

## ASSESSMENT OF ENVIRONMENTAL QUALITY IN LACU SĂRAT AREA (BRĂILA COUNTY, ROMANIA)

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**Abstract:** Lacu Sărat resort is located in Chiscani village, 6 km from Brăila town (SE of Romania). The spa is known for its natural curative factors like the mineral water from the lake, the sapropelic mud and the stimulating steppe bio-climate. The aim of the present study was to evaluate the quality of environmental factors and the impact of anthropic activities developed in Lacu Sărat area. A total of 42 samples were collected in order to analyze physico-chemical and chemical parameters such as dissolved ions and heavy metals. The radioactivity was evaluated based on <sup>222</sup>Rn and <sup>226</sup>Ra activity. The study results showed no exceeding of the maximum permissible limits for heavy metals in any of the analyzed soil samples, while the water samples collected from lake showed high levels of Pb, Cr, Ni, and NO<sub>2</sub><sup>-</sup> exceeding in some cases the limits for waters used for bathing/balneological purposes. The dominant ions from water samples are Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>. Radon and radium levels were within the limits recommended by international forums. The sapropelic mud was rich in Fe, Zn, and Ni. Ammonification was found to prevail, while denitrification occurred at low levels, especially in the water phase. The potential of local microbiota to degrade diesel compounds was high, mainly in soils not directly contaminated by petroleum hydrocarbons, with increased levels of nitrites and nitrates.

**Key words:** Lacu Sărat, mineral water, sapropelic mud, balneary tourism, heavy metals, microbiota

### 1. INTRODUCTION

Contamination with heavy metals represents a major ecological problem due to their toxic effects on environment (Morselli et al., 2003; Varol, 2011; Yi et al., 2011; Birch & Apostolatos, 2013). Even more, exposure of humans to high levels of heavy metals can cause various diseases such as malformations, growth diseases, cancer and abortion (Alomary & Belhadj, 2007). However, one of the most important pollution sources are the human activities (Bindler et al., 2011; Liu et al., 2012), coal burning, high-temperature ore processing and agricultural practices being identified as input ways of toxic elements in the environment (Dassenakis et al., 2003; Deepulal et al., 2012; Gao et al., 2005; Gunten et al., 1997).

Lake sediments are important ecological

compounds of the aquatic habitat. They are characterized by high accumulation capacity and most of the adsorbed heavy metals being not biodegradable (Singh et al., 1997; Nemati et al., 2011). Toxic elements are rapidly deposited into the sediments, remaining attached to the fine-grained components such as hydrated oxides of iron and manganese, sulfides, organic matter, and clay minerals (Tessier & Campbell, 1987; Murray et al., 1999; El Bilali et al., 2002). Some of the processes, such as desorption, redox reactions or degradation of the adsorbed substances, can result in releasing the contaminants into the water column (Zoumis et al., 2001; Simpson & Batley, 2009). Thus, sediments are acting not only as reservoirs for toxic metals, but also as pollutant sources for the aquatic systems (Varol, 2011; Nemati et al., 2011; Segura et al., 2006). Therefore, the heavy metal content of the

sediments is vital for evaluation of the pollution degree of the aquatic environment (Alomary & Belhadj, 2007).

In the past, the biogeochemical cycles were balanced due to microorganisms accomplishing their role in a favorable environment. With the increased anthropogenic influences, agricultural and industrial pollutants such as fertilizers and pesticides generate high concentrations of nitrates and nitrites in soil and in water. In addition, contamination with petroleum hydrocarbons affects the biochemical pathways of organic matter degradation and the nutrients cycle, hinders the movement of water and gas exchange, reduces the activity of bacteria and development of plants or worse, can impact drinking water sources and groundwater (Butiuc-Keul, 2015).

The aim of this study was to evaluate the quality of the environmental factors (water, soil and therapeutic mud) in the vicinity of Lacu Sărat Lake, including the industrial area where a power plant, a

paper and cellulose plant and an artificial fiber plant were active. In order to assess this aim a multidisciplinary study was done. Physicochemical parameters (pH, redox potential, electrical conductivity, total dissolved solids, salinity, dissolved oxygen), chemical parameters such as dissolved ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{S}^{2-}$ ), heavy metals (Cd, Cr, Cu, Ni, Pb, Zn, Fe), and radioactivity elements (radon and radium) as well as microbial activities were monitored. Disruption of nitrogen cycle and concurrent pollution with persistent organic contaminants were expected to occur within the study area, due to intensive agriculture and industrial activities. Therefore, biological ammonification and denitrification were investigated. In addition, the ability of local microbiota to grow in petroleum compounds was evaluated.

