

# Heavy Metal Content Analysis of Siutghiol Lake Water and Sediment

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*Siutghiol Lake, situated on the Romanian Black Sea Coast, provides socio-economical value for the surrounding area, given its various resources and uses. Seaside lakes are undergoing a significant stress from several directions, especially in the past decade, due to the enhancement of anthropic activities. Our research presents original results concerning heavy metal content determination of water and sediments by atomic absorption spectroscopy method, AAS with high resolution and continue source. In most of the sediment samples the heavy metal concentrations were above the acceptable limits stipulated of the regulation in force.*

**Keywords:** Siutghiol Lake, heavy metals, water, sediment

Siutghiol Lake, situated on the Romanian Black Sea Coast, is an important tourism attraction area. Its socio-economical value is also given by the localities surrounding it and by the necessity of using water in specific agricultural and industrial activities. Siutghiol Lake is a significant area for aquatic migratory birds (ROSPA 0057) and holds exploitable fish resources. Given the intense anthropic activity, manifested through mass tourism, nautical sports, fishing, road traffic, human settlements, the impact on this site is major, with negative effects on the Lake habitat and associated flora and fauna species [1].

Metallic elements (those metals with a density higher than 5 g/cm<sup>3</sup>: Zn, Hg, Fe, Cu, Cr, Pb, Cd) are normally present in nature and do not represent a danger for the environment, but they may become pollutants, i.e. they may alter the balance of environmental components, when they exceed a certain threshold value set by the laws [2]. They become in this way harmful for a variety of living organisms, for environment as a whole [3], possessing a risk for humans using the resources of that specific ecosystem.

The presence of metallic elements in lakes or any aquatic environment can change both aquatic species diversity and ecosystems due to their toxicity and accumulative behavior [4]. Sediments quality has been recognized as an important indicator of water pollution since they act as sink of contaminants [5]. Heavy metal contamination may have devastating effects on the ecological balance of the recipient environment and a diversity of aquatic organisms [6, 7].

For these reasons, the present study was conducted to focus light on the metallic elements levels, especially heavy metals, in water and sediment samples, taken from eleven sampling points of Siutghiol Lake, especially since data regarding the concentrations in sediments of this lake are scarce (few or single sampling points, discontinuous, etc.).

## Experimental part

Water and sediment samples were collected during 3 phases of fieldwork, in different seasons – spring, summer,

autumn: July and November 2009 and May 2010. Using a GPS (Garmin) the coordinates were recorded for each of the twelve control sections: L1-L11 inside the lake and C1 in the channel connecting Lake Siutghiol to Lake Tăbăcărie. The water samples were taken with a sampling device in a sufficient amount, from the surface to the deeper areas, and then they were transferred in sterile polyethylene bags (Whirl-Pak™) and kept in a cooler until we arrived at the laboratory. Then these were filtered through Whatman membrane filters with 0.45 mm pore diameter, using a filtering assembly.

The sediment samples were collected with Ekman or Van Veen devices, according to substrate's nature (soft, muddy, compact or sandy), transferred in labeled sterile polyethylene bags (Whirl-Pak™), and after that processed.

Atomic absorption spectrometry method in both graphite furnace and flame, with high resolution continuum source was used as a powerful tool for metallic elements determination in water and sediment samples, using atomic absorption spectrometer ContrAA 700 Analytik Jena AG. All the materials foreseen for these analytical determinations comply with the quality methodology in force.

## Results and discussions

*Water quality evaluation for Siutghiol Lake based on metallic elements determinations*

In order to evaluate the obtained data regarding the metallic elements concentrations in the water and sediments of Siutghiol Lake, we must compare them to the maximum concentrations admitted stipulated by the legislation in force [8] (table 1).

Cadmium concentrations in Siutghiol Lake water samples were in general reduced for the sampling points that have been monitored (fig. 1). Nevertheless, in the summer of 2009 higher values were observed at sampling points L2 and L3, corresponding to the IV<sup>th</sup> class of water quality. Cadmium was not encountered at stations L5 and L10.

