THE ASSESSMENT OF HEAVY METALS CONTENT IN SURFACE SEDIMENTS IN THE ALBANIAN PART OF OHRID LAKE

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ABSTRACT

The content of five heavy metals in surface sediments for three areas in the Albanian part of Ohrid Lake has been investigated from June 2015 to June 2016. As for the coastline from Lini villageto Tushemisht village these mean values (M ± SD,mg/kg) of heavy metals content were reported: Arsenic (As) 8.93±2.976;Chromium (Cr) 270.13±203.229; Nickel (Ni) 277.95±158.191;Lead (Pb) 20.71±2.552 and Zinc (Zn) 192.47±60.903. Results reported approximate mean values for the nickel and chromium content (t = 0.031;P>0.01). Analyzed according to the three shore areas of the lake, the area at the entrance of the city of Pogradec was distinguished for the higher content of metals in surface sediments. The sediments of the Lin coastal area contained less heavy metals compared to the other two sampling areas.
Keywords: Ohrid Lake, heavy metals, surface sediments, anthropogenic sources

1. INTRODUCTION

The sediments in the lake play a major role in the contamination of the lake due to the physical, chemical and hydro-geochemical and biological characteristics of the aquatic system. The geochemical composition of the sediments clearly stipulates the current condition of the lake environment

(Karthikeyan *et. al.*, 2018). There is a global concern about the pollution caused by metals due to the environmental persistence of these elements, biogeochemical recycling and the ecological hazards they pose. Sediments are the largest deposit for heavy metals in aquatic environments and sediment quality is recognized as an important indicator of water pollution (Wu *et. al.*, 2014).

The main sources for trace elements, like metals, in natural waters are related to natural processes and anthropogenic impacts. Their common feature is that even in relatively small concentrations their effects are toxic and precisely for this reason they are included in the category of very dangerous environmental pollutants (Kastori and Maksimovic, 2006). The fact that heavy metals are present in the environment does not mean that they are in any case suitable for assimilation by living things and for inclusion in their body. Determining the total content of heavy metals in sediments is insufficient to assess their impacts on aquatic ecosystems. As some of the metals are involved in the crystal structures of minerals, or are bound to other sediment substrates, they might not pose a risk to living things. Having an information on all the mobile or biologically available metals, i.e., metals that can be obtained and metabolized from the lake organisms is of great importance. The content of a metal does not necessarily reflect the severity of pollution as it depends a lot on the chemical form of the polluting metal. Here we can mention the chromium atoms with different valences (Kastratovic *et. al.*,2016).

2. MATERIALS AND METHODS

Figure 1 depicts the sampling sites in the Albanian part of the Ohrid Lake (Lin village, coastal zone in the beginning of city of Pogradec, Tushemisht village) where the present study was carried out from June 2015 to June 2016.

Fig. 1. Three sampling sites in the Albanian part of Ohrid Lake (a. coastal zone in Lin village; b. coastal zone in the beginning of city of Pogradec; c. coastal zone in Tushemisht village).

There were 5 samples seasonally collected from each area. In total, 45 samples were analyzed for the three seasons. Arsenic (As), chromium (Cr), nickel (Ni), lead (Pb) and zinc (Zn) content, in mg per 1 kg of sediment was investigated. The portable sediment grab sampler model BDN-F was used for samples collection. In general, each sample was not less than 1 kg.

The samples are put away in fixed Ziploc sacks with lake water and tests are passed to the research facility and put away at − 20 °C. Prior to the substantial metal examination method, the sample is dried at 60 °C for 48 h. A small amount of dried samples is sieved through a mesh a 63-μm nylon mesh for homogenization and stored in a fixed plastic sacks.

The analysis of metals such as As, Cr, Ni, Pb, and Zn were performed by inductively coupled plasma mass spectrometry (Ammann,2007).

Statistical analysis

Quantitative data were analyzed separately based on the sampling sites. The one-way analysis of variance (ANOVA) and Duncan's multiple range tests (Montgomery, 2013) were involved for the calculation of t-test values and determination of the significance of differences ($P<0.05$) among zones and seasons.

3. RESULTS AND DISCUSSIONS

The Figure 2 depicts the mean values (M, mg / kg) of the five heavy metals content in the surface sediments, for the three sampling sites.