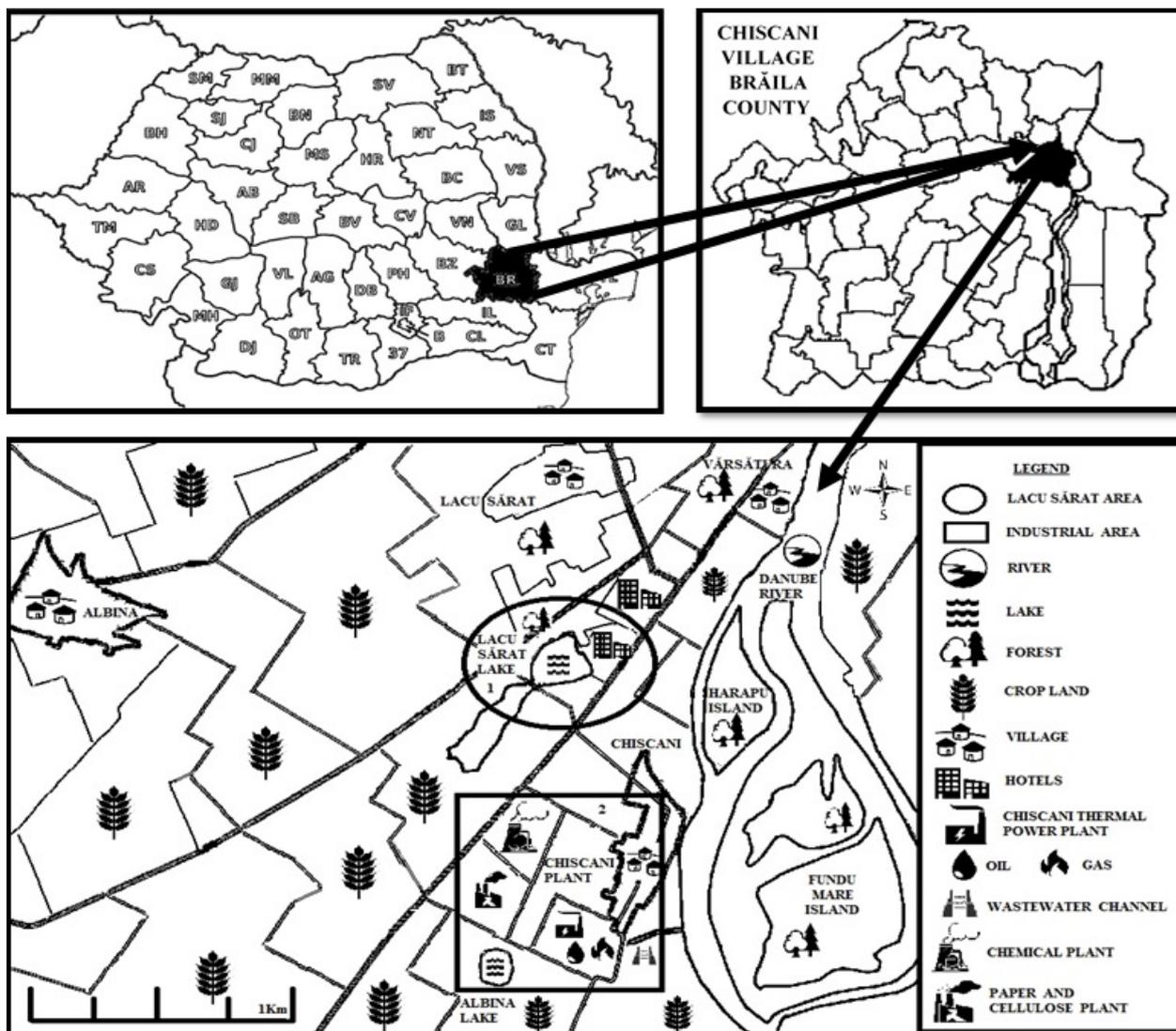


Figure 1. Location of the studied area

## 2. STUDY AREA

### 2.1. Location and description of the study area

The studied area is represented by Lacu Sărat, a lake located in the southeastern part of Romania, 6 km away from Brăila town, on the territory of Chiscani locality (Fig. 1). Lacu Sărat Lake is a hypersaline lake with a sulpho-sodium to chlorosodic and magnesium sulfate water. The water chemical analyses revealed the predominance of sulphates, chlorides, bicarbonates, sodium, calcium and magnesium, the last two elements giving high hardness to the water (Lefter, 2008). A 40cm thick level of sulphurous mud is accumulated on the bottom of the lake. The mud consists of minerals (41%) and organic matter (39%), being formed by silty clay with fine sand sediments transported by the wind, together with microscopic plants and animals which are living in high number in the water and on the lake banks (Câdea & Bădără, 1993).

### 2.2. Geographical and geological background

Geologically, the area is located on the East European Platform and it is bordered by the Fierbinți Fault in north-east and Danube River in south. Numerous sedimentary cycles have been recognized and separated: Paleozoic, Upper Permian-Triassic, Middle Jurassic-Cretaceous, Lower Badenian-Pleistocene and Quaternar (Mutihac et al., 2004).

A continental steppe climate with excessive influences and high thermal amplitudes characterizes the area. The average annual temperature is 11°C, summer average being 22.2°C. Annual relative humidity is 70% (in winter – over 80% and in summer – under 60%). Average annual precipitation does not exceed 450-500 mm during the summer, around 20 rainy days being registered (Munteanu, 2012). The small amount of precipitation is explained by the dominance of continental air masses from the Siberian anticyclones (Dan, 2010). The winds have blowing to E, N, and NE with a mean speed by 3 m/s, those from N reaching up to 100 km/h.

Hydrostatic level is situated at 2-3 m deep. During the rainy season or when the Danube River level is high, the groundwater can reach the surface being subjected to evaporation processes (Munteanu, 2012). The phreatic level is maintained either by the natural drainage through rainfall, or by irrigation and by domestic water which can be lost due to the damages from sewer system.

Due to the shallow groundwater, the soils are

saline, with a high accumulation of salts either at the land surface or within the upper horizons (Albu, 1993).

### 2.3. Human-related activity

The main industrial activity in the area is represented by the chemical one. There are two chemical plants, one producing paper and cellulose, while the other preparing artificial fiber. The construction of paper and cellulose plant began in 1956, the first unit starting to work in 1959. The basic raw material was reed and the main obtained products were represented by stationery cellulose, chemical cellulose, paper, and cardboard, hemicelluloses and lignin. There were some secondary products as a result of the activity, represented by sodium sulphate (3000 t/year), and hypochlorite (Stoiu et al., 1980). The artificial fiber plant was initiated in 1962, producing mainly cotton and wool staple, silk cord, viscose sheet, and carbon disulphide (Gâțescu & Gruescu, 1973). Today, both chemical plants are closed.

Additionally, Chiscani power plant started to work in 1973, using gas and fuel oil as the raw matter (Stoiu et al., 1980). It became one of the biggest power plants in Romania and produced, at that time, most of the electricity available at country level.

Agricultural activities have been practiced in the surrounding area, but the extensive agriculture has declined after 1989.

Today, only the touristic activities are still present on Lacu Sărat area. Lacu Sărat Lake is one of the about ten main salty lakes of Romania. The lake appears as two compartments separated by an industrial railway and a road. However, these compartments are connected through an underground channel blocked by a dam (Horneț, 1991). The lake surface is around 172 ha with a maximum depth of 1.30 m. Additional to the salty water, the sapropelic mud is used in medical treatments. The therapeutic qualities of the water and mud are used to treat various affections, such as degenerative rheumatic diseases, inflammatory, gynecological, dermatological, endocrine, respiratory diseases, disorders of the peripheral nervous system, posttraumatic states (Munteanu, 2012). Based on these qualities Lacu Sărat Lake is one of the most important spa locations of Romania.

## 3. MATERIALS AND METHODS

### 3.1. Sampling

In order to evaluate the environmental

conditions from Lacu Sărat area, a total of 42 samples have been collected during 2014-2015. The samples consisted in waters (22), soils (8) and sediments (12). Some of the sampling points have been located in the vicinity of power plant, chemical paper and cellulose plant and artificial fiber plant (Fig. 2), while other sampling points were located on/and around the Albina Lake and Lacu Sarat Lake (Fig. 3).

### 3.2. Methods

For water samples, the physico-chemical parameters (electrical conductivity, salinity, pH, redox potential and total dissolved solids) were measured *in situ* with a portable multiparameter (WTW Multi 350i). The dissolved ions ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ) were analyzed by ion chromatography (IC 1500 Dionex), while  $NO_2^-$  and  $S^{2-}$  were electrochemical analyzed.

