"Gheorghe Asachi" Technical University of Iasi, Romania

DISTRIBUTION OF METALS IN WATER, SEDIMENTS, AQUATIC PLANTS AND FISH FROM SNAGOV LAKE, ROMANIA

Daniela Simina Ştefan[1,2]*, Nicoleta Neacşu[3], Mircea Ştefan[4], Roxana Sandulovici[4], Cristina Şerbănescu[2]

[1]*University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Street, Sector 1, RO-011061, Bucharest, Romania,*
[2]*IPROCHIM SA, 19-21 Mihai Eminescu Street, Sector 1, RO-010512, Bucharest, Romania.*
[3]*Drnd. of University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Polizu Street, Sector 1, RO-011061, Bucharest, Romania,*
[4]*University Titu Maiorescu, Pharmacy Faculty, 16, Gheorghe Sincai Street, Sector 4, Bucharest, Romania.*

Abstract

This paper discussed the results of studies regarding metal ions distribution in water, sediments, aquatic plants and different tissues of fish from Snagov Lake, Romania, a natural lake situated 25-30 kilometers north from Bucharest, the capital of Romania. The concentration of several metal ions (Li, Ba, Al, Pb, As, Se) was measured in three points of the lake, namely receiving-input, middle and discharging-output ponds. The samples were collected during spring time from water, sediments, *Ceratophyllum demersum, Phragmites australis* reed, and *Scardinius Erytrophtalmus* fish.

The ecological risk, the toxicity class based on the concentration of toxic metals into sediments, according to the Sediments Quality Guidelines (SQGs) and bio-concentration factor, (*BCF*), of metals in anatomical tissues of studied fishes were assessed. Experiments have shown that aluminum and barium 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.

Key words: aquatic plants, fish, metals ions distribution, sediments, Snagov Lake

1. Introduction

The pollution of the aquatic environment with metals is of particular concern due to their persistence, biogeochemical recycling and high ecological risk, since most of them have the potential to be toxic to living organisms (Censi et al., 2006; Parzych and Cymer, 2018; Spataru et al., 2018; Storelli et al., 2005). The primary sources of metals pollution in lake water are the input from rivers, underground water and atmosphere, from both natural and anthropogenic sources. The main pathways of metal pollution are atmospheric depositions, weathering of rocks, erosions, runoff, untreated sewage, agricultures activities, industries and mining (Khan et al., 2013; Nhapi et al., 2012; Serafimovski et al., 2018; Yilmaz and Koç, 2014; Vrhovnik et al., 2013). Heavy metals concentration in aquatic ecosystems is usually monitored by measuring their concentrations in water, sediments and biota (Manu et al., 2018; Oztűrk et al., 2009). In the aquatic environment trace elements are distributed between the dissolved phase, colloids, suspended mater and sedimentary phase. Sediments have a high stored capacity for contaminants. In the hydrological cycle of metals less than 0.1% of the metals are dissolved in water and more than 99.9% are

---

* Author to whom all correspondence should be addressed: e-mail: simina_stefan_ro@yahoo.com; Phone: +40726648848

stored in sediments (Matache et al., 2018; Pradit et al., 2010).

Metals in sediments occur in different forms which have distinct mobility, biological toxicity and chemical behavior. Studies on the speciation or chemical forms of the heavy metals in sediments demonstrated the affinity of metals to make bound with sediments components (organic matter, clay, sand etc.) (Sakan et al., 2007). Biota on the whole and fish especially, can be considered as one of the most significant indicators in freshwater systems for estimation of the metal pollution level (Rashed, 2001).

Some heavy metals are essential for life processes. Metals such as Li, Ba, Al, Pb, As, and Se are important in plants and microorganisms as micronutrients (Kar et al., 2008). Lithium often occurs naturally, in trace amounts, in water supplies, particularly in areas with a high concentration of granite. In medicine, lithium salts are widely used for treatment of bipolar disorders. The amounts range between 0.7 and 59 micrograms per liter. Lithium in prescription doses (600 to 900 milligrams) helps to reduce mood swings in patients with bipolar disorder, but if it is taken even in small amounts over time has a cumulative effect, building up a resistance to the onset of mood swings in the first place (Ohgami et al., 2009).

Barium is found in water mainly in dissolved form. Barium concentrations in water are pH dependent so, the barium compounds solubility increases when the water pH decreases. Acetates, nitrates and halides are soluble in water, but carbonates, chromates, fluorides, oxalates, phosphates and sulfates are quite insoluble. The high levels found in the lake water could be associated with groundwater and solubilization of granite-like igneous rocks, alkaline igneous and volcanic rocks and manganese-rich sedimentary rocks. Concentrations are therefore expected to be relatively stable. Organic barium compounds are of ionic form and consequently they are hydrolyzed in water (Cotton and Wilkinson, 1980). The concentration of Ba ions in natural aquatic systems is limited by the presence of naturally occurring anions, and possibly also by the adsorption of these ions onto metal oxides and hydroxides (Hem, 1970). The possibility of barium poisoning is a reality among people working in and living near heavy industrial sites such as chemical plants, factories that produce rubber products and other such places. When barium accumulates in the body, it usually affects the functions of the nervous system. (Johnson and VanTassell, 1991).

Aluminium is the most abundant metal by weight in the Earth's crust and the third most abundant element after oxygen and silicon. Aluminium combined with other elements is present in environment as silicates, hydroxides and oxides. If combined with organic matter aluminium then it naturally occurs as complexes. The presence of aluminium in environment is caused mainly by natural processes. Hydrological flow paths, soil–water interactions, chemical speciation and the composition of the underlying geological materials influence aluminum mobility in environment (Chunguo and Ziuhui, 1988). A higher concentration of dissolved aluminium in the surrounding waters is determined by acid mine drainage or acid rain (WHO, 2003). It has no known role in human biology, but there is evidence that Al may be linked to acute and chronic diseases in humans (Kumar and Gill, 2014). However, problems seem to arise only in cases of kidney failure or if the kidney is underdeveloped (babies). Then Al absorption into the blood can lead to Al deposition in the brain, to dementia and even death (Wills and Savory, 1983).

Arsenic and lead are recognized as toxic pollutants. Arsenic is probably most widely known for its poisonous effect in humans. Symptoms of acute arsenic poisoning include diarrhoea, vomiting, blood in the urine, cramping muscles and eventually, death. Chronic arsenic exposure is a serious problem in many parts of the world (Naujokas et al., 2013). If inhaled or ingested, lead can affect the nervous system, and long-term exposure can result in a plethora of adverse effects including anaemia, nephropathy, colic-like abdominal pains and brain damage (Tiwari et al., 2013). The presence of arsenic in the environment is caused by industrial activities such mining and coal burning and by agricultural activities (from certain fertilizer and animal feeding). Also arsenic is used in drugs, paints, dyes, metals, soaps, semiconductors etc.