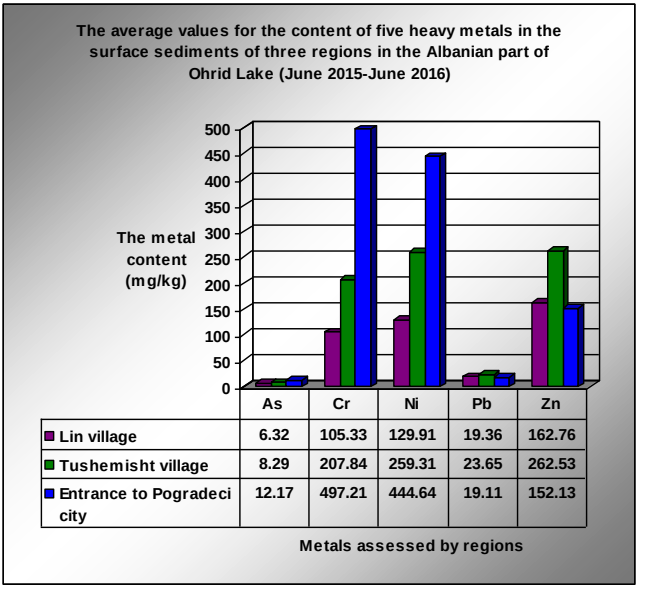

Fig. 2: The situation of heavy metal content in the surface sediments for the Albanian part of Ohrid Lake (the shoreline from Lini village to Tushemisht village).

Based on the figure we have calculated the mean values and standard deviation values (M ± SD) for each metal content, for the entire coastal area, from Lini village to Tushemisht village. The values (in mg / kg) are as following: Arsenic (As) 8.93 ± 2.976; Chromium (Cr) 270.13 ± 203.229; Nickel (Ni) 277.95 ± 158.191; Lead (Pb) 20.71 ± 2.552 and Zinc (Zn) 192.47 ± 60.903.

Analyzed according to the three shore areas of the lake, the area at the entrance of the city of Pogradec was distinguished for the higher content of metals in surface sediments. Chromium (497.21 mg/kg) and nickel (444.54 mg/kg) had the highest mean concentration rate. The sediments of the Lin coastal area had less heavy metals content compared to the other two sampling areas. In this area the chromium content was 4.7 times lower compared to the lake area at the entrance of Pogradec, and almost twice lower compared to the coastal area of Tushemisht. Meanwhile, the respective nickel contents for Lin were 3.4 and 2.0 times smaller compared to the two areas shown above.

After calculating the average values, it resulted that the surface sediments on the Albanian part of Ohrid Lake had approximate nickel and chromium content (t = 0.031; P> 0.01). These two metals, as mentioned, were found at the highest concentration rate. The arsenic content manifested an upward trend with a north-southwest extension, 6.32 mg / l and 12.17 mg / l, respectively. The arsenic, in the Albanian part of the lake, was found at a lower mean concentration rate compared to the rest of chemical elements.

After analyzing the seasonal changes of the mean concentration rate for the five metals in the surface sediments of the Albanian part of Ohrid Lake (regressions in Figures 3- 5) we found that:

The polynomial correlation with positive value of the "b" intercept (b = 12.4; r = 0.989) was typical of the dynamics of time-depending changes of arsenic concentrations. The polynomial correlation with negative value of the "b" intercept was of the dynamics of time-dependent changes of nickel (b = - 168.8; r = 0.984) and lead (b = - 9.95; 0.992) concentrations, while linear correlation was typical of the dynamics of time-dependent changes of the concentrations of chromium (b = 360.6; r = 0.989) and zinc (b = 229.37; r = 0.924) in the surface sediments of the lake.

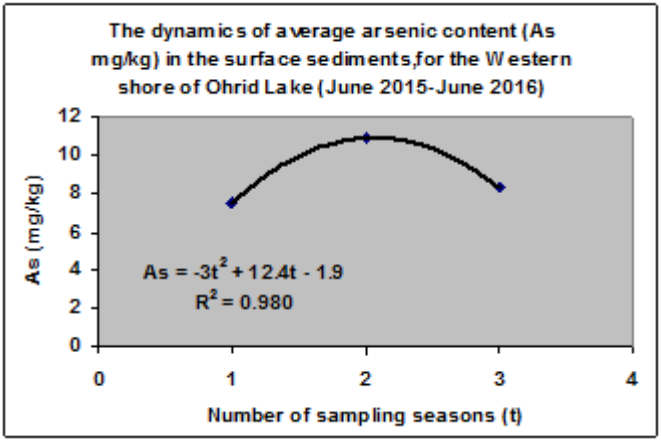

Fig. 3: The correlation between arsenic content (As, mg/kg) in the surface sediments of Albanian part of Ohrid Lake and sampling seasons (r = 0.989).

