Heavy Metals in Water, Sediments and Macrophytes in the Shkodra Lake

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Abstract – Concentrations of some heavy metals in water, sediment and macrophytes of the Shkodra Lake were investigated in two periods (July – September) of 2012 in seven different sampling sites. The concentrations of the metals were determined using ICP. Cu, Fe, Ni, Mn, Pb and Zn were detected in all the sampling stations in water, sediments, and macrophytes. Average data indicated the Cu concentration was under 0.4 µg L-1 in water, 33mg kg-1 on sediments, and 14.9 mg kg-1 in macrophytes. The Fe values in water were low in September and very high in July. The highest values were observed in sediments (up to 15g kg-1), which were consistent with values found in water macrophytes. The water values for Mn were up to 0,058 mg L-1, in sediments up to 729 mg kg-1, while the average concentration in macrophytes was 436 mg kg-1. The highest values of Ni in water were observed in July (0.262 mg L-1), in sediments was 216 mg kg-1and the highest values of the three (Cu, Ni, Zn) elements observed in water macrophytes. The data obtained for Pb were mainly in sediments, with the average value at 23.5 mg kg-1. For all sampling stations the content of Zn in water were lower than 0.2 µg L-1. Its average value in sediment was 35.4 ± 23.35 mg kg-1. The average macrophyte values of Cu (14.9 ± 13.4 mg kg-1), Ni (68 ± 68 mg kg-1) and Zn (30 ± 14.3 mg kg-1) were comparable to the corresponding values found in sediments for all stations and periods.

Keywords—Shkodra Lake, water, sediments, macrophyte, heavy metals.

I. Introduction

The problems of metal pollution is currently increasing in Shkodra Lake. It is mainly associated with intensification of agricultural activities and the lack of urban and industrial water discharge infrastructure. Under some environmental conditions, those pollutants including metals could accumulate and get biomagnified through food chain to toxic levels [1]. When heavy metals enter in water bodies, they change water quality, bind to sediments and accumulate in aquatic biota causing anemia, disturbance of physiological functions and mortalities of fish [2].

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Heavy metals also pose a serious threat to humans through ingestion of metal enriched aquatic organisms. Main anthropogenic sources of heavy metal contamination are mining, disposal of untreated and partially treated effluents contain toxic metals, as well as metal chelates from different industries and indiscriminate use of heavy metal-containing fertilizer and pesticides in agricultural fields [3], [4], [5]. At low levels in water, some elements like, Pb ($0.10 mgL^{-1}$) [6] and Cu ($0.05 mgL^{-1}$) pose threats to humans [2]. However, at high concentrations, these trace metals become also toxic [7].

The purpose of this study was to evaluate the concentrations of different selected metals (Pb, Zn, Cu, Mn, Fe and Ni) in different components such as water, sediments and three main type of macrophyte present in Shkodra Lake.

II. Study Site

The Shkodra/Skadar Lake is the largest shallow lake in southeastern Europe. It is a Managed Nature Reserve, included in the Ramsar List of international important wetlands, so its preservation and protection from pollution is very important. However, intensive industrial and urban development in the region have exposed the lake to anthropogenic pollution by organic and inorganic contaminants, including metals [5].

The largest contributors to the lake with regard to various pollutants are the rivers and creeks that pass through urban and rural settlements, and the last ones transport pollution from agricultural activity down to the lake. Previous studies have demonstrated that lake sediments are contaminated by metals, mostly Ni and Cr [5], [6].

III. Materials and Methods

A. Selection of sampling stations

The survey was carried out in two different period June and September 2012. The sampling stations was determined based on the geomorphology of the study area, tributary location, general hydrology, point and non – point source pollution identified. Based on the potential exposure of the lake to different source of agro-industrial and other source of pollutants, seven representative sampling sites: (Site-1 (**S1**): Bajçe, Site-2 (**S2**) Stërbeq, Site-3 (**S3**) Vraka, Site-4 (**S4**) Lumi Buna, Site-5 (**S5**) Bahçallëk, Site-6 (**S6**) Shirokë and Site-7 (**S7**) Zogaj : reference site by MoE) were selected (Figure1). The following criteria were applied in selection of sampling stations: (i) Sensitivity of the area, (ii) A review of existing data, (iii) Areas where rivers flows into the Lake, (iv) Known sources of pollution (point and non – point source pollution), (vi) The influence of tributaries and hydrological modifications.

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Fig. 1. Maps Location sampling stations for water, sediments and mycrophytes. Water sampling procedure with Ruttner.