Lead can be found in drinking water, airborne, and paint (Cabral et al., 2015; Pradit et al., 2013). According to the European Union regulations, maximum allowable levels in the fish are 2.5 µg/g dry wt. (EC, 2001). US EPA and FAO established the legal limit for As between 0.5-50 µg/g dry wt. depending on whether the values are expressed as inorganic fraction or total As content (EPA, 1989). The Joint FAO/WHO Expert Committee (1983), sets limit of 0.5 µg/g dry wt. for inorganic As.

Normally, the concentration of selenium in the Earth's crust is 50–90 µg/kg. A higher concentration could be determined by the presence of volcanic, sedimentary and carbonate rocks. Selenites are reduced to selenium in acidic and reducing conditions, whereas in oxidizing condition and a basic pH, selenates are obtained. Selenium and selenides are insoluble in water whereas selenites and selenates are soluble in water, so the selenium is leached from well-aerated alkaline soils (NRC, 1983). The level of selenium in groundwater and surface water varies in the range of 0.02 - 400 µg/L (Nakaguchi et al., 1985; Smith and Westfall, 1937). In natural water there were found selenium species such as selenide (Se^{2-}), elemental selenium (Se^0), selenite (Se^{4+}), selenia (Se^{6+}) and organic selenium, the chemical states of these species may vary with the redox potential of water. As a result of compounds formation with greater solubility in water, concentrations increase at high and low pH (Dulka and Risby, 1976; Larkin, 1973). Selenium is an essential element for human body. The joint World Health Organization (WHO)/Food and Agriculture Organization of the

United Nations (FAO) recommend intakes of 26 and 35 μg of selenium per day for adult females and males, 26 and 30 μg of selenium per day for adolescent females and males and 6–21 μg of selenium per day for infants and children, respectively (FAO/WHO, 1998, 2004).

This paper presents the studies regarding metals ions Li, Ba, Al, Pb, As, Se distribution in water, sediments, aquatic plants and different morpho-anatomical regions of fish sampled from Snagov Lake, Romania.

2. Materials and methods

2.1. Lake location

Snagov Lake has the coordinates 44°43.48′N 26°10.48′E, is 200 m above sea level. It has a surface area of 5.75 square kilometers, and the depth varies between 3 and 13 meters. The total volume is of 17.25 million cubic meters, and retention time is of 27 days, ("Romanian Waters" National Administration, 2016). It is a natural lake located at 25-30 kilometers from Bucharest, the capital of Romania, being a tourist location and an important nautical and agreement base. It is included in national patrimony as natural reservation. The Lake's natural sources are the underground waters and partially the snow and rain waters, therefore the water level is relatively constant through the year. Snagov Lake is exposed to agricultural and industrial effluents, leachate from synthetic and natural fertilizers and septic tanks, domestic waste, irrigations, runoff and infiltration

from animal feedlots etc. On 05/25/2013, the Lake sampling was performed. We have collected samples duplicates from water, sediments, algal, reed, and fish from three sampling sites: Şanţu Floreşti, Antena Tâncăbeşti and Complex Pacea. The details of the sampling sites are presented in Fig. 1 (Wikimapia, 2016).

2.2. Water samples

We have used a Ruttner sampler in order to collect the water samples from the water column in the photic zone. According to SR ISO 5667/2-1998 we have filtered, preserved and packed the water samples.

On site, in the water column, the following additional parameters were determined: temperature, pH, dissolved oxygen (DO) and water temperature, Secchi depth (SD, using a Secchi disk. The following parameters were analyzed in the laboratory: total Kjeldahl Nitrogen (TN), total phosphorus (TP), chlorophyll *a* (CHL), dissolved and total metals (sum of metals concentration from dissolved form and in solid form suspended in water).

The water samples used for determination of total metals concentration were acidulated to pH=2 using HNO_3 and HCl. Afterwards, the samples were preserved and packed in accordance with SR ISO 5667/2-1998. Further, the samples were mineralized by microwave assisted acid digestion, according to US EPA 3015-1994 – "Microwave assisted acid digestion of aqueous samples and extracts". Finally, they were transferred into volumetric flasks of 50 mL and brought to the mark, using bi-distilled water.

Fig. 1. Map showing sampling locations in Snagov Lake (Wikimapia, 2016)

2.3. 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". The instrument used was an Ekman grab. Afterwards, they were preserved into a cooling box and transported to laboratory for being analyzed. There, the samples were firstly weighed at room temperature, milled and sieved by means of the sieving system CISA 08 (model RP 08). From the resulting material, the fraction <0.63 μm was collected. For heavy metal analysis, the samples were then weighed and subjected to aqua-regia digestion in teflon tubes, using an ETHOS D Milestone digester type (UK). Finally, the solutions were analyzed according *Metal analysis* section.

2.4. Plant samples

Two types of plants were sampled: *Ceratophyllum demersum* (*Phylum tracheophyta*, class *Magnoliopsida*, order *Nymphaeales*, family *Ceratophyllaceae*, common name - coontail) and *Phragmites australis* (*Phylum tracheophyta*, class *Liliopsida*, order *Cyperales*, family *Gramineae*, common name - reed). *Ceratophyllum demersum* samples were taken manually from the water column, and the *Phragmites australis* on the shores of the lake, which were then transported in a cooling box to the laboratory. Here they were weighed and mineralized by microwave digestion in Teflon ampoules in the ETHOS D Milestone digester. Before digestion, the samples were washed with distilled water, dried and chopped (Stefan et al., 2017).

After mineralization, the samples were transferred into volumetric flasks of 100 mL and brought to the mark using bi-distilled water. Finally, they were analyzed according *Metal analysis* section.

2.5. Fish samples

In order to analyze the heavy metals from fish tissues, two specimens from each species were collected. Samples were taken from tissue, scales, bones and branchiae. After collection they were transported into cooling boxes to the laboratory laboratory, where their weight, length and sex were determined firstly. Then the samples were washed with deionized water, finely chopped and homogenized in order to obtain a representative sample.

Next, the samples were dried at room temperature, weighed and mineralized by microwave digestion in Teflon vials. After mineralization, the samples were transferred to 100 ml volumetric flasks and pooled using bi-distilled water for metal analysis. Table 1 shows the species of fish analyzed.

2.6. Metal analysis

Finally, the metals were analyzed by ICP-MS according to SR EN ISO 17294/2-2005, by means of an Agilent apparatus, model ICP-MS 7500 cx., the method is usual used for metals determination (Zeng and Huang, 2014). The transparence was determined using Secchi disk, a disc with 20 cm diameter, black and white design (Preisendorfer, 1986; Stefan et al, 2017). The standard methods and apparatus used for analyzing different parameters of all the considered samples are presented in Table 2.

Table 1. Characteristics of analyzed fish species

Sampling point	Sampling period	Species	Medium weight [g]	Length [cm]	Sex
Antena Tancabesti	05.25.2013	Rudd	72	16	M
		(Scardinius Erytrophtalmus)	5.33	8	M

Table 2. Standard methods and apparatuses used for analysis

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

2.7. Ecological risk determination

The ecological risk was determined for sediments from each sampling points using accumulation coefficient by the expression (1):

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

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

The pollution loading of heavy metals in sediments is indicated by the accumulation coefficients E^i_r. Häkanson method was used in order to determine the heavy metals potential ecological risk (Häkanson, 1980; Natkirutimana et al., 2013). 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) (Du et al., 2015; Huang et al., 2009; Stefan et al., 2017).

