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Comparative study of the environmental state of Ohrid and Prespa Lakes, Albania

A. Shehu*, M. Vasjari, S. Duka, L. Vallja and N. Broli
Department of Chemistry, Faculty of Natural Sciences, University of Tirana, Tirana, Albania
* *e-mail: alma.shehu@fshn.edu.al*

Abstract: The present study was undertaken to evaluate the environmental situation of Ohrid and Prespa Lakes with regard to heavy metals present in water in relation to different factors controlling their occurrence in these environments. A total of 15 water samples, collected at different stations and depths were selected to monitor Ohrid Lake whilst 4 samples were collected at Prespa Lake. Content of heavy metals such as Cr, Ni, Fe, Pb, Cd, Cu was determined in the filtered fraction of water, using the GF-AAS technique whilst chlorophyll "a" content was used as algal content estimation in both lakes. The relative abundance of heavy metals in Ohrid Lake followed the order: Fe>Cr>Ni>Pb>Cu>Cd while in Prespa Lake the metals order changed to Fe>Ni>Cr>Pb>Cu>Cd. Total mean concentration of Fe, Ni and Cr varied significantly (α=0.05) between the lakes whilst the mean concentration of Cu, Pb and Cd exhibited no significant variation. Variation of metals concentration with regard to different depths was more evident for Fe, assuming that the content of the dissolved fraction of this element was closely related to water parameters such as pH, water oxygenation, redox potential, etc. Cluster analysis confirm that positive correlation existed between stations S1-S3 and S4-S6 as well as between Fe-Cr-Ni, assuming that metals content was closely related to station location. Estimation of the quality state of the lakes was evaluated based on the European Directives of fresh surface waters such as [78/659/EEC] and (EU, 1989). Given the results, it can be concluded that waters of Ohrid and Prespa Lakes fall in Class A1 of waters quality regarding the heavy metals content, whilst low levels of dissolved oxygen, followed by higher levels of chlorophyll "a" classify deep waters of Prespa Lake in Class A2 of surface waters quality.

Key words: Heavy metals, water column, Ohrid and Prespa Lake, GFAAS

1. INTRODUCTION

Heavy metals contamination of surface water is a worldwide environmental problem because trace amounts of heavy metals are always present in fresh waters from the weathering of rocks and soils and a variety of anthropogenic activities (Achterberg et al., 1995; Loring et al., 1992).

Albania is rich in water resources, including rivers, groundwater, lakes, lagoons and seas. Although its resources exceed by far its consumption, locally water shortage and conflicts among users may occur in the dry season (Selenica et al., 2011).

Ohrid and Prespa Lakes lie in the south-eastern part of Albania. Lake Ohrid straddles the mountainous border between eastern Albania and southwestern Macedonia. It is one of Europe's deepest and oldest lakes, preserving a unique aquatic ecosystem that is of worldwide importance, with more than 200 endemic species. Lake Ohrid is the deepest lake of the Balkans peninsula, with a maximum depth of 288 m and a mean depth of 155 m (Merolli et al., 2003). Population growth and development of industry have impacted the lake ecosystem in many ways.

Prespa Lakes are a high altitude basin (850 masl) with two interconnected lakes: Micro Prespa (shared between Albania and Greece) and Macro Prespa (shared between Albania, Greece and Macedonia) (Talevski et al., 2009). The lake has suffered many pressures in the last forty years, with harmful effects on the health of the water, such as the rapid growth of biomass deriving from farming practices, erosion, untreated wastes and wastewaters.

Previous studies on Ohrid and Prespa lakes have mainly been focused on physical-chemical parameters while there are no reliable studies regarding heavy metals (Merolli, 2003; Adhami et al., 2015). The present study was undertaken to evaluate the environmental situation of Ohrid and

Prespa Lakes with regard to heavy metals present in water in relation to different factors controlling metals occurrence in these environments.

Evaluation of the contamination status of lakes waters was carried out based on two important Directives which determine the criteria for heavy metals content in fresh surface waters such as the EU Directive, 1989 and [78/659/EEC] (EPA, 2001).