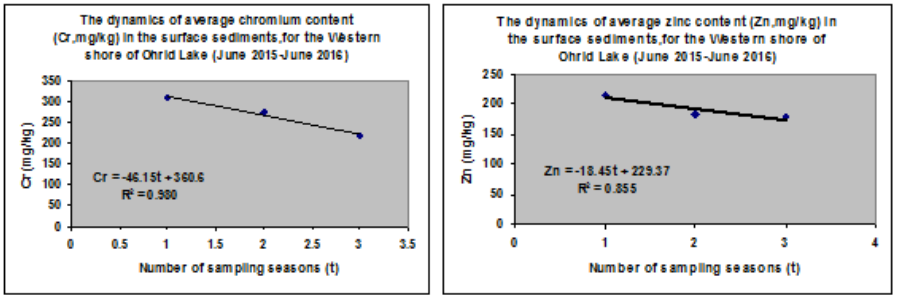

Fig. 4: The correlation between chromium content (Cr, mg/kg) in the surface sediments of Albanian part of Ohrid Lake and sampling seasons (r = 0.989) and the correlation between zinc content (Zn, mg/kg) in the surface sediments of the Albanian part of Ohrid Lake and sampling seasons (r = 0.924).

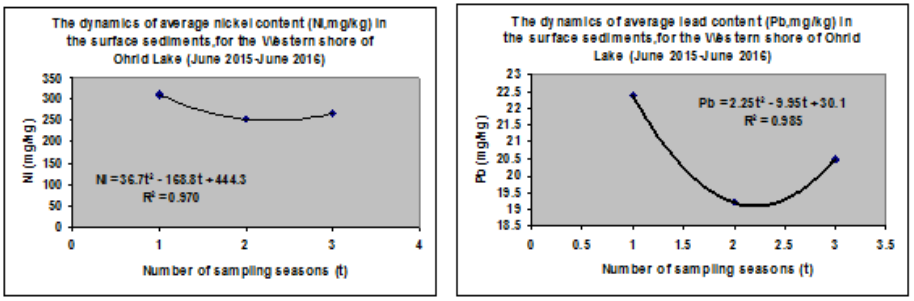

Fig. 5: The correlation between nickel content (Ni, mg/kg) in the surface sediments of Albanian part of Ohrid Lake and sampling seasons (r = 0.984) and the correlation between lead content (Pb, mg/kg) in the surface sediments of Albanian part of Ohrid Lake and sampling seasons (r = 0.992).

It could be concluded that in the one-year period, from June 2015 to June 2016, the **arsenic (As)** concentration rate has increased in the first phase of analysis (June 2015), while in the second phase (December 2015) it reached the maximum value. The third phase of analysis (June 2016) marked a decreased arsenic concentration rate. **Nickel (Ni)** has manifested a relatively significant downward trend in the first phase of analysis, has shown a minimum average value in the second phase of analysis and a slight upward trend in the third phase of analysis. **Lead (Pb):** Pb concentration rate has significantly reduced from the first to the third analyzes' phase. Despite this dynamic, the average concentration for June 2016 was lower than that of June 2015. **Chromium (Cr):** Cr concentration rate was characterized from June 2015 to June 2016 by a systematic reducing trend (the value of the angular coefficient in the regression equation (a = - 46.15) was negative.) The maximum average value of the concentration in surface sediments for this

metal was measured in the first phase of the analysis while the minimum average value was found in the third phase of the analysis. **Zinc (Zn)** showed dynamics of content in the same sediments as chromium. The value of the angular coefficient "a" in the regression equation for this metal was a = -18.45.

The results showed the highest content of arsenic (As) in the surface sediments of the shoreline of Ohrid Lake at the entrance of the city of Pogradec compared to the shoreline of Tushemisht and the shoreline of Lin. Enrichment of sediments with arsenic in the southwestern area of the lake is related to the proximity of this area to the region known as "Guri i Kuq". In this region are found the iron-nickel and chromium mines and a mineral enrichment plant. Iron compounds during precipitation take up arsenic ion, favoring its deposition in the surface sediments of the lake. Kanamori (1965) and Crecelius (1975) said that the co-precipitation of arsenic with ferric hydroxide can be an important process in removing arsenic from oxygenated water and passing it to sediments. The water of Ohrid Lake is generally distinguished for its high oxygen levels, which favors the deposition of arsenic in sediments in those areas where iron flows are high. Here we can mention the shoreline of the lake from the former iron-nickel enrichment plant to the entrance of the city of Pogradec.