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

$$R_i = \sum E^i_r \qquad (3)$$

where: C^i_f is the accumulation coefficient of element i and T^i_f is the toxic response factor of element i, T^i_f express the toxicity level for that the organisms were sensitively.

The toxic metals Pb and As have the toxic response factors 5 and 10, respectively. The criteria for establishing the ecological risk for sediment was presented in Table 3 (Du et al., 2015; Huang et al., 2009, Stefan et al., 2017)

Table 3. Criteria for determined the ecological risk level

R_i or E^i_r values	Ecological risk level
$R_i < 150$ or $E^i_r < 40$	Low
$150 \le R_i < 300$ or $40 \le E^i_r < 80$	Moderate
$300 \le R_i < 600$ or $80 \le E^i_r < 160$	Considerable
$600 \le R_i$ or $160 \le E^i_r < 320$	Very high

US EPA uses the toxicity classifications of lake water based on the concentration of toxic metals into sediments, according to the Sediments Quality Guidelines (SQGs). These criteria of US EPA toxicity classifications for Pb and As are presented in Table 4

(Baudo et al., 1990; Filgueiras et al., 2004; Pradit et al., 2013). We have used the bio-concentration factor (*BCF*) in order to characterize bioaccumulation of metals in flora and fauna. BCF can be calculated as a ratio between the concentration of a chemical substance in an organism and the concentration of the chemical substance in the surrounding environment (MacDonald and Ingersoll, 2002). The *BCF* values in different anatomical tissues of fishes are presented in Table 7.

Table 4. Criteria of US EPA toxicity classifications (concentration of metals in sediments, [mg/kg] dry wt)

Metal ⟋ Toxicity	Non Polluted	Low Polluted	Heavily Polluted
As	< 3	3 - 8	8
Pb	< 40	40 - 60	> 60

3. Results and discussions

Table 5 shows the determined values of parameters characterizing the water from Snagov Lake in the photic zone. The temperature and pH in Snagov Lake correspond to the optimal growth rate of aquatic plants, demonstrated by the high concentration of chlorophyll-*a*. The pH value is situated in the range of neutral to slow alkaline media, similar values was found in Tansa Lake from Jijia (Dughila et al., 2012). The transperence values show the existence of eutrophic conditions. The transparency increases from the input to the output of the lake.

The sediments mainly contain Al of various concentrations in the form of clay. The turbidity is higher and can be due to particles of inorganic (clay, sand, dust etc.) or organic (aquatic plants, organic matter) nature. The dissolved oxygen concentration proves that oxygen-consumption processes and oxygen production are intensive in this lake. The input N/P (ratio between concentrations, in mg/L, of the Total Nitrogen and Total Phosphorus) ratio is around 8, below 10, which shows that nitrogen limits the growth of biomass, and the nitrogen necessary for biochemical processes is provided from atmosphere. In the middle of the lake, the ratio is 17, with a higher Coontail growth, while at its output, the ratio is around 41, showing that phosphorus limits here the Coontail growth of biomass.

Table 5. Parameters characterizing the Snagov Lake water from photic zone

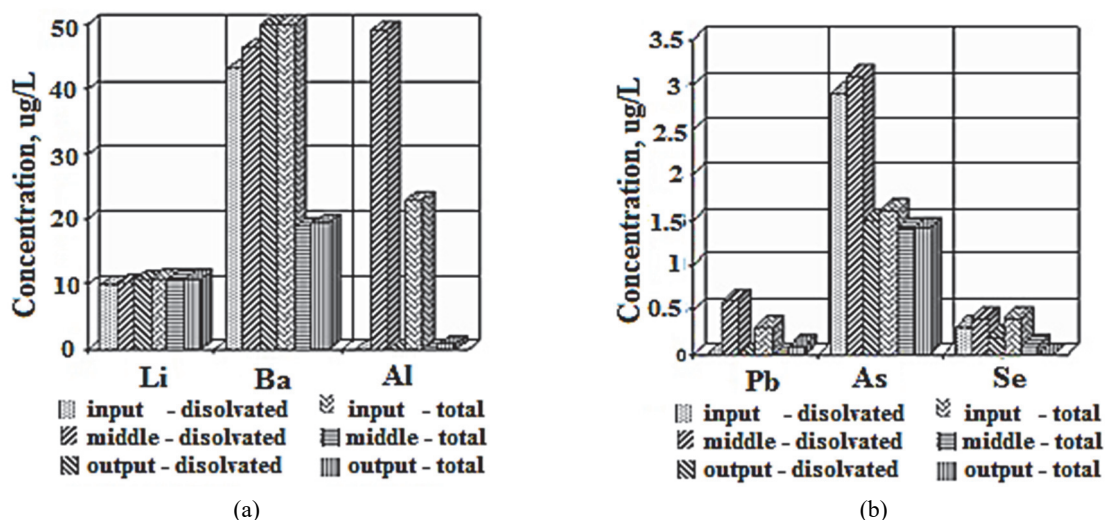| Parameter	Unit	Sampling points		
		Antena Tancabesti input	Complex Pacea middle	Santu Floresti output
Temperature	ºC	26	25	26
pH		8.43	8.28	8.9
Suspended solids matter	mg/L	18.4	18	23.20
Secchi Transperance	m	0.5	0.8	1.3
Turbidity		20	14	4.0
Dissolved oxygen	mg/L	6.5	6.4	8
Total Nitrogen	mg/L	1.32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

Fig. 2. Metal ions concentrations (a) dissolved and (b) total in Snagov Lake water

The dissolved and total average concentration of all studied metals (Li, Ba, Al, Pb, As. Se) in all the sampling points are shown in Figs. 2 (a-b).

Lithium is found in water into dissolved form and its concentrations vary around an average value of 10 µg/L, in all sampling points, being within the range of normal concentrations for lakes.

Barium concentrations varied between the input and the output of the lake. It is found in water mainly into dissolved form. The values varied as following: 4 3 µg/L (input), 55 µg/L (middle) and 19 µg/L (output). Similar values were found in Canada, Netherlands and other countries, (Subramanian and Meranger, 1984). The input water pH is around 8.5 and can precipitate barium as carbonate and sulphate. Moreover, the values of Ba concentration are slightly lower in dissolved form than in the total form. At the middle sampling point, the pH decreases at 8.3 and a part of barium solubilizes, with a concentration increased up to 55 µg/L. Finally, at the output of the lake, the pH increases at 8.9 and Ba concentration decreases at 19 µg/L, due probably to its removal by adsorption on particles (clay and/or organic matter), (Mikkelsen et al., 1989)

Aluminum is present in water only in solid phase, in particulate form (clay and sand). The Al concentration in soluble form is zero, because the value of water pH is superior to 8. This is a value higher than the precipitation pH for Al, which is 4.3 (Stefan and Meghea, 2014).