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No. crt.	Metal	Surface waters Quality Classes					
		Measure unit	I	II	III	IV	V
1	Cd	µg•L <sup>-1</sup>	0.5	1	2	5	>5
2	Cr	µg•L <sup>-1</sup>	25	50	100	250	>250
3	Pb	µg•L <sup>-1</sup>	5	10	25	50	>50
4	Cu	µg•L <sup>-1</sup>	20	30	50	100	>100
5	Mn	mg•L <sup>-1</sup>	0.05	0.1	0.3	1	>1
6	Zn	µg•L <sup>-1</sup>	100	200	500	1000	>1000
7	Hg	µg•L <sup>-1</sup>	0.1	0.3	0.5	1	>1

**Table 1**  
THE MAXIMUM CONCENTRATIONS  
ADMITTED FOR DETERMINING THE  
CHEMICAL STATUS OF WATER  
QUALITY

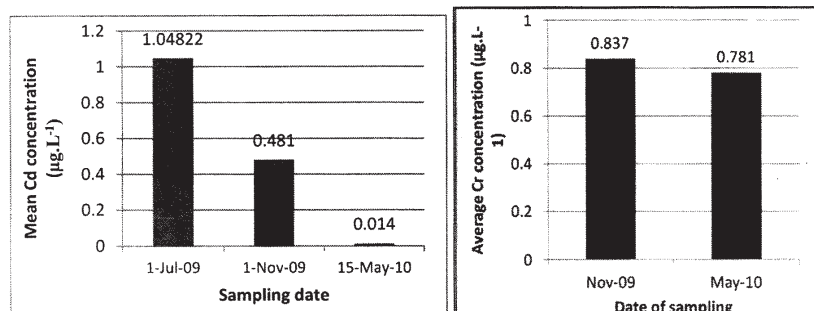


Fig. 1. The variation of the average concentration of Cadmium and Chromium in water samples for 2009 – 2010 period

Chromium presence was not detected in any of the stations in the summer of 2009, and for the other periods the values determined were extremely reduced compared to the maximum concentrations admitted for the surface waters. The values in May 2010 were slightly lower than the previous sampling period.

Lead was determined in higher concentrations in 2009, the average being  $2.54 \mu\text{g}\cdot\text{L}^{-1}$  (fig. 2). At the same time, exceeding of the maximum admitted values for the first quality class were recorded for the sampling points L5 and L8. In 2010 the concentrations were lower, rarely exceeding  $1 \mu\text{g}\cdot\text{L}^{-1}$ .

The data analyses show that higher concentrations of Copper were determined in November 2009, when the average value was  $3.12 \mu\text{g}\cdot\text{L}^{-1}$ . The sampling points L4, L7, L8 and L2 contributed mostly for obtaining these values. The maximum level was achieved at L4 sampling point, where the copper concentration was  $9.57 \mu\text{g}\cdot\text{L}^{-1}$ .

In the other two sampling periods the concentrations determined for copper were much lower, but not overcoming  $2.2 \mu\text{g}\cdot\text{L}^{-1}$  (fig. 3). The maximum concentration admitted by law for the surface waters was not exceeded.

The Manganese concentrations in the water samples were low during the entire study period (fig. 4). The maximum levels were reached in May 2010, but even so, the maximum limit for the first class of quality,  $0.5 \mu\text{g}\cdot\text{L}^{-1}$ , was not exceeded.

In the summer of 2009, Zinc was either present in samples only as traces or it was absent, as it happened for L5 and L9 sampling points. By the end of the year the situation has changed, the values rising up to  $17.08 \mu\text{g}\cdot\text{L}^{-1}$ , for the sampling point L2. The highest values for this parameter were observed in the last period of sampling, when for all sampling points, the concentration of zinc has significantly increased, the average value being  $25.92 \mu\text{g}\cdot\text{L}^{-1}$ . The maximum values were determined for L8 and L6 sampling points, which reached almost  $50 \mu\text{g}\cdot\text{L}^{-1}$  (fig. 5).