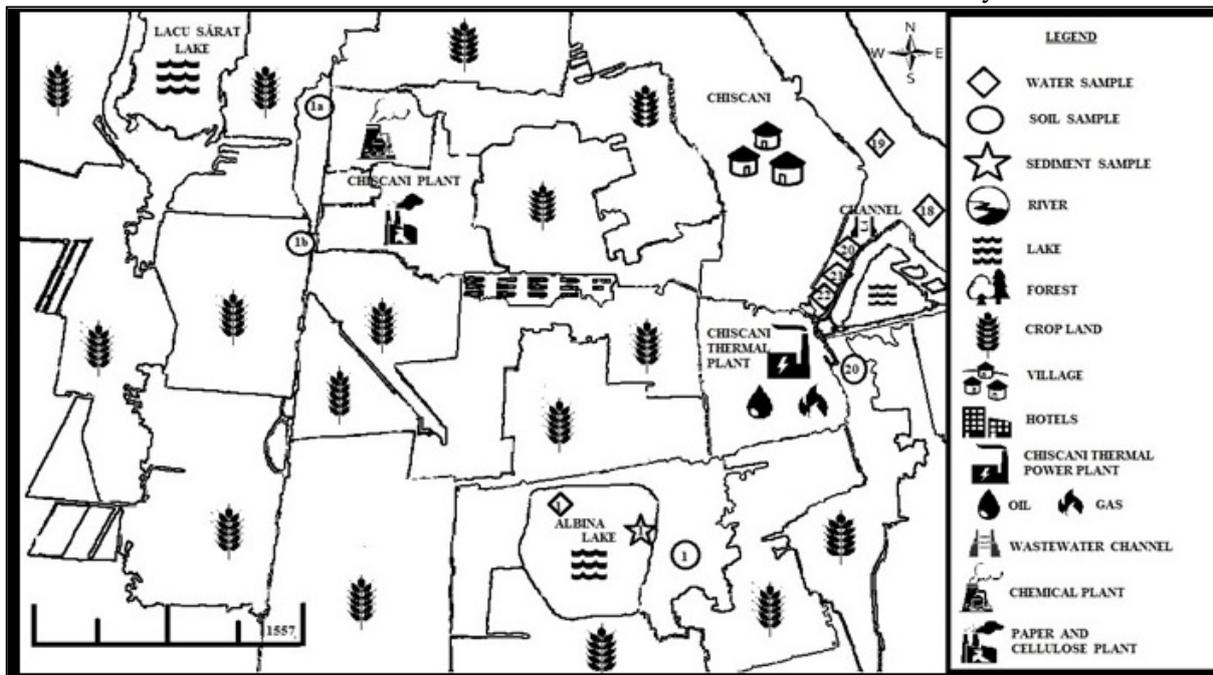


Figure 2. Location of sampling points in the Industrial Area.

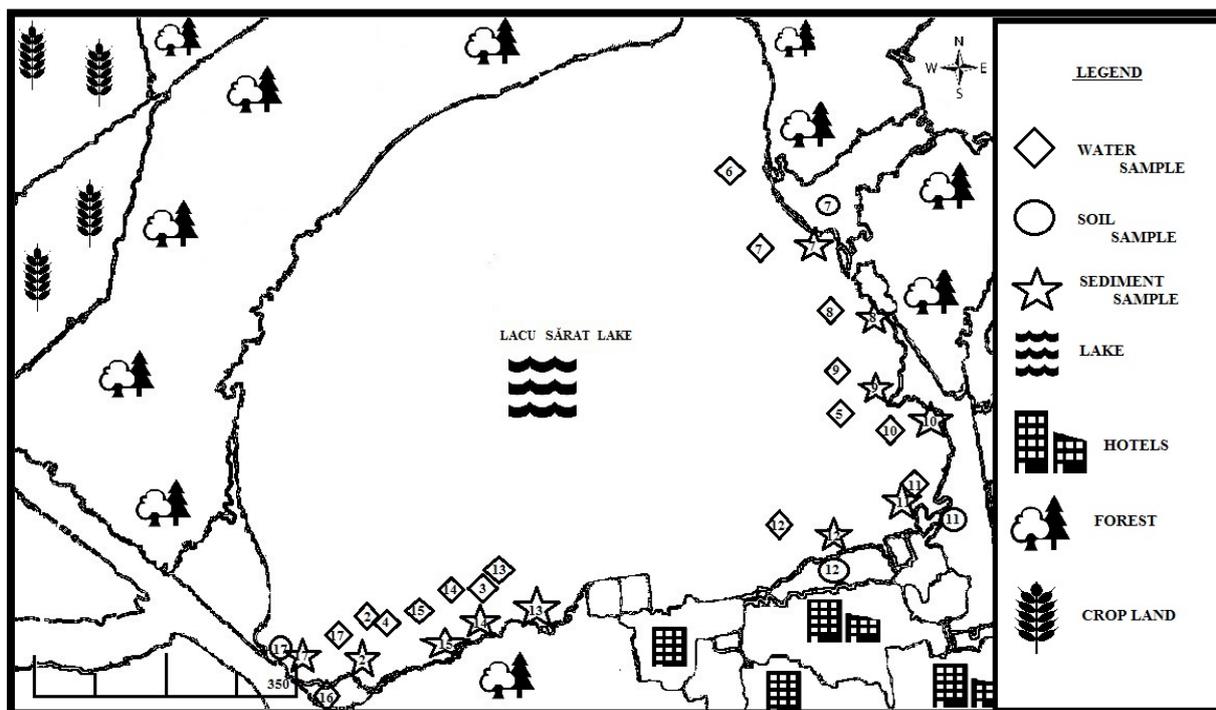


Figure 3. Location of sampling points in the Lacu Sărat Area.

The electrochemical determination of nitrites and sulphides in water, soil and sediment samples was performed using amperometric sensors based on carbon paste electrodes modified with zeolite adsorbed with Toluidine Blue (CPE-Z-TB) for nitrite and Meldola Blue, respectively (CPE-Z-MB) for sulphide. The obtained amperometric sensors CPE-Z-TB and CPE-Z-MBs were used for nitrite and sulphide detection, using the standard addition method

The electrochemical experiments (amperometry) were carried out using an AUTOLAB electrochemical analyzer (Autolab-PGSTAT10, Eco Chemie, Utrecht, Netherlands) and all measurements were performed at room temperature. The electrochemical measurements were performed in a conventional electrochemical cell with three electrodes. Carbon paste was used as working electrode, an Ag/AgCl/KCl<sub>sat</sub> as reference electrode and a Pt wire as counter electrode

Heavy metals were analyzed by atomic absorption flame spectrometry (AAS-F) using the AAS ZEE nit 700 device (Analytik Jena). Before instrumental analysis the water and soil-sediment samples were mineralized with *aqua regia*.

In order to evaluate the pollution degree of the environment in the area and the potential effects upon human health, the concentrations have been compared to the maximum permissible limits imposed by Romanian legislation for surface waters and sediments (Order no. 161/16 February 2006), wastewaters (GD no. 352/21 April 2005), and soil (Order no. 756/3 November 1997) maximum limits issued by the US Environmental Protection Agency (US-EPA).

The presence of bacteria involved in microbial processes was evaluated by the presence of end-products that are specific for certain metabolic pathways. Water samples and soil suspensions and their subsequent dilutions were inoculated in adequate culture media, considering the nutritional and energetic needs for each eco-physiological group of microorganisms (Cusa, 1996; Atlas, 2010). The most probable number of ammonifying bacteria was estimated in peptone culture broth, based on ammonia production. Accumulation of nitrogen and nitrogen oxides in Durham tubes was considered the positive reaction of denitrification, using a minimal medium for denitrifying bacteria. Bushnell-Hass broth, which lacks any carbon sources, supplemented with 1% diesel-oil and 0.01% triphenyl tetrazolium chloride as indicator was used for the assessment of microbial ability to grow in fuel phase. Inoculated tubes and controls were incubated at 22°C for 21 days.