The concentrations of soluble lead in water are zero, because the pH of water is higher than the pH of Pb precipitation. The concentrations of insoluble Pb in water are of 0.6, 0.3 and 0.1 µg/L, respectively. In all the sampling points, the concentration decreases from input to output due to sedimentation.

Arsenic is present in water only in soluble form, its concentration being variable: 2.9, 1.5 and 1.4 from input to output, respectively. The inorganic soluble forms are arsenic and arsenious acids. Under oxidizing conditions most of the arsenic is found in As(V) form, arsenic acid (H_3AsO_4), while in reducing conditions the most stable form is arsenious acid As(III; H_3AsO_3). At neutral pH, arsenious acid is more mobile than the dissociated form of the arsenic acid ($H_2AsO_4^-$ or $HAsO_4^{2-}$). In the presence of sulfide, As may precipitate and pass into insoluble form. In the presence of oxygen, bacteria can oxidize sulfides into sulphates, soluble in water. At high pH, As may be adsorbed on the surface of particles clay (NSC, 2014).

Selenium in soluble form is represented by selenite, biselenite and selenate, being normally stable in natural water (Sandy and Di Sante, 2010). Its measured concentrations varied as following: 0.3, 0.2 and 0.1 µg/L, respectively. The suspended particles contained Se(0) and selenium bonded on organic matter (Sandy and Di Sante, 2010). The concentration of this solid particle in all sampling points is of approximately 0.1 µg/L. The concentrations of variations studied metals (Li, Ba, Al, Pb, As, and Se) in sediments are presented in Fig. 3a-f. Sediment contains mainly two elements: Al, about 8000 mg/kg, and Ba, about 210 mg/kg. Other elements contained in sediment are Li, Pb, As and Se in concentrations of: 9, 7, 3.5, and 1.2 mg/kg, respectively.

The values of the accumulation coefficient, C^f_i 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. from all the sampling points are presented in Table 6. The values of the ecological risk for all sampling points and for the most toxic elements analyzed in Snagov Lake are included in the low ecological risk pollution degree.

According to the US EPA toxicity classifications criteria, Snagov Lake is framed as non-polluted due to the concentration of Pb in sediments (6.4-10.5 mg/kg), which is less than 40 mg/kg (Table 4). Moreover, the Lake is framed as moderately polluted, when considering As concentration (2.7-3.8 mg/kg), which is situated between 3 and 8 (Table 4).

Figs. 4, a-f show the variation of metals concentration of (Li, Ba, Al, Pb, As, Se) in flora

(*Ceratophyllum demersum* and *Phragmites australis*) and fauna (*Scardinius erytrophtalmus*) in Snagov Lake. The accumulation of metals in the analyzed species is affected by their total concentration in Snagov Lake water, which decreases from the entry to the exit points (Figs. 2 and 4).

The accumulation of metals decreased in the

order: Al > Ba > As > Pb > Li > Se. The most significant accumulation was found for aluminum, whose concentration ranges from 680 mg/kg at input down to about 50 mg/kg at lake's output. Barium, the second significant metal according to the measured concentrations, presents the highest accumulation in Coontail (179 -77 mg/kg).
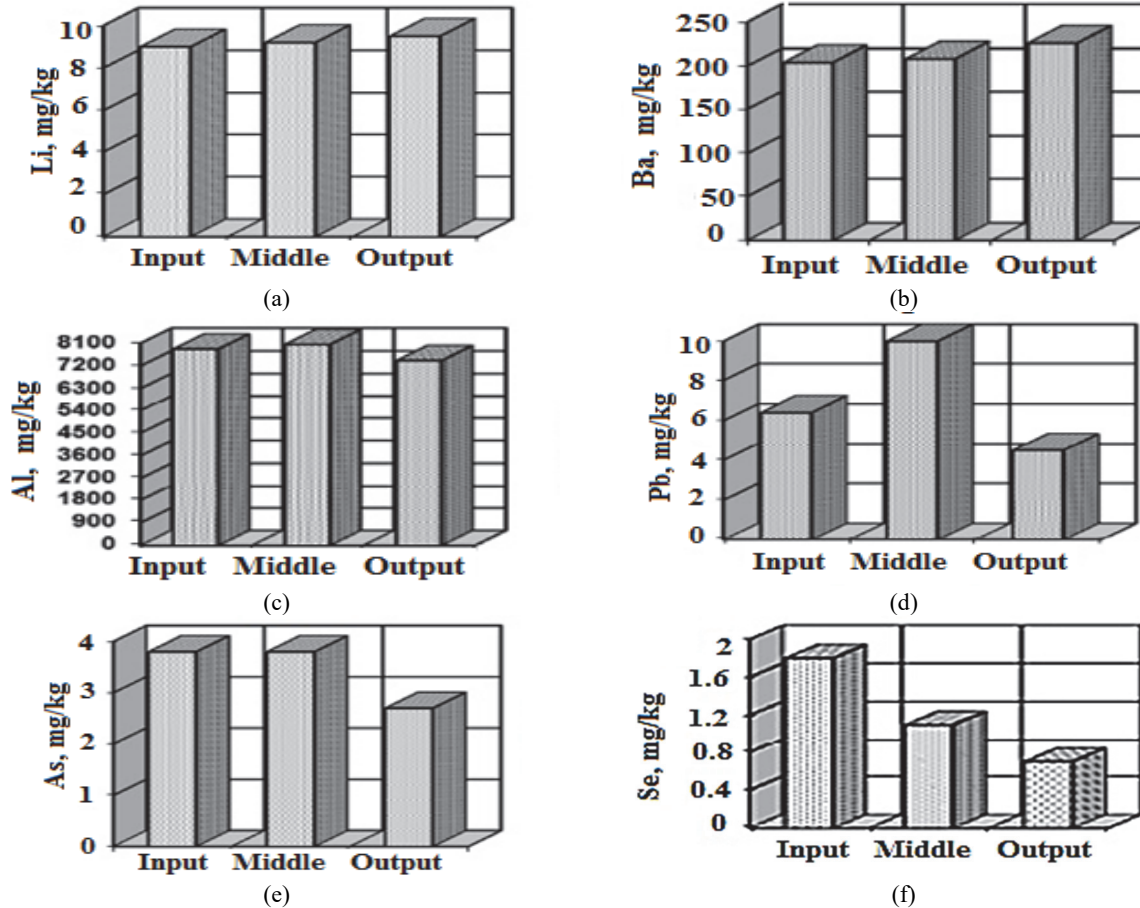

Fig. 3. Metal ion concentration in sediments for: (a) Li ; (b) Ba; (c)Al, (d) Pb, (e) As and (f) Se