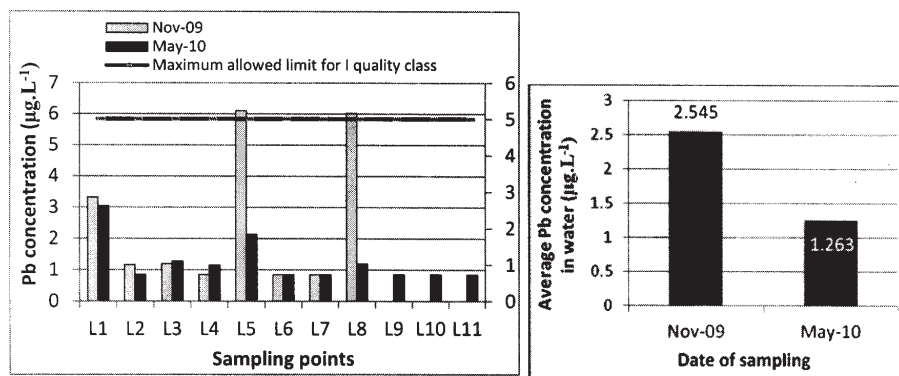


Fig. 2. The variation of Lead concentration in water (2009-2010)

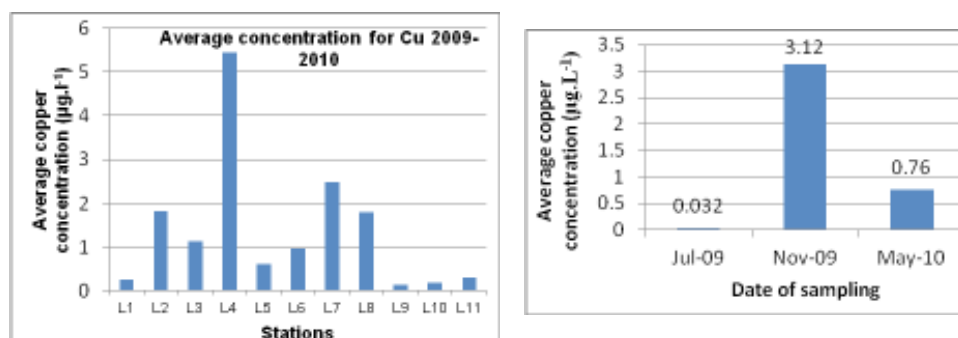


Fig. 3. The variation of Copper concentration in water for the monitoring stations (2009-2010)

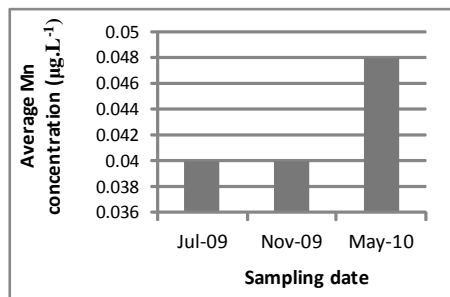


Fig. 4. The variation of the Manganese average concentration in Siutghiol Lake water samples in the period 2009-2010

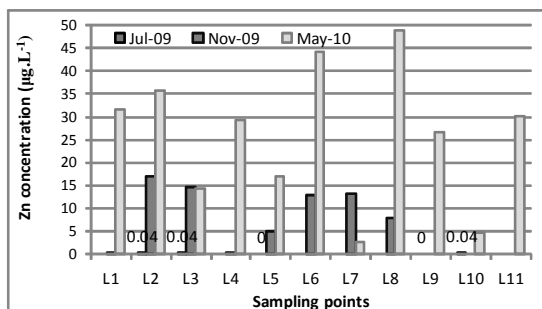


Fig. 5. The variation of Zinc concentration in water samples in the period 2009-2010

Smaller values, comparable with the ones obtained in November 2009, were found at L3, L5, L7 and L10 sampling points. However, the maximum concentrations admitted were not exceeded, the values corresponding to the first class of quality.

