DETERMINATION OF HEAVY METAL LEVELS IN WATER AND THERAPEUTIC MUD BY ATOMIC ABSORPTION SPECTROMETRY

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The aim of this study was to determine heavy metals levels (*i.e.* Pb, Cd, Cr, Ni, Mn, Zn and Fe), in different samples (*i.e.* surface water, depth water and therapeutic mud) collected from seven salt lakes from Romania. The concentrations of metals were determined by atomic absorption spectrometry. The obtained results show that heavy metal concentrations were higher in mud samples comparative with water samples. The relationships between physicochemical parameters (*i.e.* pH, conductivity, turbidity, salinity, and TDS) and heavy metal concentrations were assessed, as well.

Key words: heavy metal, AAS, therapeutic mud, salt lake.

1. INTRODUCTION

It is well-known that the salt lakes from Romania have a remarkable biodiversity, which are based on specialized microbial communities that provide the continuous operation of trophic chains as well as the complete recycling of major chemical elements. Moreover, the halotolerant and halophilic microorganisms are responsible for the achievement and regeneration of sapropelic mud (*i.e.* heterogeneous system formed from a liquid phase, a solid phase and a gaseous phase) with therapeutic effects which are very appreciated in the world. From this point of view the knowledge and understanding of chemical composition of salt lakes are very important because the accumulation of toxic elements (*i.e.*

heavy metals) in higher concentration can modify the action of halophilic microorganisms (*i.e.* algae, diatomee, *Artemia sp., Halobacterium sp,* etc.) which have a vital role in C, N, P and S circuit elements, in order to maintaining the salt lakes as healthy ecosystems [1-5]. Compared with the less salty lakes, the ones deeper have a very interesting quality, being permanently stratified [6]. Thus the concentrations of heavy metals in water and sediments of salt lakes depend on several physicochemical factors such as salinity, pH, conductivity, temperature, dissolved oxygen, redox potential and ionic strength as well [7]. Some of these metals are becoming toxics when forming complexes with organic compounds [8, 9]. Heavy metals can occur in various chemical forms (*i.e.* sulfides, metal carbonates, oxides, and ions in mineral crystal lattices) [10] especially in mud, which can modify their therapeutic properties.

The aim of this study is to determine the mean concentrations of heavy metals including Pb, Cd, Zn, Ni, Cr, Mn, and Fe in water and mud of the most known salts lakes from Romania such as Techirghiol Lake, Amara Lake, Salt Lake Braila, and Ocnita Lake, Avram Iancu Lake, Brancoveanu Lake and The bottomless Lake from Ocna Sibiului. Heavy metals concentrations were determined by atomic absorption spectrometry (AAS). The relationships between the metal levels in samples collected from different salt lakes and physicochemical parameters were assessed.

2. MATERIAL AND METHODS

2.1. SAMPLING AND ANALYTICAL TECHNIQUES

This study was carried out in October 2013. The samples were collected from seven salt lakes from Romania (Table 1). Sampling procedure involves water samples from the surface and different depths, and mud from the bottom of lakes. It was collected six samples per area (surface, different depth and bottom of lake) at 10 m around. Representative sample (1000 mL for water and 300–400 g wet weight for mud) were added in HDPE bottles, previously washed with HNO_3 solution. Muds samples were dried in oven for at least 48 hours at 60^0C, passed through a 2 mm sieve, and homogenized.

In order to determination the heavy metals concentrations all collected samples were prepared. In this respect, the digestion of water samples with aqua regia (HNO_3 67%:HCl 37% = 3:1) was achieved. Acid mixture (HNO_3 67%:H_2SO_4 98%:HCl 37%:HF 40% = 2:1:1:1) for mud samples digestion was used. Mineralization of samples was performed by using a Berghof MWS-2 microwave digester.

Atomic Absorption Spectrometry (AAS) is a very common and reliable technique for detecting metals and metalloids in environmental samples [7–9]. The total metal content of water and mud samples was performed by *Flame Atomic Absorption Spectrometry* (FAAS) or *Graphite Furnace Atomic Absorption Spectrometry* (GFAAS). The GBC Avanta AAS with flame and GBC Avanta Ultra Z (equipped with graphite furnace) spectrometers and autosampler, which provided a good sensitivity [10–15], were used. Blank and standard solutions for devices calibration were used as well. In order to measure the concentration of heavy metals in water and mud samples, a typical set of standard calibration curves with good linear regression and better relative standard deviations were achieved. Also, in order to verify the validity of the measurements, two standard reference materials, NIST SRM 1643e - Trace Elements in Water and NIST SRM 4354 - Lake Sediment Powder, were used.