TABLE I. THE LOCATION OF THE SAMPLE STATION AND THEIR COORDINATE IN UNIVERSAL TRANSVERSE MERCATOR SYSTEM (UTM).

Nr.	Location name	Coordinate X	Coorddinate Y
S1	Bajçe	364443.00	4676376.00
S2	Stërbeq	366938.00	4672993.00
S3	Vraka	373337.00	4661609.00
S4	Lumi Buna	374559.00	4657035.00
S5	Bahçallëk	375237.00	4655591.00
S6	Shirokë	372179.00	4657590.00
S7	Zogaj	367591.00	4658987.00

B. Water samples analytical method

Sampling of water was carried out in accordance with standard ISO – 5667-1. Preservation, handling transport and storage of water samples will be in accordance with standard ISO-5667-3. The water sampling were made in two levels: *top (5 cm under water surface)* and *deep (30 cm under water surface)* using a "Ruttner" sampler figure 2. All the samples will send to the laboratory in a portable fridge at 4°C.

Water samples were collected in 150 mL bottles from each station and for 25 mL of each sample were treated with 6 mL of 68% v/v HNO3 before analysis. The concentrations of the metals were determined using inductively coupled plasma optic emission spectroscopy **(ICP OES DV-Perkin Elmer)** after microwave digestion based on **EPA 3015a** were 45 mL from sample was added nitric acid (HNO_3) and hydrochloric acid (HCl).

C. Sediment samples analytical method

Sediment samples used for heavy metal fractions analysis were taken by a "Van Veen" grab sampler at the bottom of water in each sample stations in September, which were quickly packed in air tight polythene bags. Samples for analysis of heavy metals were dried, crushed and passed through 1 mm sieve in the laboratory before analysis based on **EPA 3050b**. For each digestion procedure, we have weigh to the nearest 0.01 g and transfer a 1 g sample (dry weight) to a digestion vessel and add 10 mL of 1:1 HNO_3. Heat the sample at $95^{\circ}C \pm 5^{\circ}C$ and reflux for 10 to 15 minutes without boiling. The samples was cooled, and add 5 mL of concentrated HNO_3 and 3 mL of 30% H_2O_2. After cooling, the samples was diluted to 100 mL with distilled water and then measured on Inductively Coupled Plasma Mass Spectrometry **(ICP-MS).**

D. Plant samples analytical method

At each sampling site, the aquatic plant samples of different macrophytes as *Potamogeton crispus*, *Potamogeton perfoliatus* and *Trapa natans* were collected in September for each sample station, at a constant depth of 40 cm. Each sample consisted of a pool of 2–3 plants, which were washed in the lake before being placed in polyethylene bags and taken to the laboratory in coolers.

Once there, the plants were rinsed again with distilled water to remove any material adhering to their surfaces. From samples of the dried plant material was weight (1 g ± 0.05) plant tissue and insert into a glazed porcelain crucible and into a cool muffle furnace for 2 hour. After that was digested using a mixture of 10 ml HCl (1:1) and concentrated 3 ml HNO_3 (1:1) and in the end the sample after cool was transferred to 50 ml volumetric flask with distilled water [8]. Finally, the contents of Cu, Fe, Mn, Ni, Pb and Zn were analyzed using inductively coupled plasma optic emission spectroscopy **(ICP OES DV-Perkin Elmer)**.

IV. RESULTS AND DISCUSSIONS

A. Heavy metals in water

Distributions of Cu, Fe, Mn, Ni, Pb and Zn concentrations at seven water samples for two investigated period are presented in Fig. 2 Fig. 3.