Mercury ions were determined as traces in the samples taken in November 2009 and May 2010. The situation was different in the summer of 2009, when exceeding of the maximum permitted concentration for the first class of quality was registered for all sampling points. The limit for the third class of quality regarding the concentration of Mercury in water was reached at sampling points L10 and L5 (fig. 6).

The values obtained through atomic absorption spectrometry were higher in November, the highest values being registered in the following sampling points: L1 ( $19.1 \mu\text{g} \cdot \text{L}^{-1}$ ), L4 ( $18.32 \mu\text{g} \cdot \text{L}^{-1}$ ) and L2 ( $15.4 \mu\text{g} \cdot \text{L}^{-1}$ ). The aluminum concentration in the other stations did not exceed  $11 \mu\text{g} \cdot \text{L}^{-1}$ . In May the values were relatively uniform, decreases were observed for the sampling points in which in the previous period the values were the biggest, and increases for the others (fig. 7).

#### The evaluation of the lake sediment quality based on the metallic elements determinations

Romanian Ministry Order no. 161/2006 regards some elements and standards of chemical quality for sediments (table 2) that must be considered for a correct evaluation of the sediment quality.

**Table 2**  
MAXIMUM CONCENTRATIONS ADMITTED TO ESTABLISH THE CHEMICAL STATUS OF SEDIMENT QUALITY [8]

No. crt.	Metal	Maximum admissible value (mg/kg)
1	Cd	0.8
2	Cr	100
3	Pb	85
4	Cu	40
5	Zn	150
6	Hg	0.3

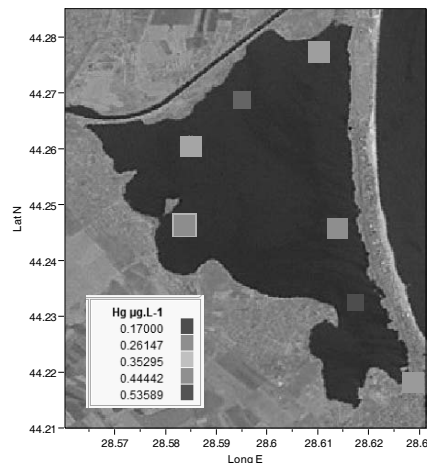


Fig. 6. The variation of mercury concentration in water for different areas of the lake in July 2009

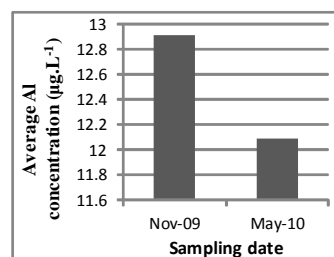
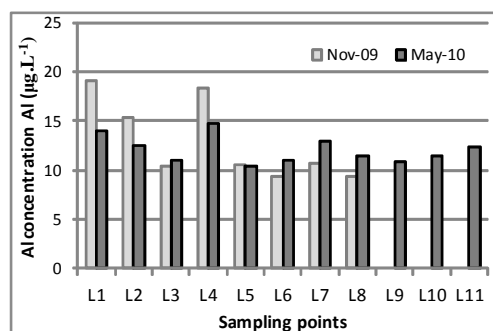


Fig. 7. The variation of aluminum concentration in water samples for the period 2009-2010

Sampling of metallic elements in sediment samples taken in the summer of 2009 was designed to see the concentration level at 0-10 and 10-20 cm depth horizon. Copper, manganese and zinc appeared in extremely low quantities, as traces, and chromium was not encountered at all. Cadmium was detected in two of the four stations monitored in small amounts, up to  $0.1 \text{ mg} \cdot \text{kg}^{-1}$  and only in the surface horizon of the sediment.

Lead was found in concentrations that exceeded the maximum allowed limit, imposed by law (fig. 8). Tops were recorded at sampling point L8:  $379 \text{ mg} \cdot \text{kg}^{-1}$  for the surface layer, respectively  $337 \text{ mg} \cdot \text{kg}^{-1}$  for the bottom layer.

South from Ovidiu Island, at sampling point L5, lead concentration was high, especially in the lower layer. At the sampling point located in Siutghiol-Tabacarie channel, C1, lead exceeded the maximum limit of about  $144 \text{ mg} \cdot \text{kg}^{-1}$ . The lowest concentrations were determined at sampling point L7, in the surface layer.