Table 1

Locations and depths of sampling for different salt lakes from Romania

Code	Salt lake	Type of sample	Sampling depth [m]	Geographic Coordinate System (GCS)	
				Latitude	Longitude
TL1	Techirghol Lake	water	surface	44° 2'27.43"	28°36'40.32"
TL2	Techirghiol Lake	water	5.0		
TL3	Techirghiol Lake	mud	bottom		
SL1	Salty Lake	water	surface	45°12'25.65"	27°53'41.16"
SL2	Salty Lake	water	1.2		
SL3	Salty Lake	mud	bottom		
OL1	Ocnita Lake	water	surface	45°52'28.03"	24° 3'59.53"
OL2	Ocnita Lake	water	15.0		
OL3	Ocnita Lake	mud	bottom		
AIL1	Avram Iancu Lake	water	surface	45°52'30.56"	24° 3'59.05"
AIL2	Avram Iancu Lake	water	15.0		
AIL3	Avram Iancu Lake	mud	bottom		
BL1	Brancoveanu Lake	water	surface	45°52'18.69"	24° 3'56.38"
BL2	Brancoveanu Lake	water	10.0		
BL3	Brancoveanu Lake	mud	bottom		
FL1	The bottomless Lake	water	surface	45°52'33.93"	24° 4'3.24"
FL2	The bottomless Lake	water	15.0		
FL3	The bottomless Lake	mud	bottom		
AL1	Amara Lake	water	surface	44°36'34.04"	27°20'26.76"
AL2	Amara Lake	water	2.0		
AL3	Amara Lake	mud	bottom		

The physicochemical parameters of water samples including pH, conductivity, salinity and Total Dissolved Solids were analyzed by using a Multi-parameter analyser C3030.

3. RESULTS AND DISCUSSION

The significant physicochemical parameters including pH, turbidity, conductivity, salinity and TDS (*Total Dissolved Solid*) are given in Table 2. The pH values ranged between 7.02 (*i.e.* SL2) and 8.24 (*i.e.* BL1). Turbidity values are higher in water samples collected from the depth of salt lakes according with values presented in Table 2. Conductivity and TDS are higher in samples collected from different depth of salt lakes as well. High salinity was observed in all samples collected from surface and different depth of Ocna Sibiului salt lakes. Lower salinity (*i.e.* 6.5 – 7.6. g/L) was observed in samples collected from Amara Lake. Relationship between conductivity and turbidity as well as between conductivity and TDS of studied salt lakes is shown in Figure 1. Relationship between pH and salinity of water samples is shown in Figure 2. From these relationships it can observe an increase tendency of salinity with the increase of lakes depth, with the decrease of pH and with the increase of conductivity.

Table 2

Physicochemical parameters of studied salt lake water

Salt Lake	pH	Turbidity [NTU]	Conductivity [mS/cm]	Salinity [g/L]	TDS [mg/L]
TL1	7.93	5.75	84.46	89.1	4223
TL2	7.81	59.6	189.45	46.6	9472
SL1	7.21	4.32	80.11	317.6	4006
SL2	7.02	102.34	108.73	262.0	5421
OL1	8.04	94.92	148.68	243.1	7434
OL2	7.59	157.3	179.46	266.3	8973
AIL1	8.13	82.19	114.31	180.3	5716
AIL2	7.73	167.12	130.47	192.4	6523
BL1	8.24	104.35	173.42	308.0	8671
BL2	7.54	155.23	218.5	319.6	10925
FL1	8.11	5.12	210.1	94.5	10505
FL2	7.82	141.7	354.1	301.5	17705
AL1	7.33	4.47	112.64	7.6	5632
AL2	7.15	8.12	102.18	6.5	5109

Thus, the studied lakes can be classified in the following category: hyposaline (3–20 ‰ that mean < 50 g/L) such as Amara Lake, mesosaline (20–50‰ which mean about 100 g/L) such as Techirghiol Lake, and hypersaline

(> 50 ‰ that mean over 200 g/L) such as Salt Lake, Ocnita Lake, Avram Iancu Lake, Brancoveanu Lake and The bottomless Lake (Table 2).