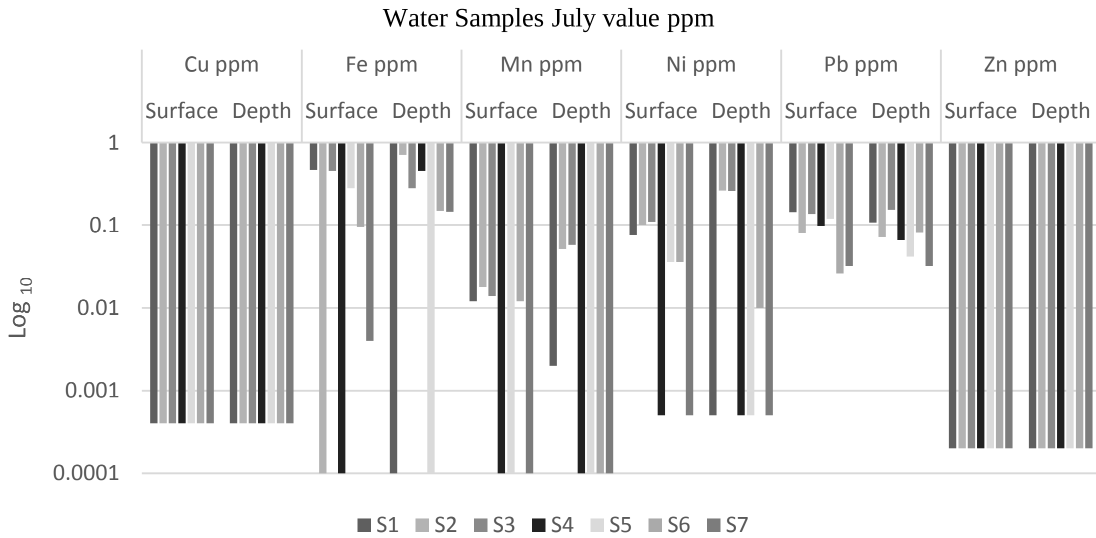

Fig. 2. Heavy metals concentration found in July measured in mgL^{-1} or ppm expressed in Logarithmic Scale base 10.

B. Copper – Cu

As we found, the Cu content is <0.4 μgL^{-1} in all cases (including the seasons and measuring stations) or the same as the limit detection value. In such conditions, the Lake does not have a significant amount of Cu, even at station 5 where due to the copper-containing minerals of Drini watershed, values of this metal were expected.

C. Iron – Fe

For September, the Fe values in water were low, smaller than 0.1 $\mu g\ L^{-1}$ or lower than the limit detection expect for three stations, at the bottom, where the highest value does not exceed 0.05 mgL^{-1}. In July, the values vary from 0.05 (station 5) to 0.708 mgL^{-1} that was the highest value found.

D. Manganese – Mn

Mn values are low. In most of the cases in September, they are under the detection limit (<0.1 μgL^{-1}), except for stations 3 and 4 with values varying from 0.002 to 0.006 mgL^{-1} Mn. In July, they vary from 0.002 (station 1) to 0,058 mgL^{-1} (station 3).

E. Nickel – Ni

Ni values in water were low; in our measurements they were lower than the limit detection (≤0.5 $\mu g\ L^{-1}$). The highest values were in July, for station 2 and 3, with 0.262 and 0.258 mgL^{-1}, respectively. Values in the other stations varied from 0.008 to 0.056 mgL^{-1}.

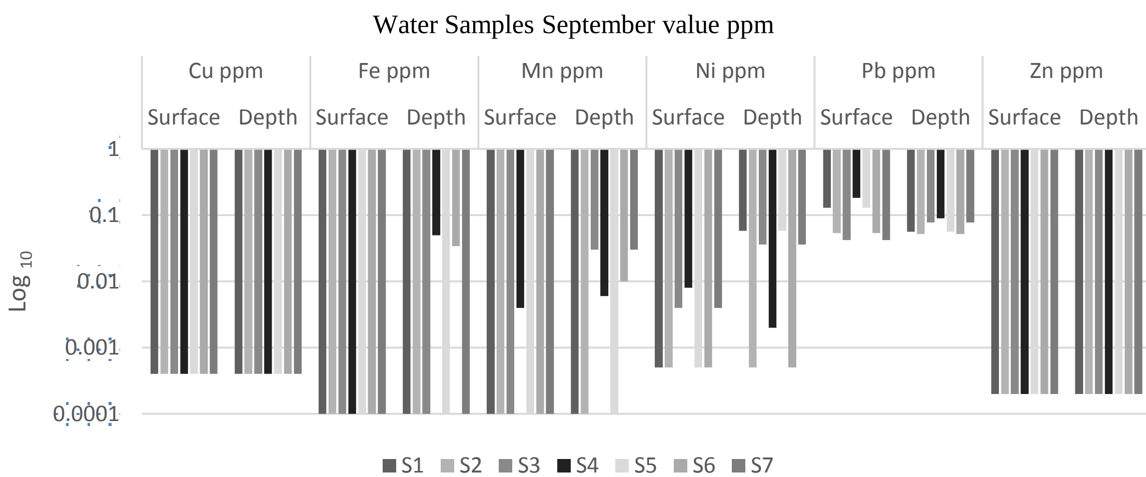

Fig. 3. Heavy metals concentration found in September measured in mgL^{-1} or ppm expressed in Logarithmic scale base 10.