2. MATERIALS AND METHODS

Estimation of the environmental situation of Ohrid and Prespa Lakes with regard to heavy metals was accomplished by determining the metals content in the filterable fraction of water samples. The field cruise was conducted during October, 2014. Sampling stations selected at each lake are illustrated in Figure 1.

Figure 1. Map of sampling stations of Ohrid and Prespa Lake

2.1 Sampling procedure of water samples

A Ruthner (Hydro – bios, Kiel, Germany) bottle was used for samples collection whilst polyethylene bottles were used for storage and transport of samples for further analyses. Sampling was conducted according to the standard method No. 105, described in APHA/AWWA, 1995. Physic-chemical parameters were measured in situ, while the chlorophyll content was determined in the suspended material after the filtration of samples, as soon as their arrival to the laboratory.
The analyzed metals were Iron, Chromium, Copper, Cadmium, Lead, Nickel and their content in water samples was determined according to the standard method No. 304 of the "Standard Methods for the Examination of Water and Waste Water" (APHA/AWWA, 1995). NOVAA 400, Atomic Absorption Spectrometer, equipped with a graphite furnace from Analytic Jena was used to carry out water analyses.

2.2 Sampling sites description

The water quality of Ohrid and Prespa Lakes was monitored in four stations in Ohrid Lake and in two stations in Prespa Lake, respectively:

Station S 1 - 4 km in the N-E part of Pogradeci City. (Max depth: 166 m). Samples were collected in six different depths of S1.

Station S 2 – 2 km far from Tushemishti city, in the north part of Ohrid Lake (Max depth: 60 m). Samples were collected in three different depths of S2.

Station S 3 - In front of Fe-Ni mine damp, Lake Ohrid, (Max depth 53 m). Samples were collected in three different depths of S3.

Station S 4 - 2 km in the East part of Lini village, Ohrid-Lake, (Max depth 72 m). Samples were collected in three different depths of S4.

Station S 5 - Prespa Lake (Gorica). 4 km in the East part, having a maximum depth of 14 m. Samples were collected in two different depths of S5.

Station S 6 - Prespa Lake. 5 km far from Gorica, in the East part, with a maximum depth of 15 m. Samples were collected in two different depths of S6.

3. RESULTS AND DISCUSSION

3.1 Analysis of physic-chemical parameters

Results of physic-chemical parameters as well as the content of chlorophyll "a" in waters of Ohrid and Prespa Lakes are presented in Table 1. Descriptive statistics was used aiming to evaluate water quality of both lakes with regard to physic-chemical parameters.

3.1.1 Temperature

In great lakes studies, variation of temperature in water column is the main indicator of lake stratification, a process occurring mainly during summer and winter (Burns et al., 1999). Based on temperature variation that existed in different depths of Ohrid Lake, from 20.8 ºC at 20 m depth to 7.5 ºC below this layer, it can be concluded that Ohrid Lake was stratified during the period of field cruise. Such situation was not observed for Prespa Lake, were the interval of temperature variation was not significant. Temperature of water in both lakes followed the normal expected values, recommended by the EU [1989] and [78/659/EEC] Directives, ranging from 7.5 – 25 ºC. Higher water temperature can reduce the dissolved oxygen concentrations in water and may thus affect the aquatic organism's life.

3.1.2 DO

Dissolved oxygen in water samples of both lakes varied significantly with regard to sampling stations depths (α=0.05). Results obtained for Ohrid Lake demonstrated that stratification occurs at 20 m depth, where the values of dissolved oxygen decrease from about 105% to about 88%, as depth increased.

The lowest concentration of dissolved oxygen (5.48 $mg.L^{-1}$) was recorded in station S5, belonging to Prespa Lake, at 10 m depth. This value was closer to the lower accepted limit (> 5 mg/l) of no risk for the support of aquatic life, [78/659/EEC]. Intensive growth of aquatic vegetation in this station has led to severe de-oxygenation of the water.

The DO levels in the other stations resulted higher than this limit, ranging from 8.36-10.48 $mg.L^{-1}$, falling consequently within the recommended levels for the support of fisheries and aquatic life (≥ 60%), EU [1989].