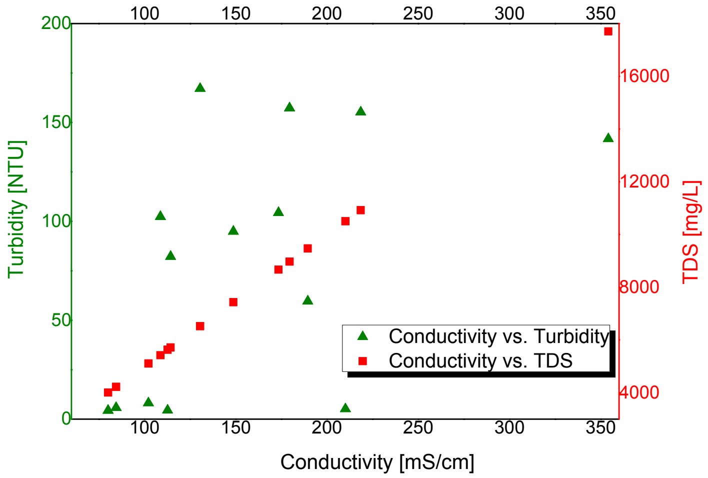

Fig. 1 – Relationship between conductivity and turbidity as well as between conductivity and TDS.

Heavy metals levels in water depend on the physicochemical parameters of water such as pH, turbidity, conductivity, salinity and TDS. It is well known that the solubility of toxic metals increases with the pH decrease (from surface to depth, from alkaline to acidic). The mean of heavy metals concentrations (*i.e.* Pb, Cd, Zn, Ni, Cr, Mn and Fe) in water samples are presented in Table 3.

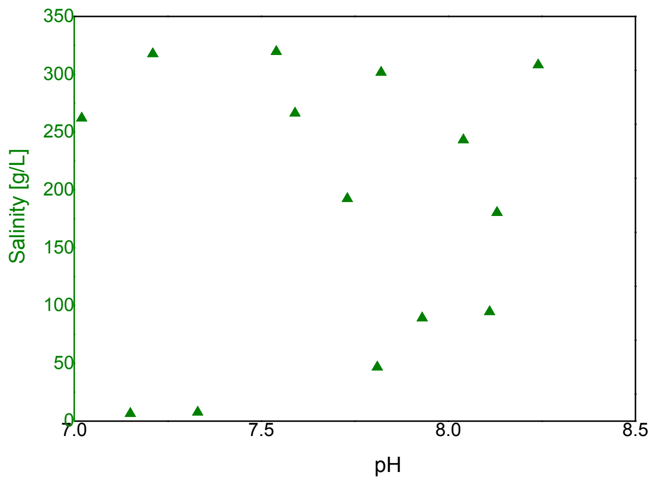

Fig. 2 – Relationship between pH and salinity for samples collected from salt lakes.

Table 3

Mean concentration of heavy metals in water samples collected from different depths