F. Lead – Pb

In Fig. 2 and Fig. **3** we can see, the Pb values in the water for two seasons, in seven sampling stations in-depth and surface, as average values. Values found in July (0.096 ±0.03) are higher than in September (0.079±0.041) except Fig. 4 for stations 4 and 7. Their variation between surface and bottom is more visible in July (two times higher in the surface compared to the bottom). Minimum and maximum values were 0.032 (station 7) up to 0.144 mgL^{-1} Pb (stations 1 and 3). The European standard for Pb content in water is ≤7.2 mgL^{-1}, EPA-USA ≤ 50 mgL^{-1} Pb, GB 3838-200 ≤5.0 mg L^{-1} and WHO ≤ 50 mgL^{-1} and the values found in Lake's water are < 0.15 mg Pb L^{-1}.

G. Zinc – Zn

For all the values found in the study (including season and station) the content of Zn in water was <0.2 µg Zn L^{-1}, lower than the detection limit.

V. Heavy Metals In Sediments

The pollution of sediments is of natural and anthropogenic origin. Erosion and leaching of phosphate rock in the surrounding areas have an important contribution [9]. In

Fig. 5 shows the content of the four heavy metals contained in the sediment.

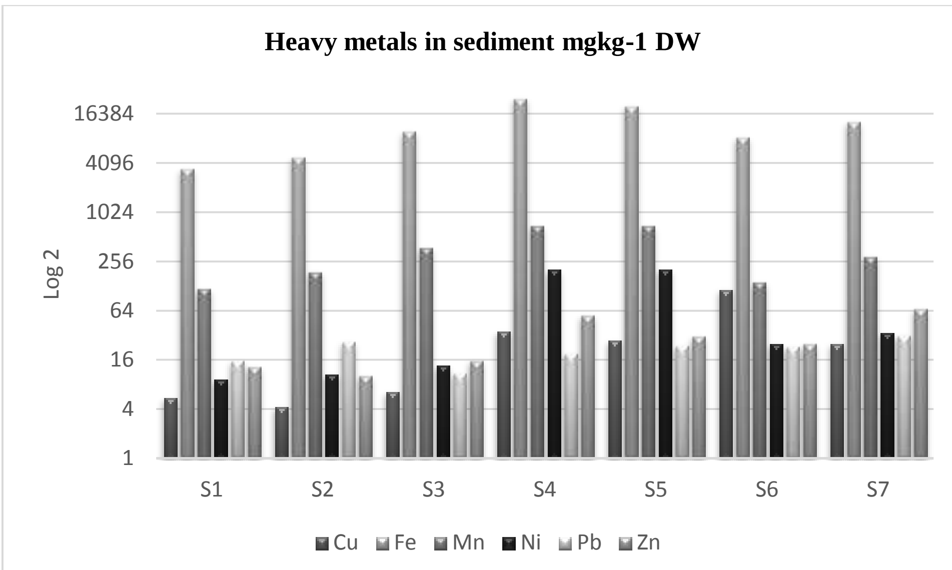

Fig. 5. The content of Cu, Fe, Mn, Ni, Pb and Zn in the sediment in $mgkg^{-1}$ dry weight (DW).

Cu content in the sediment is on average 33±37 $mgkg^{-1}$ with a minimum of 4.31 S2 and maximum 117.72 $mgkg^{-1}$ S6, both on the shallow coasts (eastern and Shiroka). The average value of Ni for the seven stations was 91±99.9 $mgkg^{-1}$ and the minimum and maximum values were 9.4 and 210.77 $mgkg^{-1}$, respectively in S1 and S5. The average value of Pb was 23.5±7.9 $mgkg^{-1}$ and with variations up to three times between the maximum (32.19 $mgkg^{-1}$) and minimum (11.1 $mgkg^{-1}$) value, with the maximum value found at the S7.

Zn varies from 10.5 to 69 $mgkg^{-1}$ with the highest content found in S7. Its average value was 35.4 ± 23.35 $mgkg^{-1}$. For Cu and especially for Ni, there are higher variations compared to the other two metals (Pb and Zn). To assess the negative effects we have considered the *guidelines* of National Oceanographic and Atmospheric Administration (NOAA-USA) [10] for the biological effects of heavy metal content in the sediment, where ERL is the Effect Range Low and ERM – Effect Range Medium [11].

TABLE II: ERL and ERM values according to heavy metals guidelines in $mgkg^{-1}$, dry weight (DW) and percentages of incidence for the biological effects in the range of concentration defined for both values.

In ERL for Cu, categorized as the limit where biological effects start to appear, is 35 while the average found was 33 $mgkg^{-1}$. In S6 the value of Cu were 40 and were within the range of the biological effects of this concentration (34-270 $mgkg^{-1}$Cu).