Regarding the annual dynamics of arsenic content of the surface sediments, winter marked an increase of arsenic content rate compared to summer. The source of such increase might be the increased inflows of this element as a result of more abundant rainfall and water flows with increased flow in the cold seasons of the year. Crecelius (1975) said that atmospheric input and flow transport account for almost half of the arsenic that is present in lakes. About 20% of the dissolved arsenic in the lake water is transferred to the sediment every year, as it is transformed into insoluble form, bound to iron and manganese.

The chromium content in the surface sediments of the lake, for the coastal area from Lini to Tushemisht varied from 94.0 mg / kg (lake area of Lin) to 534.15 mg / kg (lake area at the entrance of the City of Pogradec). Compared to the contents of this metal (35.6-127.0 mg / kg) (Kastratovic *et. al.*,2016) in the sediments of Shkodra Lake, the contents found by us for Lake Ohrid are several times higher. The main reason must be the differences in the geological features of the two areas. It is very likely that the largest amount of chromium present in the surface sediments of the lake, especially in the coastal area Pojske-Guri i Kuq, is of lithogenic origin. Mwamburi (2016) said that it is possible the dominance of lithogenic chromium sources in the surface sediments of lakes, but also the presence of possible anthropogenic sources that are transported by drainage systems and from urban areas located near their shores.

The investigation here carried out reported that the content of zinc in the surface sediments of the lake varied from 128.9 mg/kg (coastal area in the entry of Pogradec) to 285.3 mg/kg (coastal area of Tushemisht). All the analyzes concerning this metal, its levels were always above 459 mg/kg, about which MacDonald *et. al.,* (2000) said that impacts the aquatic life. The differences we have experienced for the spatial distributions of concentrations in sediments, between chromium and zinc, if not random, may express the existence of specific influences of the same sources of these two metals or the presence of their different sources. Bojakowska *et. al.,* (2014) said that there is a strong correlation between the zinc content in lake sediments and the carbon and organic sulfur content. We mention that this phenomenon of intensive organic decantation, with high content of sulfur compounds, has been known, not many years ago, for the nearby shore in the south-western area of the lake which is quite populated and has many tourist centers.

The results reported that the nickel (Ni) content in surface sediments of Ohrid Lake, was in the range 93.17-468.33 mg / kg, which is relatively high, but remain within the values reported in (Szarek-Gwiazda *et al*, 2011) about two mountain lakes in Poland with values 15.6-83.1 μg/g, giving information about the geological content of the terrain that borders the West shore of the lake, especially the lake area at the entrance of Pogradec. The mineral exploitation for a long time and the existence of the plant for enrichment of this mineral in "Guri i Kuq", very close to our sampling points in the lake area at the entrance of Pogradec have determinate the most intensive deposition of nickel in the surface sediments of this area. Nriagu and Pacyna (1988), Farkas *et. al.,* (2007) and Szarek-Gwiazda *et. al.,* (2011) claim that even some human interventions affect in nickel content in water and basin sediments. Among such interventions we mention the discharge of raw municipal waters, dumping metallurgical and mechanical industries waste in water basins, urban waste landfill placement near watercourses, watercourses discharge starting from agricultural lands especially after rainfall, etc.

4. CONCLUSIONS

The following conclusions could be drawn: i)arsenic (As) was found at a significant increasing rate between June and December for the sediments in the Lin area ($t = 8.23$; $P < 0.01$) and for the sediments of the lake area at the entrance of Pogradec ($t = 3.77$; $P < 0.01$), and at approximate rates for the sediments of the Tushemisht area ($t = 0.65$; $P > 0.01$; $n = 5$), ii) chromium content rate had insignificant differences for the period between June and December for the sediments of the coastal area of Lin ($t = 2.048$; $P > 0.05$: $n = 5$) and difference of the significant level in the surface sediments of the

coastal areas of Tushemisht (t = 11.52; P <0.001) also in the entrance to the of Pogradec city (t = 4.79; P <0.01

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