3.1.3 pH

The pH of the samples varied from 7.0 – 8.68. Observed variations of pH values were not significant and the pH ranges obtained fall within the surface water quality regulation, being respectively 5.5 - 8.5 according to the EU [1989] Directive, and ≥6 and ≤ 9 according to the Freshwater Fish Directive, [78/659/EEC].

3.1.4 Chlorophyll a

There is a strong relationship between chlorophyll, phosphorus and trophic state of lakes around the world. It was observed that the content of Chl "a" in waters of Prespa Lake resulted to be four times higher compared to its content in Ohrid Lake, ranging from 4.00 - 4.20 μgL^{-1} and from 0.6-1.40 μgL^{-1}, respectively. These values correspond to trophic state indexes, TSI, being respectively 44.19-44.68 and 25.58-33.90, according to Carlson & Simpson formula: TSI(Chl) = 9.81 ln Chl a ($\mu g.L^{-1}$) + 30.6, (Carlson and Simpson, 1996). TSI values confirm the oligotrophic state of Ohrid Lake, while waters of Prespa Lake were found to be in mesotrophic state.

Table 1. Statistical parameters for physic chemical parameters in each station of Ohrid and Prespa Lakes

Stations	Coordinates	Sample	Temp. ^oC	pH	DO (%)	Cond. ($\mu s.cm^{-1}$)	Chlorophyll "a" ($\mu g.L^{-1}$)
		Mean	14.4	8.2	98.92	238.8	0.90
S 1	N:40^{0}55'441",	Min.	7.5	7.89	83.7	227.0	0.74
	E:20^{0}41'449"	Max.	21.9	8.68	109.0	263.0	1.14
		Mean	16.7	8.10	101.3	234.7	1.40
S 2	N:40^0 54'821",	Min.	8.6	7.77	94.5	229.0	0.98
	E:20^0 42'319"	Max.	21.6	8.30	106.0	243.0	1.92
		Mean	14.8	7.80	100.4	235.0	0.70
S 3	N:40^{0}05'713",	Min.	8.0	7.00	90.9	227.0	0.01
	E:20^0 38'826".	Max.	20.3	7.30	104.7	246.0	1.20
		Mean	14.8	8.30	100.1	236.0	0.60
S 4	N:41^0 04'343",	Min.	8.0	8.03	83.4	229.0	0.26
	E:20^0 38'904"	Max.	20.0	8.40	115.4	247.0	0.93
		Mean	17.5	8.20	88.5	242.0	4.00
S 5	N:40^0 52'291",	Min.	17.0	7.88	70.7	217.0	2.99
	E:20^0 58'182"	Max.	18.0	8.47	106.3	267.0	4.97
		Mean	19.4	8.40	98.1	245.0	4.20
S 6	N:40^{0}52'917",	Min.	18.0	8.28	88.9	217.0	3.33
	E:20^0 58'642"	Max.	20.7	8.57	107.2	273.0	4.98
Recommended			A1 25	A1 5.5-8.5	≥60	1000	0.95-2.6 [O]
Value (EU, 1989)			A2 25	A2 5.5-9.0	≥50	1000	2.6-7.3 [M]
			A3 25	A3 5.5-9.0	≥30	1000	7.3-20 [E]
[78/659/EEC]				≥6 and ≤9	≥50	na	na

3.2 Distribution of heavy metals in waters of ohrid and prespa lakes

Results on heavy metals distribution in waters of Ohrid and Prespa Lakes are presented in Figures 2, 3 and 4. Boxplot graphs were used to evaluate spatial variation of each element concentration in all sampling points (Figure 2). Distribution of metals content in different depth of each station is presented in Figure 3. Mean concentrations of Fe, Ni, Cr and Cd varied significantly (α=0.05) between Ohrid and Prespa Lakes, resulting to be higher in waters of Ohrid Lake (Figure 2), while no significant changes were observed between Cu and Pb concentration in both lakes (α=0.05). According to the obtained results, the relative abundance of heavy metals in Ohrid Lake followed the order: Fe>Cr>Ni>Pb>Cu>Cd while in Prespa Lake mean concentrations of metals followed e different order, respectively: Fe>Ni>Cr>Pb>Cu>Cd.