In comparison with the situation in July 2009, the other two phases of work the situation has improved, so the maximum threshold for lead in sediment was not exceeded anymore. Higher values were observed at sampling points L1 and L4 (fig. 9).

Mercury concentration in sediment was high in all stations monitored in both horizons (fig. 10). Values were higher for the deep layer, the highest amount being recorded



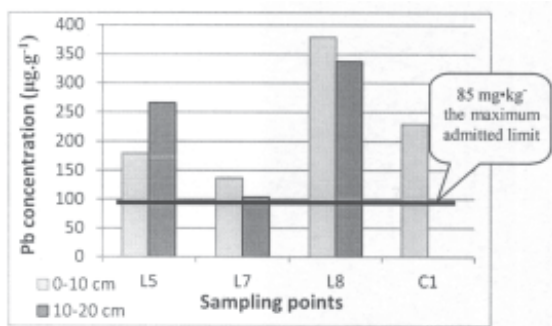


Fig. 8. The variation of Lead concentration for the deep horizon of the sediment in July 2009

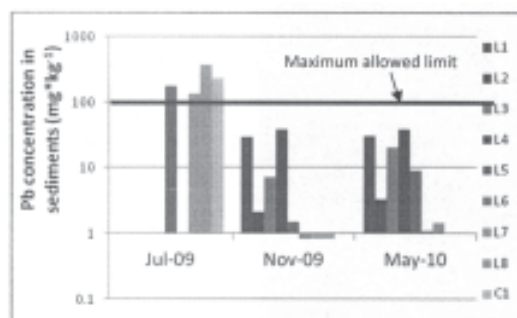


Fig. 9. The variation of Lead in sediments in the period 2009-2010

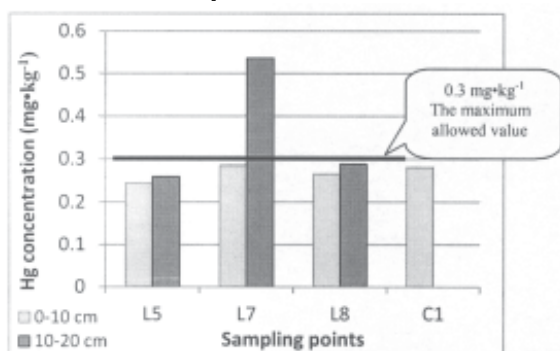


Fig. 10. The variation of mercury concentration in sediments (July 2009)

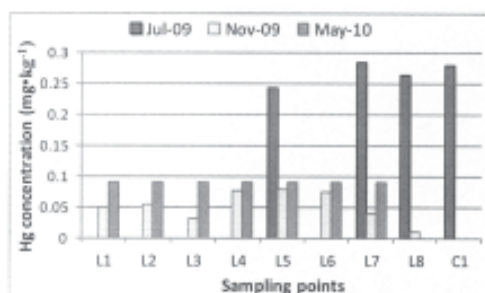


Fig. 11. The variation of Mercury concentration in sediments in the period 2009-2010

at station L7, where the maximum permissible concentration was exceeded ( $0.54 \text{ mg} \cdot \text{kg}^{-1}$ ).

The determined values for Mercury were higher in July 2009, decreasing significantly in November and then rising again, but not reaching the level of the previous summer (fig. 11). There was not recorded any exceeding of the maximum allowed concentrations; the closest sampling points to this level were L7 and C1 ( $0.28 \text{ mg} \cdot \text{kg}^{-1}$ ).

