlorophyll *a*	SR ISO 10260-1996	Molecular absorption spectrometry	SPECORD 200 Analytik Jena – molecular absorption spectrometer

Table 1
STANDARD METHODS AND APPARATURES USED FOR ANALYSIS

Order Nymphaeales, Family Ceratophyllaceae, common name - Coontail) and *Phragmites australis (*Phylum Tracheophyta Class Liliopsida, Order Cyperales, Family Gramineae, common name - Reed). They were collected mannually, *Ceratophyllum demersum* were sampled from the water column while *Phragmites australis* from the lakeshore. The samples were transported into a cooling box to the laboratory where they were washed with deionized water, dried at room temperature and chopped (leaves and strains). Further, the samples were weighted and mineralized by microwave digestion into Teflon vessels using the digester apparatus used was ETHOS D Milestone from UK.

Fish samples

In order to analyze the heavy metals from fish tissues, two specimens of Rudd, *(Scardinius Erytrophtalmus)* were collected. Samples were taken from tissue, scales, bones and branchiae. Then the samples were washed with deionized water, finely chopped and homogenized in order to obtain a representative sample. Further, the samples were dried at room temperature, weighted and mineralized by microwave digestion into Teflon vessels. The digester apparatus used was ETHOS D Milestone from UK.

Metal analysis

Finally, the solutions were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) according to SR EN ISO 17294/2-2005 – *Water Quality. Application of mass spectrometry with inductively coupled plasma. Part 2. Determination of 62 elements*, by means of an Agilent apparatus, model ICP-MS 7500 cx., the method is usual used for metals determination [7].

Ecological risk assessment

For the assessment of ecological risk, the accumulation status of heavy metals in sediments from each sampling location was computed. The equation used for accumulation coefficient calculus was [8]:

$$C^i_f = C^i_m / C^i_n \quad (1)$$

where: C^i_m is the value of heavy-metals concentration in sediment samples and C^i_n is the preindustrial background concentration values in sediments, both expressed in [mg/kg].

The accumulation coefficients, E^i_r, indicate the pollution loading of heavy metals in sediments caused by local industrialization processes. Hakanson method was used for the assessment of heavy metals potential ecological risk [9]. The potential ecological risk coefficient E^i_r of single elements and potential ecological risk index R_i of multi-element were calculated by means of eq. 2 and eq. 3.

$$E^i_r = T^i_f \times C^i_f \quad (2)$$

$$R_i = \Sigma E^i_r \quad (3)$$

where: C^i_f is the accumulation coefficient of element i and T^i_f is the toxic response factor of element *i*, that reflects its toxicity levels and bio-organism sensitivity towards it. In table 2 are given the criteria for the assessment of ecological risk degrees caused by the heavy metals present into the sediments [9-10].

Table 2
CRITERIA FOR ASSESSMENT OF ECOLOGICAL RISK DEGREES

R_i or E^i_r values	Ecological risk degree
R_i<150 or E^i_r<40	Low
150≤ R_i < 300 or 40≤E^i_r<80	Moderate
300≤ R_i < 600 or 80≤E^i_r<160	Considerable
600≤ R_i or 160≤E^i_r<320	Very high

A major parameter for characterizing bioaccumulation of metals in flora and fauna is the bio-concentration factor (*BCF*). It can be expressed as a ratio between the concentration of a chemical substance in an organism and the concentration of the chemical substance in the surrounding environment [11-12]. Further on, in table 6, are shown the *BCF* values in different anatomical tissues of studied fishes.

Results and discussions

Data analysis presented in table 3 indicate that the lake shows the maximum biological activity demonstrated by a high concentration of chlorophyll *a*, high turbidity, the

Parameter	*Unit*	*Sampling points*		
		Antena Tancabesti input	*Complex Pacea middle*	*Santu Floresti output*
Temperature	°C	26	25	26
pH		8.43	8.28	8.9
Suspended solids matter	mg/L	18.4	18	23.20
Secchi Transparence	m	0.5	0.8	1.3
Turbidity		20	14	4.0
Dissolved oxygen	mg/L	6.5	6.4	8
Total Nitrogen	mg/L	1.32	1.12	0.792
Total Phosphorus	mg/L	0.154	0.065	0.019
Chlorophyll *a*	μg/L	23.69	35.54	8.29

Table 3
PARAMETERS CHARACTERIZING THE SNAGOV WATER FROM PHOTIC ZONE

temperature and *p*H are optimum for their development. Organical carbon compounds concentration is high proves by low dissolved oxygen concentration. The transparency increases from input to output of the lake, all the values of transparence indicating the existence of eutrophic.