Radon analyses were conducted using a LUK-

VR system with Lucas cells and a special device for radon extraction (scrubber) (Plch, 2002). The following relationship (1) was established for a temperature of 20°C, between the radon concentration in water (A) and the number (N) of counts/second (c/s) recorded by the device – LUK 3A:

$$A \text{ (Bq/l)} = 7.6 \times N \text{ (c/s)} \quad (1)$$

Considering the uncertainty due to measurements and statistics, the minimum detection limit (MDL) has been estimated to be 0.2 Bq/l for the radon analysis, this value for the LD is below the expected lowest radon concentration levels that are found in surface water (normally ~ 1 Bq/l). Statistical errors associated with the radon analysis were 5–6% (Cosma et al., 2008).

Radium was analyzed based on radon concentration after 30 days from sampling, when the secular equilibrium is reached and radium concentration is equal to radon concentration.

Because of the relatively low radium activity in water compared with the radon activity in fresh water, lower detection and quantification limits were required. Thus, by increasing the measuring time to 2400 seconds the quantification limit was brought down to 0.05 Bq/l and a new calibration constant of 5.3 was determined through experiments in our laboratory (Niță et al., 2014).

The radium concentration in water (Bq/l) was determined using the following equation (2) (Moldovan et al., 2009):

$$A \text{ (Bq/l)} = 5.3 \times N \text{ (c/s)} \quad (2)$$

where N (c/s) is the number of measured counts/second.

## 4. RESULTS

### 4.1. Measurement of physico-chemical and chemical parameters

The results of the physico-chemical parameters for water, soil and sediments samples are summarized in Table 1.

#### *Surface water*

Most of the analyzed surface water samples have a pH more than 8.0, the lowest one being 6.5 in the water samples collected from Danube River. The low pH is given, probably by the fact that the waste water from the power plant (Chiscani), located in the Danube plain is discharged in the sampled area. The highest pH (8.4) was registered in water from Lacu Sărat Lake.

Table 1. Summarize of the physico-chemical parameters for water, soil and sediments samples.

Sample type		pH	Eh (mV)	EC ( $\mu\text{S}/\text{cm}$ )	TDS (mg/l)	Salinity (‰)
Surface water	Danube River	6.5 – 6.6* (6.6)	-5.3 – -5.2 (-5.3)	315 – 323 (319)	201 – 206 (203.5)	0.0
	Albina Lake	6.7	-12.2	3230	1421	1.0
	Lacu Sărat Lake	7.2–8.4 (8.1)	-100.6 – -42.8 (-87.3)	419 – 142400 (98411)	268 – 89000 (61714)	0.0 – 101.2 (71.6)
Waste water		6.1 – 7.3 (6.9)	-49.4 – 7.5 (-29.6)	256 – 3390 (2329)	164.0 – 2169.6 (1490.4)	0.0 – 1.7 (1.1)
Soil		3.3 – 7.7 (6.8)	-68.5 – -189.9 (-16.2)	132.6 – 5570 (1972)	85.0 – 8912.0 (1844.4)	0.0 – 3.0 (0.9)
Sediments		6.1 – 7.7 (7.4)	-73.8 – -17.3 (-55.9)	354 – 24200 (17602)	237.0 – 15125.0 (10994.4)	0.0 – 14.6 (10.4)

\*min – max (average)

Regarding the salinity of the collected surface water samples it can be underline the high amount of salts from Lacu Sărat Lake where the obtained values are between 0‰ and 101.2‰. Value 0‰ was identified in the samples collected from Lacu Sărat Lake II (sample 18) which is in connection with Lacu Sărat Lake I, the first one giving a water input into the second one. The other water samples, from Albina Lake and Danube River have a lower salinity ranging between 0 and 1‰.

Electrical conductivity follows the same pattern as salinity, with high values for Lacu Sărat Lake waters (between 419 and 142400  $\mu\text{S}/\text{cm}$ ). Albina Lake contains waters with an electrical conductivity of 3230  $\mu\text{S}/\text{cm}$  and for Danube River the average value is 319  $\mu\text{S}/\text{cm}$ . The values for total dissolved solids are between 268 and 89000 mg/l for Lacu Sărat Lake and between 164.0 and 2169.6 mg/l for Albina Lake and between 201 and 206 mg/l for Danube River. Redox potential has negative values for all the analyzed water samples, ranging between -5.2 and -100.6 mV.

Some differences in physico-chemical parameters of Lacu Sărat Lake waters can be observed between the samples collected from western part of the lake and the samples collected from the eastern part. This is due to the water input from Lacu Sărat Lake II which decrease the salinity, electrical conductivity and total dissolved solids in that part of the lake.

The detection of anions from the collected samples has been done using two methods: ion chromatography for most of the chemical compounds and amperometry for  $\text{NO}_2^-$  and  $\text{S}^{2-}$ . Regarding the  $\text{NO}_2^-$  content the waters from Danube River and Albina Lake can be classified into the 5<sup>th</sup> quality class based on Romanian legislation, and Lacu Sărat Lake into the 4<sup>th</sup> and 5<sup>th</sup> quality classes (Fig. 4). The different values of nitrites from Lacu Sărat Lake are related to the sediment lake content and the extraction location of curative mud.

Other chemical compounds which exceed the

maximum permissible limits are:  $\text{Na}^+$  with the high value reaching 65887 mg/l,  $\text{Mg}^{2+}$  with the highest values of 14340 mg/l,  $\text{Ca}^{2+}$  reaching 1670 mg/l in one sample,  $\text{Cl}^-$  with the highest value of 129481 mg/l,  $\text{NO}_3^-$  with 77.03 mg/l in only one sample (sample 11 from Lacu Sărat Lake),  $\text{NO}_2^-$  with most of the values higher than 1 mg/l and  $\text{SO}_4^{2-}$  with 127356 mg/l in sample 16. Regarding the quality classes for surface waters those from Lacu Sărat Lake can be included into 5<sup>th</sup> one in the western part of the lake, and into 3<sup>rd</sup> class for the western part of the lake from  $\text{Na}^+$  and  $\text{Cl}^-$  content point of view, and those from Danube River and Albina Lake into the 5<sup>th</sup> quality class from  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  content point of view. Generally, the anions and cations distribution in surface waters was:  $\text{Cl}^- > \text{SO}_4^{2-} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{Ca}^{2+} > \text{NO}_2^- > \text{S}^{2-} > \text{NO}_3^-$  (Fig. 4).