Table 6. Ecological risk degree assessment

| Sampling points	Pb			As			R_i	Ecological pollution degree
	C^i_f	E^i_T	Ecological pollution degree	C^i_f	E^i_T	Ecological pollution degree		
Antena Tancabesti	0.1	0.45	Low ecological risk	0.25	2.5	Low ecological risk	≈ 3	Low ecological risk
Complex Pacea	0.15	0.75	Low ecological risk	0.25	2.5	Low ecological risk	3.25	Low ecological risk
Santu Floresti	0.06	0.3	Low ecological risk	0.2	2	Low ecological risk	≈2.5	Low ecological risk
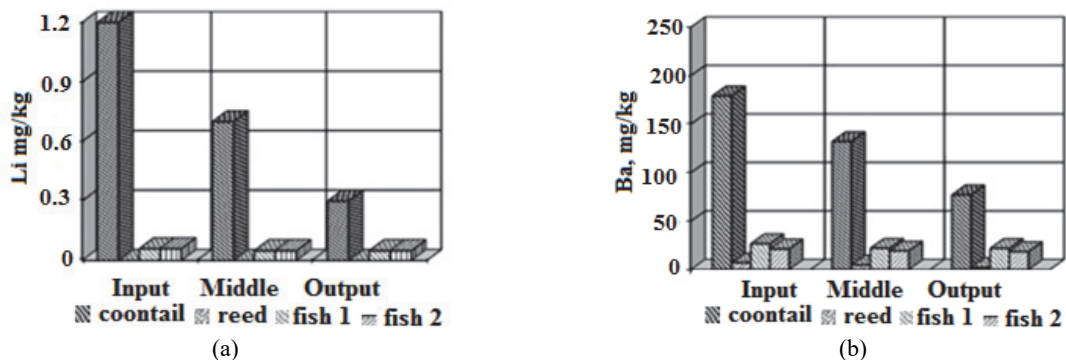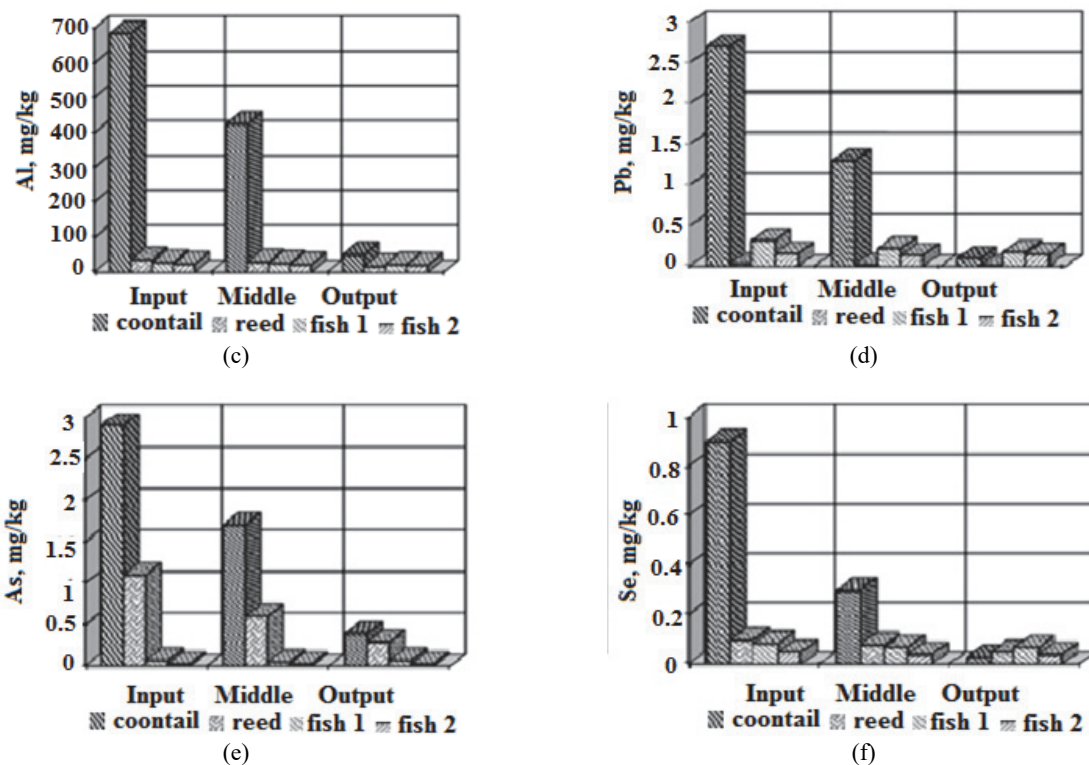
Fig. 4. Metal ion concentrations in aquatic flora and fauna: to input, middle and output
for coonail, reed, fish 1 and fish 2 for: (a) Li; (b) Ba; (c)Al, (d) Pb, (e) As and (f) Se

In Reed, the metals accumulation decreased in the following order: Al > Ba > As > Se > Pb > Li. Reed presented an important accumulation of aluminum (36.5-17.4 mg/kg), followed by barium (6.8-2.1 mg/kg) and arsenic (1.1-0.3 mg/kg). The decreasing accumulation order in fish 1 was found to be: Al > Ba > Pb > Se > As > Li, while in fish 2: Al > Ba > Pb > Li=Se >As. Consequently, no significant difference was observed in trace element concentration between the two fish types. The average concentration of lead in fish taken from the input of water in the lake, 2.7 μg/g dry wt is higher than the limit imposed by EU regulation, 2.5 μg/g dry wt, while in the other points, the concentration is below the imposed limits. The highest concentrations of aluminum, found in particle form in the water, involved a significant accumulation of this element in aquatic flora and fauna. Generally, the highest degree of metals accumulation was found

in Coontail, followed by fish and Reed. The average concentration of arsenic in fish in all sampling points is 0.07 μg/g dry wt, far less than the limit imposed by US EPA regulation, between 0.5-50 μg/g dry wt. The metal cations concentrations in anatomical parts of the fish (rudd) are presented in Fig. 5.

The metals Li, Ba, Al, Pb, As, Se accumulate in fish in different concentrations in the anatomical parts. The concentration decreased in order:
- Branchiae: Ba > Al > Pb=Li > Se > As
- Muscles: Ba > Al > Se > As > Pb > Li
- Scales: Al > Ba > Pb > Li > Se=As
- Bones: Ba=Al=Pb > As > Li=Se