Water sample	Mean concentration of heavy metals [µg/mL]						
	Pb*	**Cd****	**Zn***	**Ni***	**Cr***	**Mn***	**Fe***
TL1	5.478±1.2	0.771±0.1	234.211±4.5	11.156±1.5	1.257±0.1	21.498±3.5	301.16±5.5
TL2	0.412±0.1	0.051±0.01	266.347±3.0	2.204±1.0	0.326±0.1	7.031±1.5	351.22±5.0
SL1	5.458±1.6	0.935±0.8	218.023±5.3	7.435±0.8	7.103±0.4	20.324±2.3	267.11±3.4
SL2	2.862±0.1	0.052±0.01	248.976±6.0	3.452±1.0	1.908±0.1	17.903±2.4	260.99±4.0
OL1	3.456±1.0	0.212±1.0	214.113±4.5	8.032±1.5	1.744±0.5	28.355±3.5	365.77±4.0
OL2	0.244±0.01	0.042±0.01	233.512±4.2	0.874±0.5	0.341±0.1	19.845±2.5	381.66±3.5
AIL1	4.014±1.5	0.799±0.05	228.514±4.1	10.251±1.5	2.867±0.5	29.147±3.0	321.61±4.5
AIL2	0.381±0.1	0.073±0.01	297.850±6.0	1.113±0.5	0.621±0.1	20.138±2.5	399.05±5.5
BL1	4.321±1.0	0.698±0.1	216.243±4.5	10.183±1.5	2.371±0.5	28.221±3.0	374.22±6.5
BL2	0.412±0.1	0.068±0.01	286.095±3.0	1.035±0.1	0.422±0.05	21.847±2.7	419.29±4.0
FL1	5.331±0.5	0.738±0.1	222.355±4.1	9.961±0.5	2.038±0.5	26.158±2.0	381.66±5.0
FL2	0.421±0.1	0.062±0.01	271.267±3.3	1.253±0.1	0.436±0.1	19.833±3.0	376.59±4.0
AL1	6.017±1.0	1.881±0.5	261.221±4.5	9.336±1.5	4.755±0.5	23.665±2.5	314.41±5.0
AL2	4.458±1.6	0.855±0.1	278.558±3.5	7.284±0.5	1.133±0.4	20.371±2.0	287.01±3.8

Flame Atomic Absorption Spectrometry (FAAS)
**Graphite Furnace Atomic Absorption Spectrometry (GFAAS)*

From Table 3 it can see that when the pH values decreased on the surface to depth, only Fe and Zn levels increased. Thus, the conductivity values had a significant positive relationship with all heavy metals except Cd (as divalent cation). There were significant differences between salinity and Ni, Cd, and Cr levels. It can found negative relationships between pH and some metals such Ni, Cr, and Mn, as well. It could be concluded that the changes of physicochemical parameters depend on how seasons affect the levels of some metals.

The presence of toxic metals including Pb and Cd in mud samples comparative with surface water can be explained by precipitation of sulfides (PbS and CdS), which are commonly found in higher concentrations in salt lakes (Table 4, Figures 3 and 4).

Table 4

Mean concentration of heavy metals in therapeutic mud samples collected from the bottom of salt lakes

Mud sample	Mean concentration of heavy metals [mg/kg d.w.]						
	Pb*	**Cd***	**Zn***	**Ni***	**Cr***	**Mn***	**Fe***
TL3	12.13±1.5	9.11±2.5	1721.28±5.2	17.51±1.5	17.33±1.4	92.47±3.0	34572.66±4.0
SL3	17.69±4.2	6.07±2.1	2465.44±6.5	19.90±1.0	15.43±1.2	89.88±2.8	33568.43±4.5
OL3	11.03±1.1	8.22±2.0	1848.11±6.5	15.44±1.5	12.19±1.5	55.13±2.5	21901.73±3.0
AIL3	10.87±1.5	9.08±1.5	1345.67±4.5	17.67±1.0	13.85±2.0	54.32±2.2	21834.52±3.5
BL3	9.66±1.0	10.77±2.8	1504.18±5.5	17.90±1.5	12.41±1.0	56.66±2.0	23410.24±4.0
FL3	10.48±1.0	9.71±3.5	1721.32±5.0	17.11±1.2	12.77±2.0	53.28±2.5	21730.30±4.5
AL3	13.31±2.6	7.69±2.0	2246.41±4.5	14.22±1.5	10.33±1.0	76.68±5.0	39574.78±5.5

Flame Atomic Absorption Spectrometry (FAAS)

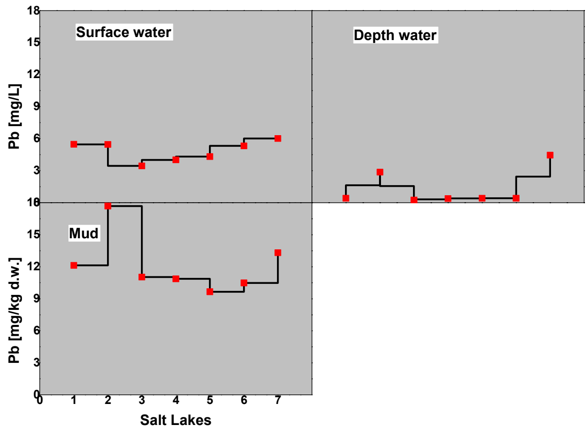

Fig. 3 – Lead concentration in samples collected from seven salt lakes.