The concentrations of heavy metals into the analyzed surface water samples were relatively high for chromium (2.2 – 142.9  $\mu\text{g}/\text{l}$ ), zinc (50.7 – 260.8  $\mu\text{g}/\text{l}$ ), and iron (29.4 – 812.4  $\mu\text{g}/\text{l}$ ). The highest values have been registered for lead (15.9 – 1546.0  $\mu\text{g}/\text{l}$ , average of 303.2  $\mu\text{g}/\text{l}$ ) and nickel (27.6 – 1443  $\mu\text{g}/\text{l}$ , average of 389.6  $\mu\text{g}/\text{l}$ ) (Fig. 5), these two metals exceeding the maximum permissible limits for 1<sup>st</sup> quality class (5  $\mu\text{g}/\text{l}$  and 10  $\mu\text{g}/\text{l}$ ), even by 309 times (e.g. sample 4) and 144 times respectively.

These high levels can be due to the high dilution of the samples (up to 500 times) which were done prior to AAS analysis; such high dilution can lead to analytical errors. Similar results were obtained in the study conducted by Rădulescu et al. (2014) in the Lacu Sărat area. Because of the high levels of lead and nickel, these waters can be classified into the 5<sup>th</sup> quality class. Lead poisoning is one of the most dangerous forms of intoxication at the global level, this metal can be accumulated in blood and it can be transmitted from mother to child during pregnancy. The most exposed are the children, who may suffer from deficiencies in their cognitive development (Tong et al., 2000).

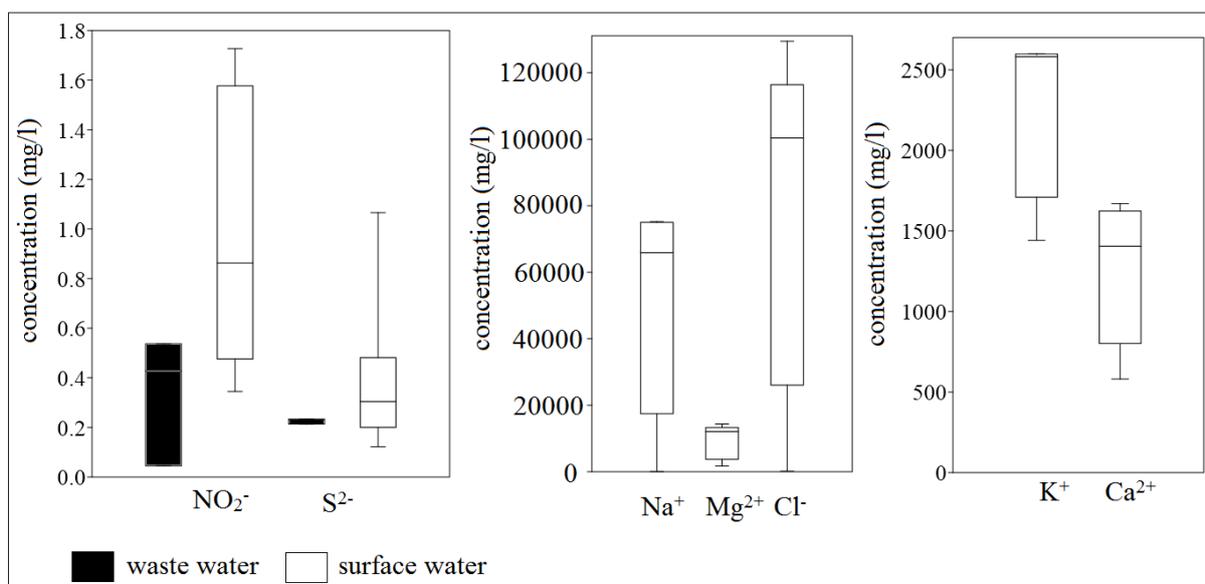


Figure 4. Concentration of the major dissolved ions in water samples.

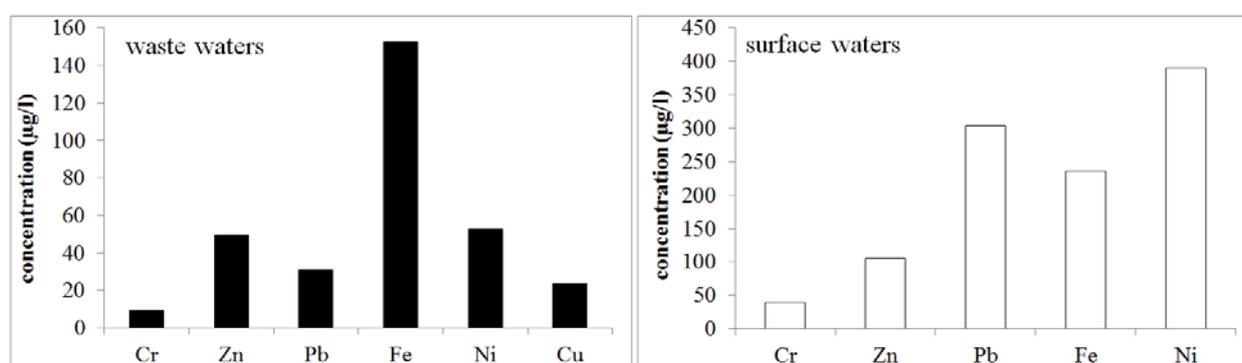


Figure 5. Heavy metals content in waste water (left) and surface waters (right) samples.

#### **Waste water**

Waste water samples have been collected from the evacuation channels from the power plant. These waters are discharged in Danube River without any treatment. Anyway, the lowest pH is under the limits imposed by the national legislation (6.5-8.5) being 6.1, having a positive (7.5 mV) redox potential. The waste waters had relatively high levels of electrical conductivity (256 – 3390  $\mu\text{S}/\text{cm}$ ) and total dissolved solids (164 – 2169.6 mg/l) (Table 1).

Analyzed waste waters are within permissible limits regarding Romanian legislation, for both  $\text{NO}_2^-$  and  $\text{SO}_4^{2-}$  point of view (Fig. 4). For the analyzed waste water samples, no exceeding of the heavy metals content can be outlined, all the values are into the permissible limits. The highest value has been recognized for Fe (Fig. 5).

#### **Soil and sediments**

The soil samples can be divided into sensitive and less sensitive soils. Thus, those collected from power plant and former paper and cellulose chemical

complex are included into the less sensitive soils category and those from Lacu Sărat area into the sensitive soils category. Physico-chemical parameters for soils are as follows: pH between 3.3 and 7.7; salinity between 0 and 3.0‰; electrical conductivity between 132.6 and 5570  $\mu\text{S}/\text{cm}$ , total dissolved solids between 85 and 8912 mg/l, and redox potential between -68.5 and 189.9 mV. A correlation can be observed between all the analyzed parameters in order that the sample with low pH has the highest salinity, electrical conductivity and total dissolved solids, and a positive redox potential (Table 1).

The values of physico-chemical parameters for sediment samples are different from Albina Lake to Lacu Sărat Lake. While the salinity of sediments from Albina Lake was 0, the sediments from Lacu Sărat Lake have a considerably higher salinity (4.8 - 14.6 ‰). Registered pH is within permissible limits (6.5-8.5), redox potential is negative for all the studied samples, electrical conductivity and TDS is high for Lacu Sărat Lake (reaching 24 200  $\mu\text{S}/\text{cm}$ , and 15.125 mg/l respectively).