Barium is found in higher concentration in water dissolved form, and also bio accumulated into fish's branchiae, muscles and bones. Due to the large contact surface, the highest metals accumulation has been found in scales and branchiae.
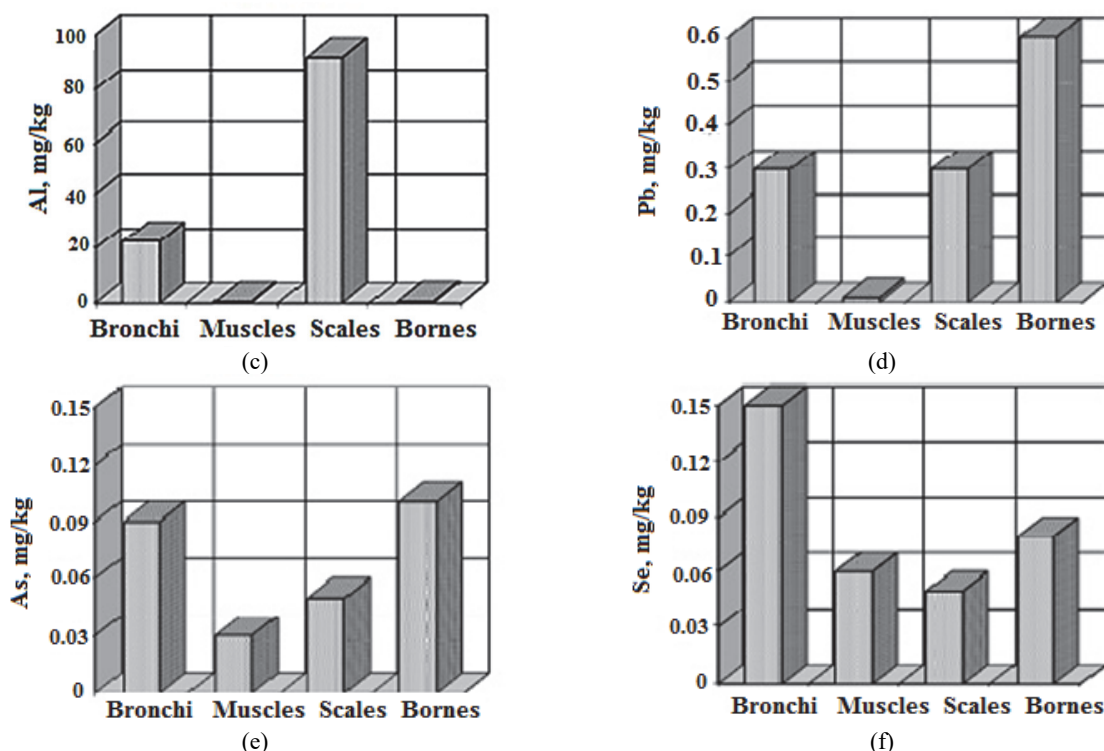
(c)

(d)

(e)

(f)
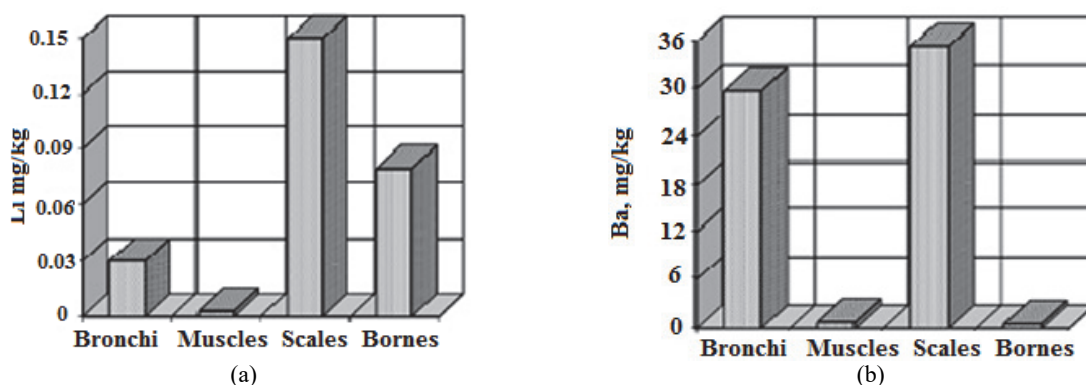
Fig. 5. Metal ions concentrations in different anatomical parts bronchi, muscles, scales, and borne of fish from Snagov Lake for: (a) Li ; (b) Ba; (c)Al, (d) Pb, (e) As and f) Se

The accumulative processes observed can be due to bio-concentration, bioaccumulation and biosorption of metals in the different anatomical parts (EPA, 2003; Mohammed et al., 2014). The BCF values (expressed in liter per kilogram wet tissue) for anatomical parts of the fish are presented in Table 7.

Table 7. BCF values for fish in its different anatomical parts

Metal \ BCF	Branchiae	Tissues	Scales	Bones
Al	785.9	17.3	3168	20.7
As	49.3	16.5	27.37	54.9
Ba	1085.8	29.2	1297.8	21.93
Li	5.0	0.5	25	13.2
Pb	850	28.4	850	1700
Se	127.5	12.75	637.5	340

The growth order of metals bio-concentration factor into different anatomical parts of fish is:

- for Branchiae: $BCF_{Li} < BCF_{As} < BCF_{Se} < BCF_{Al} < BCF_{Pb} < BCF_{Ba}$
- for Muscles: $BCF_{Li} < BCF_{Se} < BCF_{As} < BCF_{Al} < BCF_{Pb} < BCF_{Ba}$
- for Scales: $BCF_{Li} < BCF_{As} < BCF_{Se} < BCF_{Pb} < BCF_{Ba} < BCF_{Al}$
- for Bones: $BCF_{Li} < BCF_{Al} < BCF_{Ba} < BCF_{As} < BCF_{Se} < BCF_{Pb}$

It can be observed that barium presents a greater tendency of bio-concentration in branchiae and muscles, aluminum in scales, and lead in bones.

4. Conclusions

The temperature and pH of Snagov Lake corresponds to the optimal growth rate of Coontail, demonstrated by the high concentration of chlorophyll-*a*. The value of its pH ranges from neutral to slow alkaline media. The transparency values indicate the existence of eutrophic conditions. The turbidity is higher and can be due to inorganic (clay, sand, dust etc.) or organic (Coontail or organic matter) particles.

The N/P ratio indicates that, at the Snagov Lake input, nitrogen limits the growth of biomass, at its middle, the Coontail growth is higher, and at its output, phosphorus limiting the growth of biomass.

The metals in water were found in dissolved form (lithium), dissolved and particulate form in low amount (barium, arsenic and selenium), and in solid form (aluminum and lead).

Aluminum was found in water in concentration of the order of milligrams per liter, barium in concentrations of the order of hundreds of micrograms per liter and lithium, lead, arsenic and selenium in concentrations of the order of micrograms per liter.

The sediments present a major mineral component in the form of clay, due to the presence of aluminum ions in high concentrations (~ 8000 mg/kg). Barium is found in sediments at elevated concentrations (~ 210 mg/kg), in the form of carbonates and sulphates, but also absorbed on different types of particles. The average concentrations of Li, Pb, As and Se in sediments vary around 9, 7, 3.5, and 1.2 mg/kg, respectively. Arsenic is found in sediments in the form of sulphates or

absorbed on clay particles and organic matter. After the assessment of the ecological risk pollution degree based on the toxic metals concentrations (As, Pb) in the sediments, Snagov Lake can be included in the low ecological risk pollution class.

According to the US EPA toxicity classifications criteria, the Snagov Lake is framed as non-polluted due to the concentration of Pb in sediments (6.4-10.5 mg/kg), which is less than 40 mg/kg. Moreover, it is framed as moderately polluted when considering As concentration (2.7-3.8 mg/kg), which is situated between 3 and 8 mg/kg.

The most significant accumulation in Coontail was found for aluminum, whose concentration ranges from 680 mg/kg at input down to about 50 mg/kg at lake's output. Barium, the second significant metal according to the measured concentrations, presents the highest accumulation in Coontail (179 -77 mg/kg). Lead, lithium and selenium were found in small quantities in this lake.