The ratio between concentrations, in mg/L, of the total nitrogen and total phosphorus, TN/TP varied to input in range 8-10, optimal algae growth, to middle around 17 and output around 40 while phosphorus limits here the growth of biomass. The values of chlorophyll *a*, transparence and total phosphorus indicating the eutrophic-hypertrophic conditions in lake, according CARLSON criteria [13].

In table 4 are shown the dissolved and total average concentrations of studied metals (Cu, Zn, Cd, Ti, V, Cr, Mo, Co and Ni) in all the sampling points.

United States Environment Protection Agency, EPA, established a water quality criteria for aquatic life in freshwaters for Cd, Cr, Cu, Ni and Zn as priority pollutants[14]. According to this criteria, freshwaters must have specific continuous concentrations (CC) and maximum concentrations (MC) of each of these pollutants, as presented in table 4). According EPA criterion we can say that none of the elements analyzed does not exceed the two limits.

Molibdem is found only in dissolved form throughout the lake route, the concentrations of soluble Ti in water are nearly zero, while the ones of insoluble form as mineral or organic compounds. At the input to the lake other metals are found both in dissolved form and in solid organic and mineral particles. On route the concentration of dissolved metal ions decreases and to output are found in lower concentrations, only in dissolved form, due to sedimentation and precipitation them. So, in sediment reaches more than 90% of the metal ions of Zn, Cd and Ti, about 80% of V, around 60% of Cr and Cd, around 50% Cu and Mo, and only 30% of Ni relative to the amount of input.

Concentrations of Cu, Zn, Cd, Ti, V, Cr, Mo, Co and Ni metals ions in sediments are showed in figure 2. The sediments mainly contain Ti, of concentration around 400 mg/kg, with the highest value in the middle of the lake, i.e. around 600 mg/kg. Another major element in the sediments is V, with a concentration around 20 mg/kg. The average concentrations of Cd, Co, Cr, Cu, Ni, Mo and Zn in sediments vary: 0.1, 3, 11, 7, 9, 1 and 10 mg/kg, respectively.

Sampling point	Antena Tancabesti		Complex Pacea		Sant Floresti		Concentration limit	
Metal	Dis. μg/L	Total μg/L	Dis. μg/l	Total μg/L	Dis. μg/L	Total μg/L	*CMC, μg/L	** CCC, μg/L
Cu	1.2	1.5	1.4	1.4	0.77	0.78	-	-
Zn	5.3	23.6	4.9	11.3	<	1.37	120	120
Cd	0.014	0.03	0.007	0.012	<	0.001	1.8	0.72
Ti	<	2.20	0.01	0.93	<	0.075	-	-
V	1.5	1.8	0.86	0.96	0.37	0.39	-	-
Cr	0.09	0.33	0.087	0.21	0.10	0.118	586	85
Mo	4.2	4.01	2.84	2.9	1.93	1.98	-	-
Co	0.15	0.25	0.14	0.15	0.085	0.094	-	-
Ni	0.9	1.16	0.72	0.79	0.71	0.80	470	52

*CMC = criterion maximum concentration, ** CCC = criterion continuous concentration