For Ni, ERL and ERM values are 21 and 52 $mgkg^{-1}$, respectively while the average content of Ni is 23 mg kg and values for stations S4, S5, S6 and S7 were > or >> than 21 $mgkg^{-1}$ (207 and 210 $mgkg^{-1}$ for S4 and S5). In the last stations (S4 and S5) Ni concentrations threaten the biota with values exceeding the accepted range as ERM (52 $mgkg^{-1}$).

For Pb, the average value (23.5 $mgkg^{-1}$) was significantly higher than ERL for this metal (8.0) but lower than ERM (217 $mgkg^{-1}$). In stations S2 and S7 the ERL value is significantly exceeded which means that the biological effects are felt. The average value for Zn was 35 $mgkg^{-1}$and the maximum value 69 $mgkg^{-1}$or much lower than the ERL value for this metal, which means that there are no biological effects caused by this metal. The average value of Fe was about 14 $mgkg^{-1}$ of dry sediment with a standard deviation (±9114 $mgkg^{-1}$while the variability is higher. The maximum value was 26807 and the minimum only 3538 $mgkg^{-1}$, or 8 times less. The highest values were found on stations S4 and S5 (>15 gkg^{-1}sediment). Mn values compared to Fe were much lower; the average value was 405±269 $mgkg^{-1}$with a maximum and minimum 729 and 120 $mgkg^{-1}$, respectively. As for Fe, stations S4 and S5 where characterized by high concentrations of Mn

VI. Heavy Metals In Macrophytes

Macrophytes are considered as important component of the aquatic ecosystem since they serve as food source for aquatic invertebrates and can act as efficient accumulator of heavy metals [12].

Distribution of metals in aquatic macrophytes depends primarily on the macrophytes species, plant organs and the type of metal [13]. Fe and Mn are considered as major elements for the plant physiology and metabolism.

Moreover, at a lower level also Cu, Zn and Ni are important for the process of photosynthesis and are considered as essential microelements in macrophytes. On differing, Pb is a toxic element and inhibitory to the metabolic processes; in large concentrations in plants it may pass to the food chain from water products to humans.

The average values of Fe in macrophytes were high (11363±6337 $mgkg^{-1}$) dry matter plant tissues with maximum and minimum values 18768 and 4306, respectively. The highest values were found in stations 4 and 5. Compared to the content of this metal in sediments, content levels in plant tissues were lower.

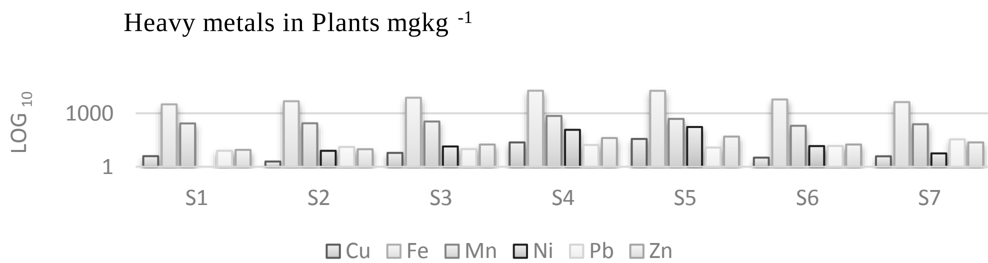

Fig. 6. The content of Cu, Fe, Mn, Ni, Pb and Zn in different macrophytes ($mgkg^{-1}$ Dry Mater).

The average content of Mn in plants was 436±205 mg kg^{-1} with a variation of maximum and minimum values, 721 and 202, respectively. Values found in macrophytes are almost similar with those found in sediments. The average values of Cu (14.9±13.4 $mgkg^{-1}$), Ni (68±68 $mgkg^{-1}$) and Zn (30 ±14.3 $mgkg^{-1}$) were comparable to the corresponding values found in sediment. The highest values of the three elements correspond to stations 4, 5 and 8, all located along Buna river flow. The average value of Pb was 17.95 ± 8.36 or a little bit lower than the average content value in sediment (23.5 $mgkg^{-1}$) and the station with the highest concentration was station 7 (Zogaj). Heavy metals accumulate more in sediments than in aquatic organisms and water [2], [14], [15] and as such sediments act as sinks and sources of supply of heavy metals to overlying water columns. In view of the fact that heavy metals such as Pb, and Zn are good markers of contamination from human activity detection of these metals in Shkodra Lake indicates contamination of the lake's water by human activities.

Data obtained indicated that the heavy metals were accumulating more in sediments than in aquatic organisms and water column, hence the sediments act as sinks and sources of heavy metals to overlying water.

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