More specifically:

3.2.1 Iron

Among the studied metals, Fe resulted to have the highest concentration in waters of both lakes, ranging from 9.34 - 54.63 $\mu g.L^{-1}$ in waters of Ohrid Lake and from 1.63-16.92 $\mu g.L^{-1}$ in waters of Prespa Lake. Mean concentration of Fe in Ohrid Lake was approximately 3.4 times higher than its concentration in Prespa Lake. Former mining activities of nickel, chromium, iron and coal production may contribute to the higher levels of iron in waters of Ohrid Lake compared to Prespa Lake. Concentration of Fe varied significantly in samples collected at different depths, being more evident for Ohrid Lake, reaching the maximum value at the deepest point of (S1, 150 m depth), (Figure 3). Concentration of dissolved Fe in bottom waters of deep lakes increases as the dissolved oxygen and redox potential lowers (Davidson et al., 1984; Morel et al., 1985). The shapes of the dissolved metal profiles indicate that dissolved Fe is supplied to the deeper layer during stratification by diffusion of Fe (II) from the sediments into the overlying anoxic water as well as reduction of Fe oxide particles settling through the anoxic water column (Balisteri et al., 1992; Murray, 1987).

It was observed that mean concentration of Fe in different stations of both lakes did not exceeded the recommended values for Fe content in surface waters (being respectively 0.1 mg.L^{-1}), according to the Directives [78/659/EEC] and EU, 1978.

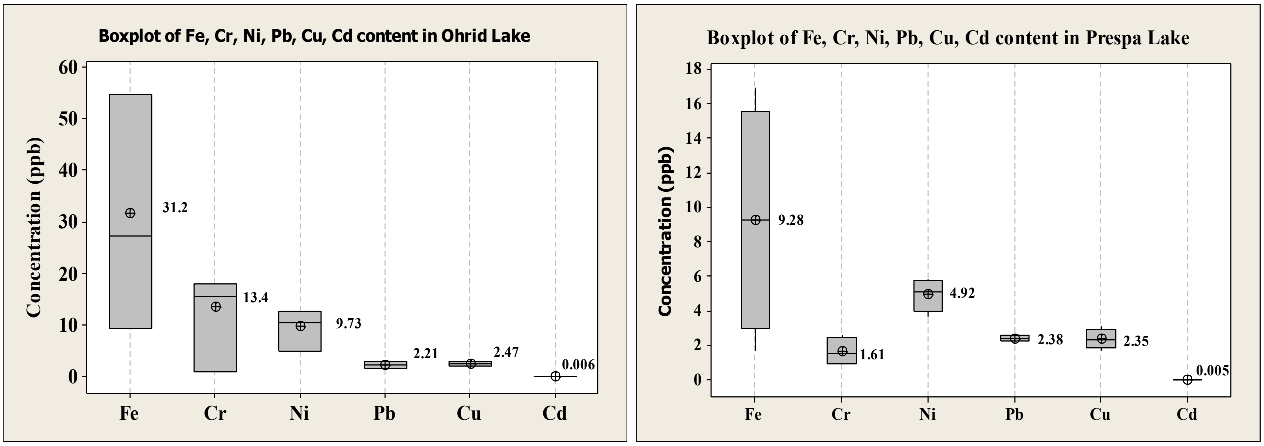

Figure 2. Variation of metals concentration in Ohrid and Prespa Lakes.

3.2.2 Chromium

Chromium content varied from 0.98-17.93 μg.L^{-1} in samples of Ohrid Lake and from 0.9-2.6 μg.L^{-1} in waters of Prespa Lake. Mean concentration of Cr in Ohrid Lake resulted to be about 8 times higher compared to its content in waters of Prespa Lake (Figure 2). Intensive former and actual mining activities can contribute to the levels of chromium in Ohrid Lake. Stations S1-S3 of Ohrid Lake were characterized by higher levels of Cr compared to stations S4-S6. Station S4 is regarded as the reference point for Ohrid Lake. Situated at the northern part of the lake, it is more isolated from the other stations which suffer more the effects of anthropogenic contamination. It is evident that the content of chromium in waters of Prespa Lake, represented by stations S5 & S6, was more related to natural factors such as the geology of the area. Higher concentrations were recorded at samples collected at 20 m depth, while its concentration decreased as the depth increased. Sedimentation and precipitation processes followed by reductive conditions of water such as low oxygen levels and redox potential contribute to lower chromium levels in bottom waters (Murray, 1987). Obtained results show that concentration of this metal falls below the recommended value (0.05 mg.L^{-1}) of chromium content in surface waters, according to the [78/659/EEC] EU Directive.