Cadmium was determined in low concentrations, which were generally below  $0.40 \text{ mg} \cdot \text{kg}^{-1}$  (fig. 12). The exception was L5 sampling point, where the maximum permissible

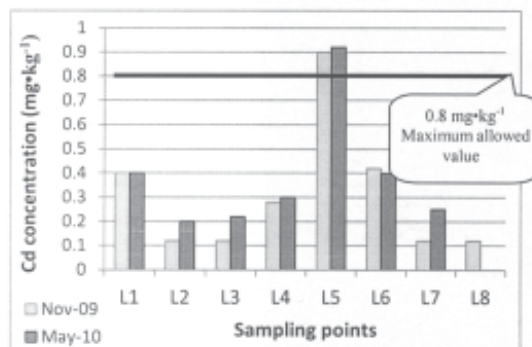


Fig. 12. The variation of Cadmium in sediments for different zones of the lake

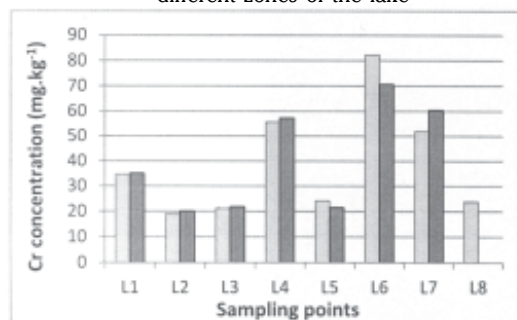


Fig. 13. The variation of Chromium in sediments from different zones of the lake (2009-2010)

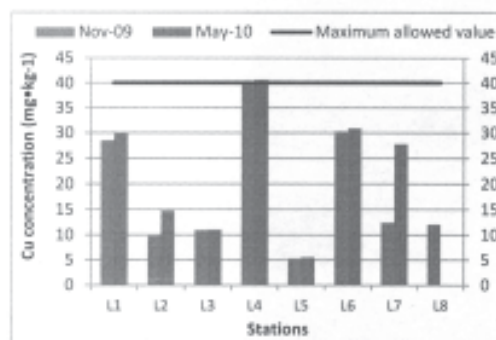


Fig. 14. The variation of Copper in sediments for different zones of the lake (2009-2010)

concentration was exceeded in lake sediments in both stages of sampling ( $0.90$ , or  $0.92 \text{ mg} \cdot \text{kg}^{-1}$ ).

If in the summer of 2009 Chromium was not observed in any of the monitored sampling points, in other work stages it was present in quantities around  $20 \text{ mg} \cdot \text{kg}^{-1}$  (sampling points L2, L3, L5 and L8). In the remaining sampling points the concentrations were higher, the maximum values being recorded at L6 ( $82.2 \text{ mg} \cdot \text{kg}^{-1}$ , in November). Sampling points L4 and L7 are next, with average values of  $56.4$ , or  $56.2 \text{ mg} \cdot \text{kg}^{-1}$  (fig. 13). In the case of this element the maximum concentration admitted has not been exceeded.

As in Chromium case, the situation is similar for the determination of Copper in sediments. If in July 2009, this metallic element was present as traces, in the next periods the concentrations have increased. The differences have been observed at sampling points L7 and L2, where concentrations were higher in May. The highest concentrations were found at L4 sampling point (fig. 14), where the maximum limit required for copper in lake sediments was slightly exceeded ( $40.63 \text{ mg} \cdot \text{kg}^{-1}$ ).

Order no. 161/2006 does not specify a maximum value admitted for Manganese in the sediments. In most cases values exceed  $200 \text{ mg} \cdot \text{kg}^{-1}$  (fig. 15) and concentrations generally increased over time. The only sampling point where the concentration was very low ( $0.04 \text{ mg} \cdot \text{kg}^{-1}$ ) was L8.

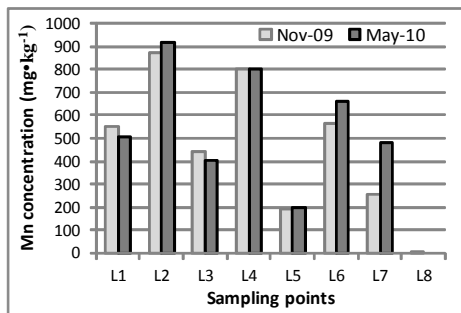


Fig. 15. The variation of Manganese concentration in sediments in the period 2009-2010