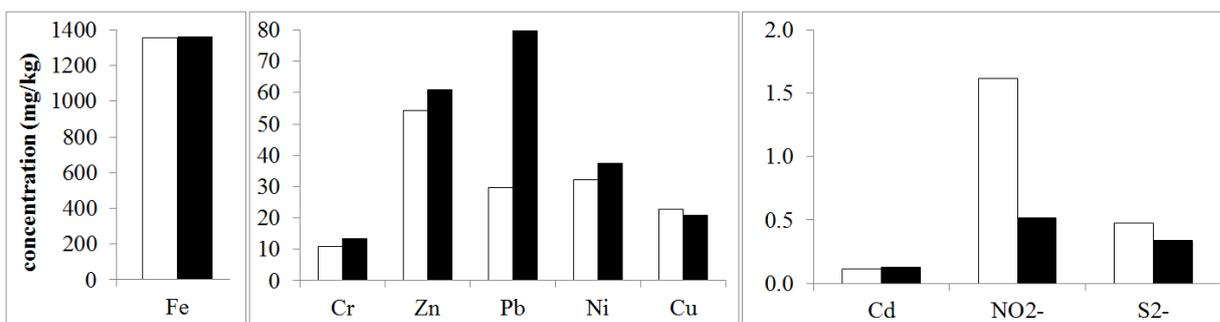


Figure 6. Average levels (mg/kg) of heavy metals, NO<sub>2</sub><sup>-</sup> and S<sup>2-</sup> in soil and sediment samples.

The highest content of NO<sub>2</sub><sup>-</sup> was registered into the less sensitive soils (between 0.54 mg/kg and 4.38 mg/kg). For SO<sub>4</sub><sup>2-</sup> the values are ranging between 0.05 mg/kg and 1.08 mg/kg into the sample collected from power plant. Sediment samples have NO<sub>2</sub><sup>-</sup> content between 0.12 mg/kg and 1.10 mg/kg (average of 0.52 mg/kg) (Fig.6) and SO<sub>4</sub><sup>2-</sup> content between 0.19 mg/kg and 0.55 mg/kg. It is necessary to mention that both nitrites and sulphides are not normalized by the Romanian legislation.

The soils had a low content of heavy metals. With the exception of Pb, Ni and Cu, the other metals were within normal values mentioned in national legislation (Fig. 6). The levels of all analyzed heavy metals were within alert threshold.

Sediments proved to have higher heavy metal content than soils. Regarding the heavy metal content a contamination was detected into the sediment samples from both analyzed lakes, especially with Ni (average of 37.32 mg/kg) and Pb (average of 79.75 mg/kg) (Fig. 6). Lead content is double than maximum permissible limit for some samples collected from Lacu Sărat Lake.

#### 4.2. Measurement of radioactivity

The results for the radioactivity measurements are summarized in Table 2. Water from the sewer resulted from "technological processes" is not substantially enriched with radon and radium. Radon and radium concentration measured in two different points show values which do not endanger the environment in which this water is discharged.

Table 2. Radon and radium concentration in sewer waters and Albina Lake from Brăila County

Source	Radon concentration (Bq/l)	Radium concentration (mBq/l)
Sewer	7.06 ± 0.9	79.50 ± 12
Sewer towards the road	5.62 ± 0.7	77.29 ± 11
Albina Lake	4.84 ± 0.6	53.2 ± 0.9

The recommended radon concentrations for surface water range between 1-10 Bq/l (US EPA, 1999) while the recommended concentration for radium range between 50-100 mBq/l (WHO, 2008). Therefore, the values obtained for the concentration of radon and radium is within the limits recommended by international forums regarding surface water.

#### 4.3. Bacteria involved in the nitrogen cycle and degradation of petroleum compounds

Four water samples have been included in the microbial assay, two waste water samples collected from the power plant inlet and outlet channels, together with two surface water samples from Lacu Albina and Lacu Sărat Lake. Four soil samples (paper mill area, power plant area, Albina Lake bank and agricultural soil in the area of Lacu Sărat Lake) were also analysed in order to estimate the most probable numbers of ammonifying (AMB), denitrifying (DB) and diesel-degrading bacteria (DDB).

Ammonification was observed as the most prevalent microbial process in both the water and soil consortia (Fig. 7). In water samples, minimum 54 ammonifying bacteria/ml were found in the power plant inlet channel and 9.2 x 10<sup>3</sup> bacteria/ml in Lacu Sărat Lake. Larger values of ammonifying bacteria were found to characterize the soils, between 11.29 x 10<sup>4</sup> cells/g of dry soil around the power plant and 8.89 x 10<sup>8</sup> cells/g of soil from Lacu Albina bank.

Meanwhile, microbial denitrification occurred at very low intensities, especially within the water phase, between 0.2 cells/ml (power plant inlet channel and Lacu Sărat Lake) and 1.4 denitrifying bacteria/ml (power plant outlet channel) being detected. In soil samples, minimum 2.21 x 10<sup>2</sup> and maximum 17.56 x 10<sup>4</sup> denitrifying bacteria were found per gram of soil around the paper mill and nearby Lacu Albina, respectively.

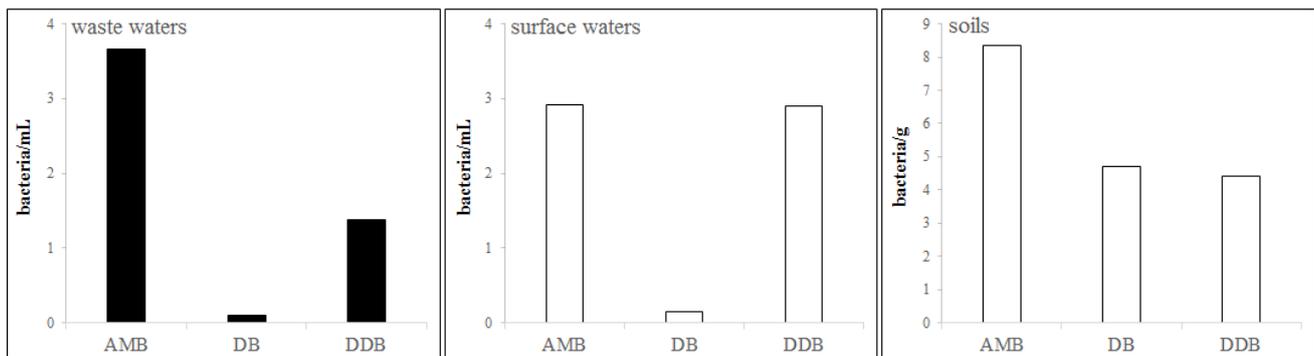


Figure 7 - Microbial activity in surface waters and soils, average values. AMB: ammonifying bacteria; DB: denitrifying bacteria; DDB: diesel degrading bacteria.