Table 4
METAL IONS CONCETRATIONS (DISSOLVED- DIS. AND TOTAL) IN SNAGOV LAKE WATER

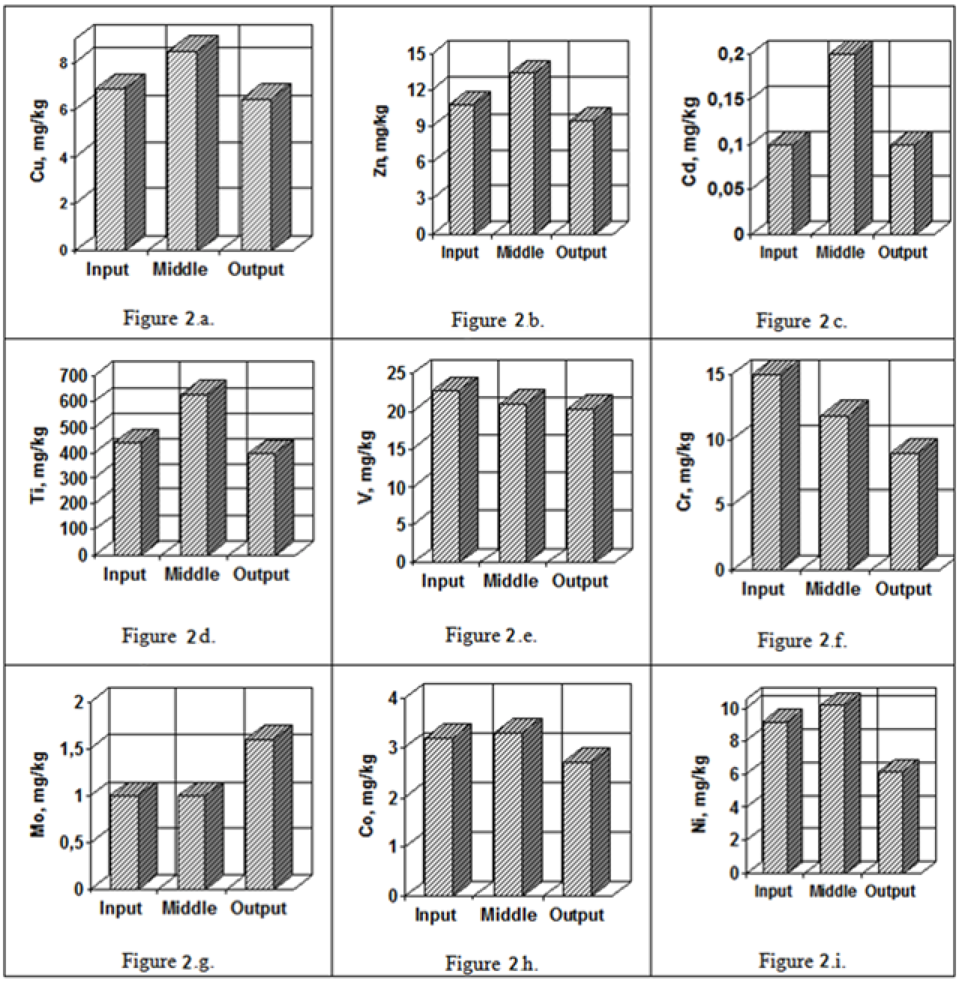

Fig. 2. Metal ion concentration in sediments

Table 5
ACCUMULATION COEFFICIENT, C^i_f OF THE ECOLOGICAL RISK POTENTIAL FOR EACH ELEMENT, E^f_r, AND OF THE ECOLOGICAL RISK POTENTIAL FOR MULTI ELEMENTS, R_{fi} FOR THE TOXIC STUDIED METALS

HM	Antena Tancabesti			Complex Pacea			Santu Floresti		
	C^i_f	E^i_T	E.R.D.*	C^i_f	E^i_T	E.R.D.*	C^i_f	E^i_T	E.R.D.*
Cu	0.23	1.15	LER**	0.287	1.41	LER	0.22	1.08	LER
Zn	0.037	0.037	LER	0.13	0.13	LER	0	0	LER
Cd	0.23	6.96	LER	0.31	9.38	LER	0.18	5.52	LER
V	0.41	0.82	LER	0.38	0.77	LER	0.37	0.74	LER
Cr	0.30	0.60	LER	0.24	0.47	LER	0.18	0.36	LER
Co	0.21	1.1	LER	0.22	1.1	LER	0.18	0.9	LER
Ni	0.372	1.85	LER	0.41	2.05	LER	0.25	1.25	LER
Ri		**12.51**	LER		**15.31**	LER		**9.85**	LER

***E.P.D** - Potential ecological risk, ** *LER* - Low ecological risk

The accumulation coefficient, C^i_f, of the ecological risk potential for each element, E^i_T, and of the ecological risk potential for multi-elements, R_i for the most toxic studied metals are presented for in table 5. Preindustrial background concentration values in sediments [ppm], C^i_n for studied metals has Cu, Zn, Cd, V, Cr, Co and Ni has respectively: 30, 100, 0,5, 2100, 50, 15 and 25 [15 - 18]. T^i_f is the metal toxic response factor, according to Hakanson the values for each element are in the order of Zn=1, V=Cr=2, Co= Cu=Ni=5, Cd=30 [9].

Accumulations coefficient in sediment varied in order V>Ni>Cr>Cu=Cd>Co>Zn. Cd present the highest ecological risk potential around 7 but much less to determine an ecological risk. Ecological risk potential for multi-elements, R_i are values around 12 to input, 15 to middle and 10 to output, that showing a low ecological risk.