In Reed, the accumulation of metals decreased in the following order: Al > Ba > As > Se > Pb > Li. Reed presented an important accumulation of aluminum (36.5 - 17.4 mg/kg), followed by barium (6.8-2.1) and arsenic (1.1 -0.3 mg/kg). No significant difference in trace element concentrations was found between the two types of fish studied.

The highest concentrations of aluminum, found in particle form into the water, involved a significant accumulation of this element in the aquatic flora and fauna. The highest degree of metals accumulation was found in Coontail, followed by fish and Reed.

It is noted that barium, which has a higher concentration in its dissolved form, accumulates more than aluminum and other metals in branchiae, muscles and bones of fish. The greatest accumulation of metals was found in scales and branchiae, as a consequence of the large contact surface on these anatomical parts. Barium showed a greater tendency of bio-concentration in branchiae and tissues, aluminum in scales and lead in bones.

Therefore, the lower content of heavy metals is found in muscle, which proves that it presents no risk for human health.

References

Baudo R., Griesy J.P., Muntau H. (Eds.), (1990), *Sediments: Chemistry and Toxicity of In-Place Pollutants*, Lewis Publishers, USA.

Cabral M., Toure A., Garçon G., Diop C., Bouhsina S., Dewaele D., Cazier F., Courcot D., Tall-Dia A., Shirali P., Diouf A., Fall M., Verdin A., (2015), Effects of environmental cadmium and lead exposure on adults neighboring a discharge: Evidences of adverse health effects, *Environmental Pollution*, **206**, 247-255.

Censi P., Spoto S.E., Saiano F., Sprovieri M., Mazzola S., Nardone G., Di Geronimo S.I., Punturo R., Ottonello D., (2006), Heavy metals in costal water system. A case study from the northwestern Gulf of Thailand, *Chemosphere*, **64**, 1167-1176.

Chunguo C., Ziuhui L., (1988), Chemical speciation and distribution of arsenic in water, suspended solids and sediment of Xiangjiang River, China, *Science of the Total Environment*, **77**, 69-82.

Cotton F.A., Wilkinson G. (Eds.), (1980), *Advanced Inorganic Chemistry: Comprehensive Text*, 4th Edition, John Wiley, New York.

Du M., Wei D., Tan Z., Lin A, Du Y., (2015), The potential risk assessment for different arsenic species in the aquatic environment, *Journal Environmental Science,* **27**, 1-8.

Dughila A., Iancu O.G., Rascanu I.D., (2012), Geochemical Evaluation of Quality indicators for the water of the Tansa Lake from the Jijia Catchment, Romania, *Carpathian Journal of Earth and Environmental Science*, **7**, 79-88.

Dulka J.J., Risby T.H., (1976), Ultratrace metals in some environmental and biological systems, *Analytical Chemistry*, **48**, 640A-653A.

EC, (2001), Commission Regulation 466/2001, of 8 March 2001 setting maximum levels for certain contaminants in foodstuffs, *Official Journal of European Communities*, 1.77/1.2001, 16.03.2001, Brussels, On line at: http://ec.europa.eu/food/fs/sfp/fcr/fcr02_en.pdf.

EPA, (1989), Assessing Human Health Risks From Chemically Contaminated Fish and Shellfish, A Guidance Manual. EPA/503/8-89-002 US, Environmental Protection Agency, Washington, D.C., On line at: https://www.google.ro/search?q=EPA,+(1989),+Assessing+Human+Health+Risks+From+Chemically+Contaminated+Fish+and+Shellfish,+A+Guidance+Manual.+EPA/503/8-89-002.

EPA, (2003), Methodology for Deriving Ambient Water Quality Criteria for Protection of Human Health, "2000 Methodology", Technical support Document, Volume 2: Development of National Bioaccumulation Factors, Office of Research and Development, EPA/822/R-03/030, U.S., Washington, Environmental Protection Agency, Washington, D.C., On line at: https://archive.epa.gov/scipoly/sap/meetings/web/pdf/methodology.pdf.

FAO/WHO Expert Committee, (1983), Expert Committee on Food Additives Evaluation of certain food additives and contaminants (Twenty-seventh report of the Joint). WHO Technical Report Series, No. 696, On line at: http://apps.who.int/iris/bitstream/10665/39165/1/WHO_TRS_696.pdf.

FAO/WHO, (1998), Preparation and use of food-based dietary guidelines. Report of a joint FAO/WHO consultation. Geneva, World Health Organization (WHO), Technical Report Series, No. 880, On line at http://apps.who.int/iris/bitstream/10665/42051/1/WHO_TRS_880.pdf.

FAO/WHO, (2004), Vitamin and mineral requirements in human nutrition, 2nd ed. Report of a Joint FAO/WHO Expert Consultation, Bangkok, Thailand, 21–30 September 1998, Geneva, World Health Organization, On line at: http://whqlibdoc.who.int/publications/2004/9241546123.pdf.

Filgueiras A.V., Lavilla I., Bendicho C., (2004), Evaluation of distribution, mobility and binding behavior of heavy metals in superficial sediments of Louro River (Galicia, Spain) using chemometric analysis: A case study, *Science of Total Environment*, **330**, 115-129.

Häkanson L., (1980), An ecological risk index for aquatic pollution control. A sedimentological approach, *Water Resources*, **14**, 975-1001.

Hem (Eds), (1970), *Study and Interpretation of the Chemical Characteristics of Natural Water,* 2nd Edition*,* Geological survey water supply paper 1473*,* U.S. Geological Survey, U.S. Government Printing Office*,* Washington*.*

Huang X., Hu J., Li C., Deng J., Long J., Qin F., (2009), Heavy metals pollution and potential ecological risk assessment of sediments from Baihua Lake, Guidhou, P.R. China, *International Journal of Environmental Health Resources*, **19**, 405-419.

Johnson C., Van Tassell V., (1991), Acute barium poisoning with respiratory failure and rhabdomyolysis, *Annals of Emergency Medicine*, **20,** 1138-1142.

Kar D., Sur P., Mandal S.K., Saha T, Kole R.K., (2008), Assessment of heavy metals pollution in surface water, *International Journal of Environmental Science and Technology*, **5**, 119-124.

Khan K., Lu Y., Khan H., Zakir S.I., Khan S., Khan A.A., Wei L., Wang T., (2013), Health risks associated with heavy metals in the drinking water of Swat, northern Pakistan, *Journal of Environmental Science,* **25**, 2003-2013.

Kumar V., Gill K., (2014), Oxidative stress and mitochondrial dysfunction in aluminium neurotoxicity and its amelioration: a review, *NeuroToxicology*, **41**, 154-166.

Larkin H.W., (1973), Trace elements in the environmental, American Chemical Society, *Advances in Chemistry Series*, **123**, 96-102.

MacDonald D.D., Ingersoll C.G., (2002), A Guidance Manual to Support the Assessment of Contaminated Sediments in Freshwater Ecosystems Volume I – An Ecosystem-Based Framework for Assessing and Managing Contaminated Sediments, United States Environmental Protection Agency, Great Lakes National Program Office 77 West Jackson Boulevard (G-17J), Chicago, Illinois 60604, On line at: http://www.cerc.usgs.gov/pubs/sedtox/VolumeI.pdf.