3.2.3 Nickel

Similar situation was concluded for nickel, where the mean concentration resulted to be approximately two times higher in waters of Ohrid Lake, varying from 4.93 to 12.26 μg.L^{-1}, whilst in Prespa Lake its content varied from 3.64 to 5.81 μg.L^{-1}. Even for this element, the main contributors are the wastes derived from mining activity. Stations S1-S3 were characterized by higher levels of Ni compared to stations S5 and S6 which belong to Prespa Lake. Variation of Ni content in different depths of each station resulted to be low, assuming that its content was not related to water depth. Values of nickel concentration in waters of Ohrid and Prespa Lakes fall below the value 0.1 mg.L^{-1}, which is the upper limit recommended by the surface fresh waters Directive [78/659/EEC].

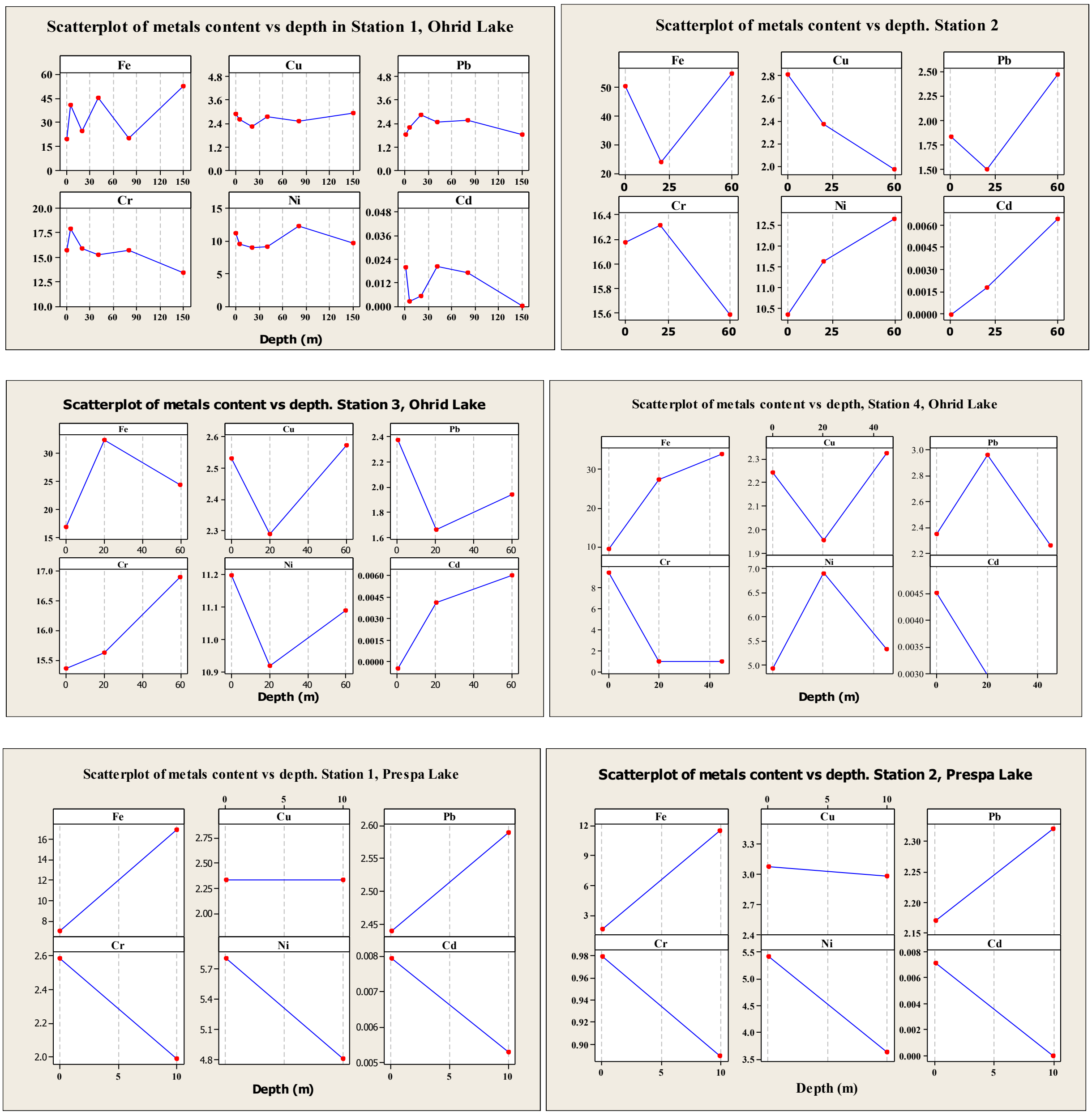

Figure 3. Distribution of heavy metals in different depths of each station (μg.L^{-1})

3.2.4 Copper and Lead

There were no significant differences between the mean concentrations of these metals in waters of both lakes. Copper content varied from 1.97-2.96 μg.L^{-1} in Ohrid Lake and from 2.99-3.08 in Prespa Lake waters, having very close mean values of its content. Lead concentration exhibited small variation in both lakes, being respectively 1.50-2.96 μg.L^{-1} and 2.17-2.59 μg.L^{-1}.

3.2.5 Cadmium

Mean concentration of cadmium in both lakes didn't exhibit significant differences, but the concentration of this metal resulted to be higher in some points of station S1. Cadmium content in Ohrid Lake varied between values below the detection limit of the AAS/ETA method to 0.020 $\mu g.L^{-1}$, while in Prespa Lake the maximum concentration observed was 0.008 $\mu g.L^{-1}$.

Concentration of cadmium in waters of Ohrid and Prespa Lake did not exceed the recommended value of its content in surface waters, being respectively 5 $\mu g.L^{-1}$, according to the European Council Directive, EEC, 1989.

4. CONCLUSIONS