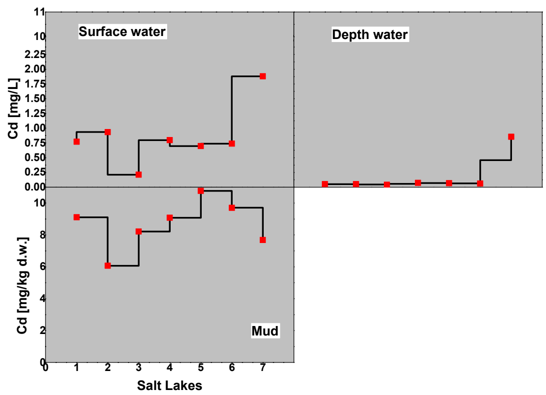

Fig. 4 – Cadmium level in samples collected from seven salt lakes.

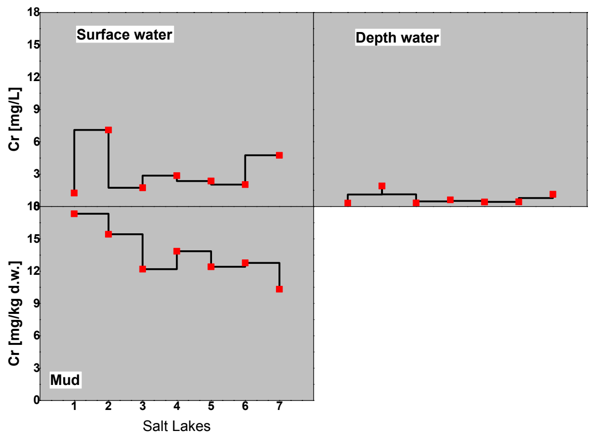

Fig. 5 – Chromium content in samples collected from seven salt lakes.

The Ni concentration in mud samples (Figure 6 and Table 4) is higher comparative with the Ni concentration in water samples collected from different depth (Table 3 and Figure 6). This can be explained by the fact that the suspended particulate matter from depth water is the main agent that promotes the transport of this metal in natural aqueous medium.

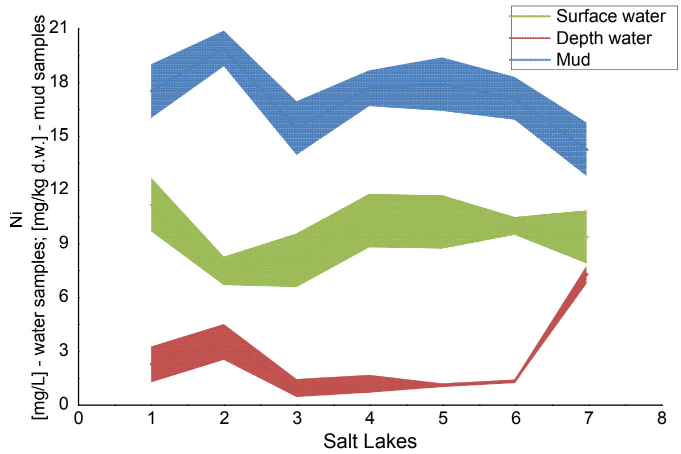

Fig. 6 – Nickel concentration in samples collected from studied salt lakes.

High concentration of Mn in muds (Table 4 and Figure 7) comparative with Mn level in water samples (Table 3 and Figure 7) was obtained for Techirghiol Lake (92.47 mg/kg d.w.) and Salt Lake (89.88 mg/kg d.w.).