Manu M., Onete M., Băncilă R.I., (2018), The effect of heavy metals on mite communities (Acari-Gamasina) from urban parks - Bucharest, Romania, *Environmental Engineering and Management Journal*, **17**, 2023-2284.

Mikkelsen R.L., Page A.L., Bingham F.T., (1989), *Factors Affecting Selenium Accumulation by Agricultural Crops*, In: *Selenium in Agriculture and the Environment*, Jacobs L.W. (Ed.), Soil Science Society of America Special Publication, 23, Madison, Wisconsin, 65-94.

Mohammed M.A., Shitu A., Tadda M.A., Ngabura M., (2014), Utilization of various agricultural waste materials in the treatment of industrial wastewater containing heavy metals: a review, *International Research Journal of Environment Sciences*, **3**, 62-71.

Nakaguchi Y., Hiraki K., Tamari Y., Fukunaga Y., Nishikava Y., Shigematsu T., (1985), Fluorimetric determination of inorganic Selenium (IV), Selenium(VI) and organi selenium in natural waters, *Analytical Sciences*, **1**, 247-252.

Natkirutimana T., Du G., Guo J., Gao X., Huang L., (2013), Pollution and potential ecological risk assessment of heavy metals in a lake, *Polish Journal of Environmental Studies*, **22**, 1129-1134.

Naujokas M., Anderson B., Ahsan H., Aposhian H., Graziano J., Thompson C., Suk W., (2013), The broad scope of health effects from chronic arsenic exposure: update on a worldwide public health problem, *Environmental Health Perspectives*, **121**, 295-302.

Nhapi I., Wali UG., Usanzineza D., Kashaigli J.J., Banadda N., Kimwaga R., (2012), Distribution of Heavy metals in Lake Muhazi, Rwanda, *Open Environmental Engineering Journal*, **5**, 96-102.

NRC, (1983), *Selenium in Nutrition, Chapter: 8 Selenium and Human Health*, Revised Edition, Washington, DC, National Research Council, National Academy Press, 17, doi:10.17226/40.

Ohgami H., Takeshi T., Shiotsuki I., Ishii N., Iwata N., (2009), Lithium levels in drinking water and risk of suicide, *Brithish Journal of Psychology*, **194**, 464-465.

Oztűrk M., Ozőzen G., Minareci O., Minareci E., (2009), Determination of heavy metals in fish, water and sediments of Avsar Dam Lake in Turkey, *Iran Journal of Environmental Health Science and Engineering*, **6**, 73-80.

Parzych A., Cymer M., (2018), heavy metals content in the sprouts of *Glyceria maxima* (Hartm.) Holmb and in river sediments (Northern Poland), *Environmental Engineering and Management Journal*, **17**, 1743-1752.

Pradit S., Wattayakorn G., Angsupanich S., Leemaker M., Baeyens W., (2010), Distribution of trace elements in sediments and biota of Songkhla Lake, southern Thailand, *Water, Air and Soil Pollution*, **206**, 155-174.

Pradit S., Pattarathomrong M.S., Panutrakul S., (2013), Arsenic, cadmium and lead concentrations in sediment and biota from Songkhla Lake: A Review, PSU-USM International Conference on Humanities and Social Sciences, *Procedia-Social Behavioral Science,* **9**, 573-580.

Preisendorfer R.W., (1986), Secchi disk science: Visual optics of natural waters, *Limnology and Oceanography*, **31**, 909-926

Rashed M.N., (2001), Monitoring of environmental heavy metals in fish from Nasser Lake, *Environmental International*, **27**, 27-33.

Sakan S., Gržetic I., Dordevic D., (2007), Distribution and fractionation of heavy metals in the Tisa (Tisza) river sediments, *Environmental Science Pollution Resources*, **14**, 229-236.

Sandy T., Di Sante C., (2010), Review of available technologies for the removal of Selenium from water, Prepared for North American Metals Council, 2-3, On line at: www.mamc.org/docs/00062756.PDF.

Serafimovski T., Stafilov T., Tasev G., (2018), Soil metal pollution related to active Buchim copper mine, Republic of Macedonia, *Environmental Engineering and Management Journal*, **17**, 2597-2608.

Smith M.I., Westfall B.B., (1937), Further field studies on the selenium problem in relation to public health, *United States Public Health Report*, **52**, 1375-1384.

Spataru P., Povar I., Lupascu T., Alder A. C., Mosanu E., (2018), Study of nitrogen forms in the seasonal dynamics and kinetics of nitrification and de-nitrification in Prut and Nistru river waters, *Environmental Engineering and Management Journal*, **17**, 1521-1772.

Stefan D.S., Meghea I., (2014), Mechanism of simultaneous removal of Ca^{2+}, Ni^{2+}, Pb^{2+} and Al^{3+} ion from aqueous solutions using Purolite S930 ion exchange resin, *Comptes Rendus de Chimie*, **17**, 403-502.

Stefan D. S., Neacsu N., Serbanescu C., Pascu L.F., Stefan M., (2017), Assessment of heavy metals pollution of Snagov Lake, *Revista de Chimie*, **68**, 215-220.

Storelli M.M., Storelli A., D'ddabbo R., Marano C., Bruno R., Marcotrigiano G.O., (2005), Trace elements in loggerhead turtles (*caretta caretta*) from the eastern

Mediterranean Sea: Overview and evaluation, *Environmental Pollution*, **135**, 163-170.

Subramanian K.S., Meranger J.C., (1984), A survey for sodium, potassium, barium, arsenic, and selenium in Canadian drinking water supplies, *Atomic Spectroscopy,* **5**, 34-37.

Tiwari S., Tripathi I.P., Tiwari H.L., (2013), Lead poisoning: a review, *Research Journal of Chemical Science*, **3**, 86-88.

Wikimapia, (2016), Snagov, Lake Map, On line at: http://wikimapia.org/417011/Snagov-Lake.

Wills M., Savory J., (1983), Aluminium poisoning: dialysis encephalopathy, osteomalacia, and anaemia, *Lancet*, **322**, 29-34.

WHO, (2003), Aluminium in Drinking Water, Guidelines for Drinking –water Quality 2003, On line at: http://www.who.int/water_sanitation_health/dwq/chemicals/en/aluminium.pdf.

Vrhovnik P., Arrebola J.P., Serafimovski T., Dolenec T., Rogan Šmuc N., Dolenec M., Mutch E., (2013), Potentially toxic contamination of sediments, water and two animal species in Lake Kalimanci, FYR Macedonia, *Relevance to Human Health*, **180**, 92-100.

Yilmaz E., Koç C., (2014), Research on Water Quality of Lake Bafa in Turey, *Environmental Engineering and Management Journal*, **13**, 153-162.

Zeng Z., Huang W., (2014), Cloud points extraction procedure for flame atomic absorption spectrometric determination of heavy metals in surface sediments of Chaohu Lake, China, *Environmental Engineering and Management Journal*, **13**, 1041-1046.