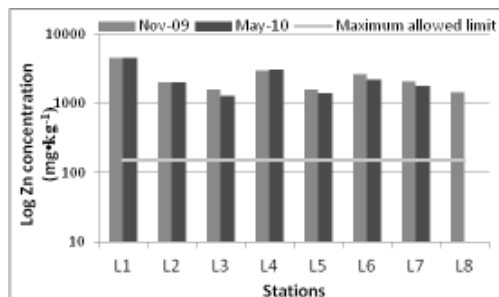


Fig. 16. The variation of Zinc concentration in sediments in the period 2009-2010

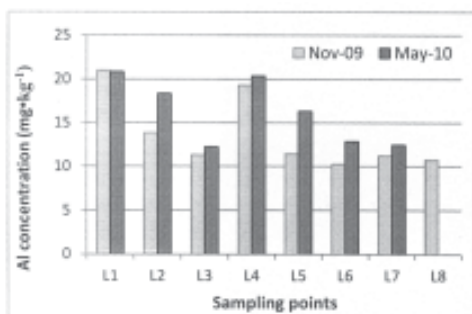


Fig. 17. The variation of Aluminum concentration in sediments in the period 2009-2010

**Table 3**  
SAMPLING POINTS WITH DETERMINED EXCEEDING OF MAV

Heavy metal	Sampling points with exceeding MAV	Date of sampling
Cd	L5	Nov and May
Pb	L5, L7, L8, C1	July
Cu	L4	May
Zn	L1 - L8	Nov and May
Hg	L7, L8	July
Mn	L1-L7, especially L2, L4, L6, L7	Nov and May

Zinc was found in the sediments in high concentrations, exceeding  $1000 \text{ mg} \cdot \text{kg}^{-1}$  (fig. 16). All the values determined for this element, regardless of the zone of the lake, have exceeded by at least an order of magnitude the maximum concentration admitted for sediment of  $150 \text{ mg} \cdot \text{kg}^{-1}$ . The highest concentrations were reached at station L1 ( $4620 \text{ mg} \cdot \text{kg}^{-1}$ ).

The law does not stipulate a maximum allowed concentration for Aluminum. In Siutghiol Lake's sediments the concentrations found were much lower compared to the literature data. The concentrations were higher at stations L4 and L1, around  $20 \text{ mg} \cdot \text{kg}^{-1}$ ) and the others