Comparative study conducted on heavy metals concentration as well as on physic-chemical parameters of Ohrid and Prespa Lakes assumes that the quality of lakes water is threatened by both human and anthropogenic activities. Heavy metals resulted to be of great concern for Ohrid Lake due to higher levels of Fe, Cr, Ni, Cu, and Cd compared to Prespa Lake. The comparison of our results with former reported values was rather difficult because of the lack of existing data.

Considering the geology of the zone, large areas of central Albania are covered by serpentine soils which are highly enriched in heavy metals such as Cr, Cu, Ni, Fe, and Zn (Miho et al., 2005; Cullaj et al., 2007). On the other hand, some known anthropogenic sources of nickel, chromium and iron deriving from former mining activities, contribute to the levels of these metals in waters of Ohrid Lake. To the east of Pogradeci, a number of old mines that used to produce chromium, nickel, iron and coal are situated. Of these, only one remains in operation, but the mining sites still have many large piles of waste material that is exposed to the rain, which washes the pollutants from the piles into the lake.

Results on parameters such as oxygen saturation as well as content of Chl "a" give important information regarding the trophic state of the lake. In large and deep lakes such as Ohrid Lake, chances of water deterioration are very low compared to small and shallow lakes like Prespa. Levels of dissolved oxygen as well as the content of Chl "a" classify waters of Ohrid Lake in A1 class of waters quality, according to EU Directive [78/659/EEC] while low levels of dissolved oxygen, reaching the minimum value 5.83 $mg.L^{-1}$ (70.7%) at station S5, as well as high levels of Chl "a" suggest that nutrient loadings are deteriorating the quality of Prespa Lake waters.

Based on the obtained results as well as on EU Directives regarding the quality of surface waters, it can be concluded that waters of Ohrid and Prespa Lakes fall in Class A1 of waters quality regarding the heavy metals content, whilst low levels of dissolved oxygen, followed by higher levels of chlorophyll "a" classify deep waters of Prespa Lake in Class A2 of surface waters quality.

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