The variation of metals concentrations from flora (*Ceratophyllum demersum* and *Phragmites australis)* and fauna (fish species *Scardinius Erytrophtalmus*) is shown in figure 3. Can be observed that metals accumulation in the analyzed species is affected by their total concentration in the Snagov Lake water, the concentrations decreasing from input to output.

Metals accumulation within coontail decreased in the order: Zn > Ti > Cu > V = Ni > Mo = Cr > Co > > Cd . The

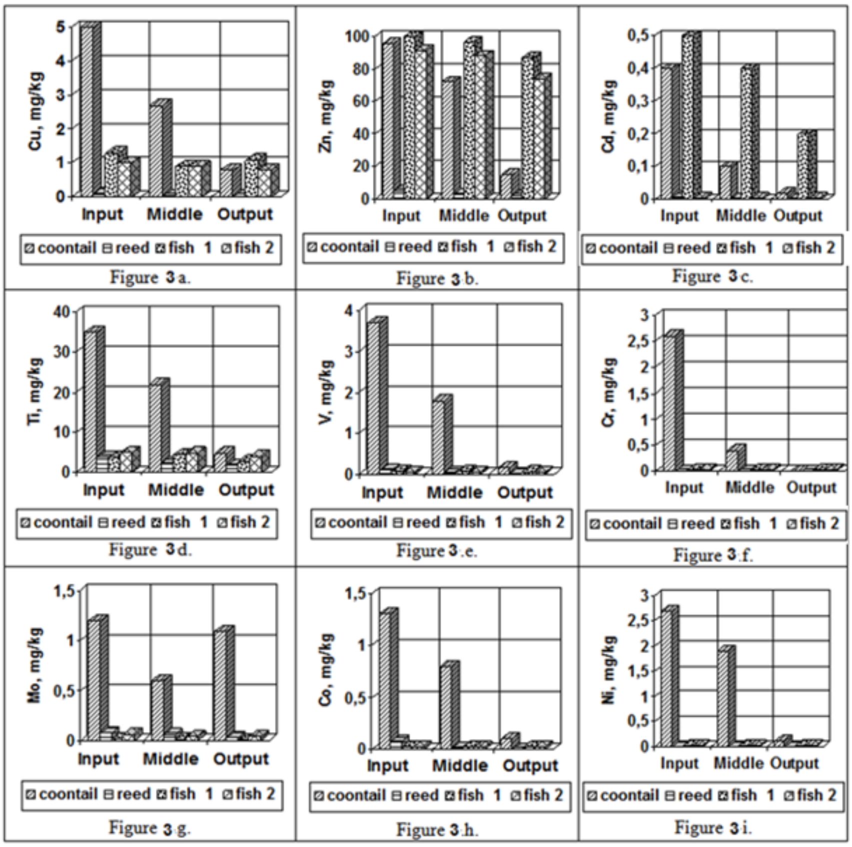

Fig. 3. Metal ion concentrations in aquatic flora and fauna

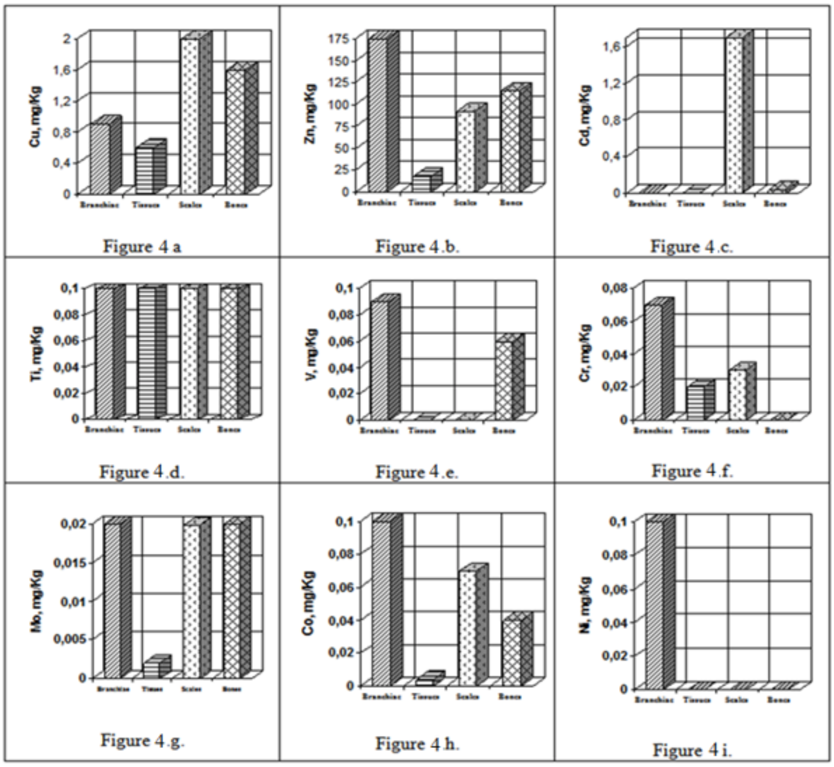

Fig. 4. Metal ions concentrations in different anatomical parts of fish from Snagov Lake