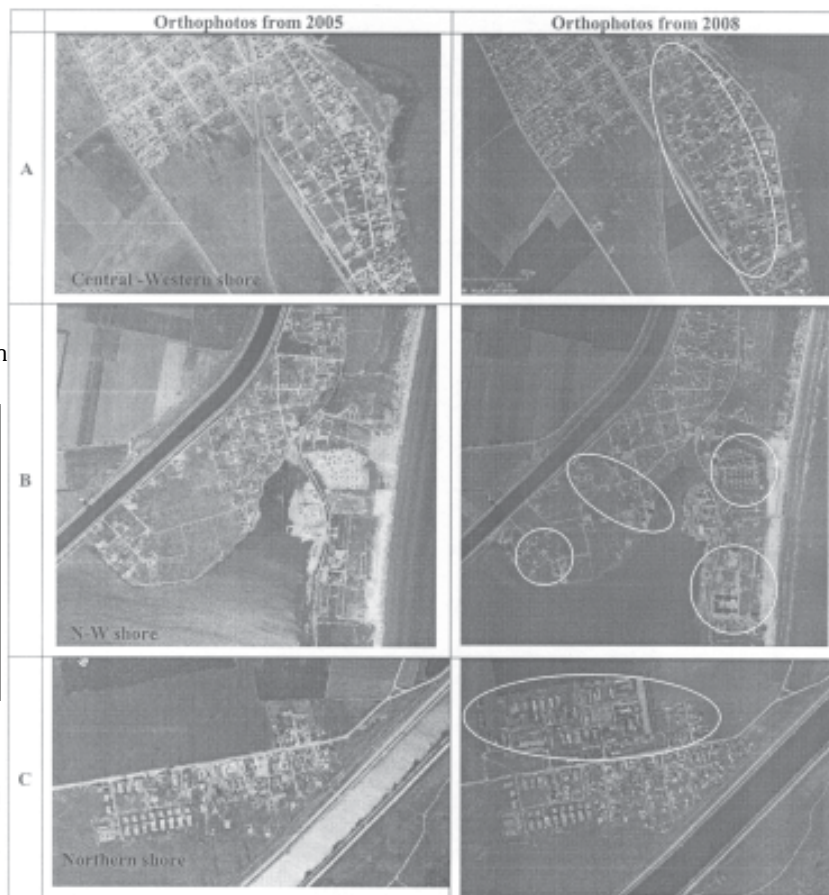


Fig. 18. Orthophotos from different areas around Siutghiol Lake showing increasing buildings and construction sites density for the years 2005 and 2008 (source: www.arcgis.ro)

were not exceeded in 2009 (fig. 17). Overall, the values had an increasing trend from one determination phase to another.

As an overall image, we noticed that there are certain stations with high levels of concentration for several heavy metals. In this respect we distinguished L4, L5, L7 and L8 sampling points (table 3). Very interesting is that in the shoreline areas corresponding to the stations where exceeding of the maximum concentration allowed were observed, the main anthropogenic activity was represented by constructions. We believe that heavy metal buildup is happening due to surface drainage from the catchment area and not due to the underground feeding of the lake. In this respect, bibliography data [9] on underground water caption determinations show low levels of metallic elements, even lower than in the lake water, thus not representing the source.

The area corresponding to the stations L4 and L5 is Ovidiu locality, namely its southern extremity, which has known an astounding development (fig. 18A). Here, in the past five years, a new neighborhood was practically built, that does not have at all the appropriate equipment: no sewage system, several houses have septic tanks; during the significant rainfall episodes (eg. the latest - July 2010, May 2012) the Canara and Caragea Dermen valleys were simply washed out by the heavy rain, everything draining into the lake.

For the sampling points L7 and L8 the situation is similar to the previous one, meaning that the original purpose of the northeastern shore of the Lake was modified, the place of the green space being taken within 4-5 years by relatively large buildings with living quarters or arranged for tourism activities (fig. 18).

## Conclusions

Literature data especially regarding the content of heavy metals in sediments of Lake Siutghiol are very poorly represented. The levels determined for the heavy metal content in water are in normal parameters, normal variations can be observed from one stage of monitoring to another. Exceeding of the limits imposed by law for Cd in water were recorded in the southern stations L2 and L3, respectively for Hg in the west and north-west areas, at stations L5 and L10 [10].

Exceeding of the maximum permissible concentration stipulated by law for sediments was observed for cadmium, lead, copper, zinc, mercury and manganese. chromium and aluminum were within normal limits.

Our data confirm that the accumulation of heavy metals in sediments usually occurs at concentrations much higher in the water of the same ecosystem [11]. Contaminated lake sediments cause concern, due to toxic potential, especially if an important fraction of metallic elements becomes bio-available [12]. Metallic elements may be transported from sediments back to the surface environment through diffusion [13], but this would be the subject of a further study for sediment metal mobility.

We can conclude that the sediments toxicological potential is very high, especially for the organisms inhabiting lake sediments, but also for the other components of the ecosystem also because of the re-suspension phenomenon accentuated mainly due to the NE winds, but also due to the decrease of the lake depth (maximum depth of 17 m in 1998 to about 6 m in 2007).

The contamination of freshwater with a wide range of pollutants has become a matter of great concern over the last few decades, not only because of the threats to public water supplies but also the damages caused to the aquatic life [14]. The natural aquatic systems may extensively be contaminated with heavy metals released from domestic and industrial wastes, agricultural activities, physical and chemical weathering of rocks, soil erosions, as well as sewage disposal and atmospheric deposition [15].

In this respect, it is indicated to determine also the total metal/dissolved metal ratio and their correlation with pH values because the metal present in solution in the precipitated stage could be re-precipitated if the pH value or other water quality condition changes [16].

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