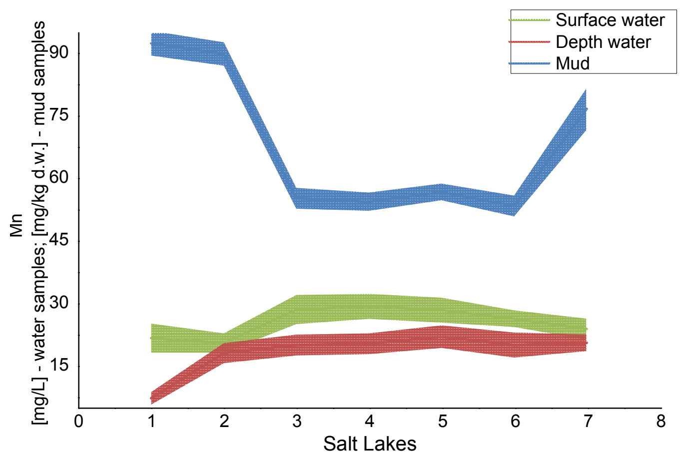

Fig. 7 – Manganese concentrations in samples (water and mud) of salt lakes.

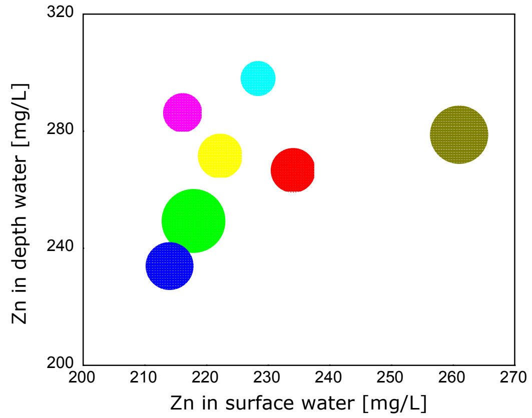

Figure 8 – Zinc concentration in water samples of studied salt lakes.

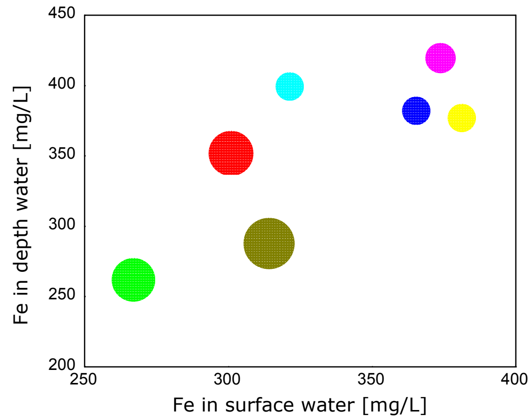

Fig. 9 – Iron concentration in water samples of studied salt lakes.

In water samples Zn levels ranged between 214.113 μg/mL (Ocnita Lake) to 261.221 μg/mL (Amara Lake), in samples collected from surface of lakes, and 233.512 μg/mL (Ocnita Lake) to 297.850 μg/mL (Avram Iancu Lake), in samples collected from different depth of lakes. Zn contents varied significantly from surface to depth of lakes (Figure 8). In this study, heavy metals in mud collected from Techirghiol Lake, Ocnita Lake, Avram Iancu Lake, Brancoveanu Lake, and The bottomless Lake would appear as Fe > Zn > Mn > Ni > Cr > Pb > Cd. In comparison, heavy metals in mud collected from Salt Lake and Amara Lake would appear as Fe > Zn > Mn > Ni > Pb > Cr > Cd.

Generally, Fe is the most abundant and common element in the Earth's crust. This can be one of the reason for which iron was obtained in highest levels in mud sample especially (Table 4). High concentration of iron was obtained in water samples as well (Figure 9). It is well known that the pyrite by oxidation can produce sulphate (Fe^{2+}) and then Fe^{2+} ion, is oxidized to Fe^{3+} by microorganisms such as *Thiobacillus ferrooxidans*.

4. CONCLUSIONS

This study shows that the mud collected from seven salt lakes from Romania (*i.e.* Techirghiol Lake, Salt Lake, Ocnita Lake, Avram Iancu Lake, Brancoveanu Lake, The bottomless Lake, and Amara Lake) consists of a high content of heavy metals when compared with their levels in water. Due to their strong affinity for particles, metals tend to be accumulated by suspended matter or trapped immediately by therapeutic mud from the bottom of lakes. Several metals including Pb, Cd, Cr and Ni have a strong toxicity for aquatic biota, modifying the therapeutic properties of studied salt lakes. In this study a significant relationships between physicochemical parameters (*i.e.* pH, conductivity, turbidity, salinity, and TDS) and heavy metal concentrations were assessed.

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