most significant accumulation was found for zinc, whose concentration ranges from 90 mg/kg at input down to about 15 mg/kg at lake's output. The second significant metal accumulated in ccontail is Ti, whose concentration ranges from 35 mg/kg at lake's input down to 7 mg/kg at lake's output.

Into reed, metals accumulation decreased in the following order: Ti > Zn > Mo = Co = V >> Cu = Cd = Cr = Ni. Reed presented highest accumulation values for titanium (~ 4 mg/kg), followed by zinc (~ 2 mg/kg).

The metal concentration in fish decreasing in order: Zn > Ti > V > Cu >> Cr = Co = Ni = Mo. Generally, the highest metals concentration was found in Coontail followed by fish and Reed. Figure 4 gives the metal ions concentrations measured in different anatomical parts of the studied fish (rudd).

Metals accumulate in different concentrations in the anatomical parts of fishes. Thus, the concentration of metals in different anatomical parts of the fish decreased in the following order:

- Branchiae/gills: Zn > Ti > Cu > Ni > Cu = V = Cr > Mo >> Cd
- Muscles: Zn > Cu > Ti >> Cr >> Co > Mo > Cd > Ni = V
- Scales: Zn > Ti > Cu > Cd >> Co > Cr > Mo >> Ti = Ni
- Bones: Zn > Ti > Cu > >> V > Cd = Co > Mo >> Ni = Cr.

Metal / BCF	Branchiae	Tissues	Scales	Bones
Cu	632.1	378.6	1354.1	1059.0
Zn	7403.8	755.8	3954.6	4921.3
Cd	194.0	45.6	55830.0	1379.7
Ti	1959.6	147.0	4203.4	3682.7
V	47.3	-	-	34.0
Cr	228.5	66.0	85.5	-
Mo	6.1	0.6	4.5	4.7
Co	114.8	18.9	331.9	163.2
Ni	98.2	-	-	-

Table 6
BCF VALES FOR FISH ON ITS DIFFERENT ANATOMICAL PARTS

It can be observed that Zn had higher concentration in dissolved form, and it is accumulated more than Ti and other metals into fish's branchiae, muscles and bones. The highest metals accumulation has been found in scales and branchiae, which is mainly due to the large contact surface on these anatomical parts.

Bioconcentration factor BCF values for fish on its different anatomical parts, expressed in liter per kilogram wet tissue are showed in table 6. According United States EPA under the Toxic Substances Control Act (TSCA) a substance is considered to be not bioaccumulative if it has a BCF less than 1000, bioaccumulative if it has a BCF from 1000–5000 and very bioaccumulative if it has a BCF greater than 5000, [19].

It can be observed that the branchiae of *Scardinius Erytrophtalmus* fish are very accumulative for Zn and biaccumulative for Ti and not bioaccumulative for other elements. Tissues are not bioaccumulativ for all elements, scales are very bioaccumulative for Cd and bio-accumulative for Cu, Zn and Ti. Bones are very bioaccumulative for Zn and bioaccumulativ for Ti, Cd and Cu.

Conclusions

Snagov lake fall into the category eutrophic-hypertrophic according CARLSON criteria. The concentrations of metal ions in the water, both total and dissolved form are much lower than the maximum limits set by EPA. This proves that the level of pollution of Lake Snagov with metal ions is reduced. Potential environmental risk for each metal ion and the cumulative effect is less than 40 lake which proves that shows a low ecological risk. Zinc and titanium are accumuleaza best in flora and fauna of the lake and given greater concentration of these ions in water.

The branchiae of *Scardinius Erytrophtalmus* fish are very accumulative for Zn and biaccumulative for Ti and not bioaccumulative for other elements. Tissues are not bioaccumulativ for all elements, scales are very bioaccumulative for Cd and bioaccumulative for Cu, Zn and Ti. Bones are very bioaccumulative for Zn and bioaccumulativ for Ti, Cd and Cu.

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Manuscript received: 18.10. 2016