The ability of local microbiota to degrade petroleum compounds was observed to roughly follow the ammonification potential: from 11 cells/ml (power plant inlet channel) to  $1.6 \times 10^2$  bacteria/ml (power plant outlet channel) in water samples, and from  $11.28 \times 10^3$  cells/g (power plant area) to  $4.5 \times 10^4$  bacteria/g of soil (Lacu Albina area).

The increased frequency of ammonifying bacteria indicate enhanced mineralization processes, as expected to occur in environments with high organic content. This occurs mainly within Lacu Sărat Lake where the sapropelic mud is an important source of nutrients. The soils in the Lacu Albina area and the rich agricultural soils nearby Lacu Sărat Lake are also dominated by ammonifying bacteria able to degrade the organic matter rich in ammonia up to nitrogen oxides and nitrogen gas.

The prevalence of ammonification among the microbial processes was also described in previous studies investigating the nitrogen cycle in freshwater reservoirs (Curticăpean et al., 2005) and biofilms (Farkas et al., 2013). Recently, Zhao et al., (2015) revealed that ammonification occurs mostly in lakes impacted by aquaculture, agriculture or residential areas, where the source of ammonia might be associated with nitrogen compounds used in agriculture runoffs or human waste. Denitrification prevails in environments with increased anthropogenic inputs of nitrogen arising from such diverse sources such as fertilizer run-off, selvage discharges or aquaculture, but can also be related to natural factors associated with the base erosions, soil erosion and atmosphere deposition. The high levels of denitrifying bacteria found around Lacu Albina and also in the agricultural soil, together with the elevated levels of nitrites may be explained by the local situation, characterised by the intensive use of fertilizers in the past. Denitrification occurred at very low rates in the water phase, in all sampling locations.

Enhanced activity of diesel degrading bacteria

was expected to occur in samples collected from the Chiscani power plant, related to hydrocarbon contamination. This association was observed only for the water phase, while increased potential of diesel oil decomposition occurred in less disturbed soils. Current bioremediation strategies of petroleum contaminated sites demonstrate that increased microbial degradation of petroleum hydrocarbons occurs in enhanced nitrate environments, in parallel with denitrification (Holtze, 2011). In this study the potential of local microbiota to degrade diesel oil was observed to merely follow the ammonification rates, and to occur at higher rates in soils not directly impacted by petroleum compounds, with increased levels of nitrites and nitrates.

## 5. CONCLUSIONS

In the current study the concentration of dissolved ions, heavy metals, radioactivity, and activity of bacteria have been investigated in Lacu Sărat area.

Based on the high level of  $\text{NO}_2^-$ ,  $\text{Cl}^-$ , Pb, and Ni the waters from southwestern part of the Lacu Sărat Lake can be classified into the 5<sup>th</sup> quality class while the waters from eastern part are assigned to 2<sup>nd</sup> and 3<sup>th</sup> class based on the level of  $\text{NO}_2^-$  and Fe content. The surface waters (Danube River and Albina Lake) from Chiscani area can be classified into the 2<sup>nd</sup> quality class regarding the concentration of  $\text{Cl}^-$ , Pb and Ni levels. High levels of  $\text{NO}_2^-$  (between 29.5–45.5 mg/l) have been identified into the discharged channel from Thermoelectric Power Plant.

The concentration of heavy metals into the sediment samples from Lacu Sărat Lake is low for most of the analyzed elements, exceeding the maximum permissible limits only for Ni and Pb. High levels of Fe and  $\text{NO}_2^-$  have been identified in all the investigated sediment samples.

High levels of Fe and  $\text{NO}_2^-$  were determined into the sediment samples from Albina Lake, but only Ni is exceeding the maximum permissible limits.

Low levels of heavy metals (except Fe) are identified into the soil samples from Chiscani area, with no exceeding of maximum permissible limits. Regarding the dissolved ions, only NO<sub>2</sub><sup>-</sup> exceeds the normal values from Romanian legislation.

The values obtained for the concentration of <sup>226</sup>Ra and <sup>222</sup>Rn are within the limits recommended by international forums regarding surface water.

Microbial activity tracking may serve as an important tool to assess the variety and magnitude of natural or anthropogenic disturbances in impacted areas. In this study, the high prevalence of ammonifying bacteria indicate increased potential for decomposition of organic matter by local microbial consortia from Lacu Sărat Lake, Albina Lake and adjacent soils. The low levels of denitrification occurred in the water phase, while enhanced activity was present in soils previously affected by extensive agriculture. The potential of local microbiota to degrade diesel compounds was observed to merely follow the ammonification rates, and to occur mainly in soils not directly contaminated by petroleum hydrocarbons, with increased levels of nitrites and nitrates.

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#### REFERENCES

- Albu, D.**, 1993. *Natural reservations, protected areas, and natural monuments from Brăila county*. Ed. Alma, Galați, 128. (in Romanian)
- Alomary, A. A. & Belhadj, S.**, 2007. *Determination of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, Zn) by ICP-OES and their speciation in Algerian Mediterranean Sea sediments after a five-stage sequential extraction procedure*. Environ. Monit. Assess. 135, 265–280.
- Atlas, R. M.**, 2010. *Handbook of Microbiological Media*, 4th ed., CRC Press, New York, 286p.
- Bindler, R., Rydberg, J. & Renberg, I.**, 2011. *Establishing natural sediment reference conditions for metals and the legacy of long-range and local pollution on lakes in Europe*. J. Paleolimnol. 45, 519–531.
- Birch, G. F. & Apostolatos, C.**, 2013. *Use of sedimentary metals to predict metal concentrations in blackmussel (*Mytilus galloprovincialis*) tissue and risk to human health (Sydney estuary, Australia)*. Environ. Sci. Pollut. Res. 20, 5481–5491.
- Butiuc-Keul, A.**, 2015. *General biology* Presa Universitară Clujeană, Cluj-Napoca, 203-215 p (in Romanian).
- Cândeia, I. & Bădără, D.**, 1993. *Brăila annals*. I (I) Ed. Istros a Muzeului Brăilei, Brăila, 270. (in Romanian).
- Cosma, C., Moldovan, M., Dicu, T. & Kovacs, T.**, 2008. *Radon in water from Transylvania (Romania)*. Radiation Measurements, 43, 1423–1428.
- Curticăpean, M. & Drăgan-Bularda, M.**, 2005. *The quantitative distribution of some ecological groups of bacteria from the Tarnita dam reservoir*, Stud. Univ. Babeş-Bol. Biologia, 2, 147-163.
- Cusa, V.**, 1996. *Methodological instructions for microbiological analysis of aquatic sediments*, Institute for Research and Environmental Engineering, Bucharest, 14-20 p, (in Romanian).
- Dan, S.**, 2010. *The valorification of balnear potential of Brăila county*. Lakes, Reservoirs and Ponds, 10, 276 – 283, (in Romanian).
- Dassenakis, M., Andrianos, H., Depiazzi, G., Konstantas, A., Karabela, M., Sakellari, A. & Scoulios, M.**, 2003. *The use of various methods for the study of metal pollution in marine sediments, the case of Euvoikos Gulf, Greece*. Appl. Geochem. 18, 781–794.
- Deepulal, P. M., Kumar, T. R. G., Sujatha, C. H. & George, R.**, 2012. *Chemometric study on the trace metal accumulation in the sediments of the Cochin Estuary, Southwest coast of India*. Environ. Monit. Assess. 184, 6261–6279.
- El Bilali, L., Rasmussen, P., Hall, G. & Fortin, D.**, 2002. *Role of sediment composition in trace metal distribution in lake sediments*. Appl. Geochem. 17, 1171–1181.
- Farkas, A., Drăgan-Bularda, M., Muntean, V., Ciatarâș, D., Țigan, Ș.**, 2013. *Microbial activity in drinking water-associated biofilms*. Central European Journal of Biology, 8(2) 201-214.
- Gao, N., Armatas, N. G., Shanley, J. B., Kamman, N. C., Miller, E. K., Keeler, G. J., Scherbatskoy, T., Holsen, T. M., Young, T., McIlroy, L., Drake, S., Olsen, B. & Cady, C.**, 2005. *Mass balance assessment for mercury in Lake Champlain*. Environ. Sci. Technol. 40, 82–89.
- Găstescu, P. & Gruescu, I. S.**, 1973. *Brăila county*. Ed. Academiei Republicii Socialiste România, București, 149, (in Romanian).
- Gunten, von H. R., Sturm, M. & Moser, R. N.**, 1997. *200-Year record of metals in lake sediments and natural background concentrations*. Environ. Sci. Technol. 31, 2193–2197.
- Holtze, D. L.**, 2011. *Demonstration of nitrate-enhanced in situ bioremediation at a petroleum hydrocarbon contaminated site*. PhD thesis, University of Waterloo, Ontario, 321.
- Horneț, N.**, 1991. *The monography of Chiscani village – Brăila county*. Ed. Porto-Franco, Galați, 90. (In Romanian), 90.
- Lefter, D. V.**, 2008. *Contributions to the knowledge of*

- the epidemiological aspects of the clinical and socio-economic arthrosis diseases registered in Brăila county and the therapeutical efficiency of the physico-chemical factors from "Lacu Sărat" spa. Ed. Olimpiada, Brăila, 78, (in Romanian).
- Liu, E., Shen, J., Birch, G., Yang, X., Wu, Y. & Xue, B.,** 2012. Human-induced change in sedimentary trace metals and phosphorus in Chaohu Lake, China, over the past halfmillennium. *J. Paleolimnol.* 47, 677–691.
- Moldovan, M., Cosma, C., Encian, I. & Dicu, T.,** 2009. Radium-226 concentration in Romanian bottled mineral waters, *J. Radioanal. Nucl. Chem.* 279, 487–49.
- Morselli, L., Olivieri, P., Brusori, B. & Passarini, F.,** 2003. Soluble and insoluble fractions of heavy metals in wet and dry atmospheric depositions in Bologna, Italy. *Environ. Pollut.* 124, 457–469.
- Munteanu, I.,** 2012. *Lacul Sărat - Istoricul stațiunii.* Ed. EX LIBRIS., 145.
- Murray, K. S., Cauvet, D., Lybeer, M. & Thomas, J. C.,** 1999. Particle size and chemical control of heavy metals in bed sediment from the Rouge River, Southeast Michigan. *Environ. Sci. Technol.* 33, 987–992.
- Mutihac, V., Stratulat, I. M. & Fechet, R. M.,** 2004. *Geology of Romania.* Ed. Didactică și Pedagogică, București, 38????, (in Romanian).
- Nemati, K., Abu Bakar, N. K., Bin Abas, M. R., Sobhanzadeh, E. & Low, K. H.,** 2011. Comparison of unmodified and modified BCR sequential extraction schemes for the fractionation of heavy metals in shrimp aquaculture sludge from Selangor, Malaysia. *Environ. Monit. Assess.* 176, 313–320.
- Niță, D., Cosma, C. & Moldovan, M.,** 2014. Radon measurement in carbonated water with the Lucas cell and charcoal adsorption methods. *Journal of radioanalytical and Nuclear Chemistry*, 299, 25-30.
- Plch, J.,** 2002. *Radon Detector LUK 3A. Manual for Operating LUK 3A.* Jiri Plch M Eng SMM, Prague, 48p.
- Rădulescu, C., Dulamă, I. D., Stîhi, C., Ioniță, I., Chilian, A., Necula, C. & Chelărescu, E. D.,** 2014. Determination of heavy metal levels in water and therapeutic mud by atomic absorption spectrometry. *Rom. Journ. Phys.* 59(9-10), 1057-1066.
- Segura, R., Arancibia, V., Zúñiga, M. C. & Pastén, P.,** 2006. Distribution of copper, zinc, lead and cadmium concentrations in stream sediments from the Mapocho River in Santiago, Chile. *J. Geochem. Explor.* 91, 71–80.
- Simpson, S. L. & Batley, G. E.,** 2009. Predicting metal toxicity in sediments: a critique of current approaches. *Integr. Environ. Assess. Manag.* 3, 18–31.
- Singh, M., Ansari, A., Müller, G. & Singh, I.,** 1997. Heavy metals in freshly deposited sediments of the Gomati River (a tributary of the Ganga River): effects of human activities. *Environ. Geol.* 29, 246–252.
- Stoiu, V., Anastasiu, F., Berian, S., Constantinescu, V., Furtună, A., Harțuche, N., Hîrjoghe, C., Mocioiu, N., Petică, E., Popescu, A., Popescu, C., Rusesvu, V. & Țîru, I.,** 1980. *Brăila - monography.* Ed. Sport - Turism, București, 363, (in Romanian).
- Tessier, A. & Campbell, P.,** 1987. Partitioning of trace metals in sediments: relationships with bioavailability. *Hydrobiologia* 149, 43–52.
- Tong, S., Schirnding, von Y. E. & Prapamontol, T.,** 2000. Environmental lead exposure: a public health problem of global dimensions. *Bulletin of the World Health Organization*, 78(9), 1068-1077.
- US EPA,** 1999. *National primary drinking water regulations: radionuclides (Proposed Rule) Federal Register.* 56(138), 33050.
- Varol, M.,** 2011. Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *J. Hazard. Mater.* 195, 355–364.
- WHO,** 2008. *Guidelines for drinking-water quality* (third edition), Volume 1, 668p.
- Yi, Y., Yang, Z. & Zhang, S.,** 2011, Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. *Environ. Pollut.* 159, 2575–2585.
- Zhao, X. Y., Wei, Z., Zhao, Y., Xi, B., Wang, X., Zhao, T., Zhang, X. & Wei, Y.,** 2015. Environmental factors influencing the distribution of ammonifying and denitrifying bacteria and water qualities in 10 lakes and reservoirs of the Northeast, China. *Microbial Biotechnology*, 8(3), 541-548.
- Zoumis, T., Schmidt, A., Grigoroza, L. & Calmano, W.,** 2001. Contaminants in sediments: remobilisation and demobilisation. *Sci. Total Environ.* 266, 195–202.

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