

DETERMINATION AND ASSESSMENTS OF PHYSICO-CHEMICAL PARAMETERS OF THE WATER FROM ANTHROPO-SALINE LAKES LOCATED IN THE PROTECTED AREA “SALINA TURDA”, ROMANIA

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ABSTRACT. It was carried out the monitoring of the qualitative parameters for the "Ocnei" and "Rotund" lakes located in the protected area "Salina Turda", Romania, and as well it was made a comparative analysis of the results with previous determinations. It was determined the evolution of the physico-chemical parameters on 5 segments of depth. The monitoring was carried out within 2 measurement campaigns. It has been determined that the lakes tend to lose basicity and it was found that the heliotherm phenomenon represents a stable index in comparison with previous determinations.

Keywords: *anthropo-saline lakes, water quality, physico-chemical parameters*

INTRODUCTION

Saltwater is a natural resource useful for health, its therapeutic qualities being known from the 19th century, and its exploitation must be done in an appropriate way. Improving human's health and prophylactic action is the major objective of the therapeutic use of water with a high salinity content. Salty lakes are the basis of the spa activity.

As a result of the increased demands of the body, generated by the modern lifestyle, new aspects of morbidity appear, with the predominance of degenerative diseases, sequelae after trauma or accidents, diseases that have a debilitating potential picked up. In these cases, balneary medicine is not limited to medicinal treatment, widening the scope of therapeutic interventions by applying natural remodeling, here as well as the therapeutic action of salt lakes and baths in salted water.

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Saline aquatic systems are classified into two categories: thalassohaline (derived from sea water) or athalassohaline (i.e., of land origin) [1].

"Ocnei" and "Rotund" lakes are anthropo-saline and they have chlorinated-sodic mineral waters, with mineralization ranging between 19.27 mg/l and 225 mg/l. These lakes are sensitive to climate change through alterations, precipitation patterns and evaporation potential that may lead to dilution, further concentration, or even drying [2].

The therapeutic value of organic-rich sediments and the physico-chemical peculiarities of salt waters (e.g., heliotherapy) represents one of the most important two characteristics of values, so that they contribute to their scientific valorization [3]. Stratification and currents in lakes are determined by the weather conditions [4].

Ocnei lake was formed by the collapse of an old salt mine around 1800 [3].

The high chlorine concentration in these lakes is reflected in the salinity of the water, which is why the lake is very pleasant during the hot season for salt baths for therapeutic purposes [5].

Sodium chloride (NaCl), which is a thermophile molecule has an impact on the salinity of the warm layer by increasing it during the day [6].

Where salt lakes occur, they represent the dominant aquatic resource and they also are the critical components of the natural environment. What makes them important research model systems in microbial niche differentiation and biogeochemical cycling is their physical stability coupled with vertical water column partitioning [7].

The purpose of this paper is to determine the water quality status of the salty lakes located in the protected area "Salina Turda" after 7 years from opening.

There have been 2 measurement campaigns for the physico-chemical parameters of the lakes water, on 5 segments of depth, in order to determine their quality status.

For the knowledge of the water quality of the lakes located in the protected area "Salina Turda", namely "Ocnei" and "Rotund" lakes, during the course of the research, were organized 2 measurement campaigns in order to determine the basic parameters.

The lakes are fed by rainfall and freshwater springs and the level of the water is maintained constant by an artificial drainage channel towards the sărata Valley [8]. They are located in Transylvania which is an area with residual relief and diapiric areas [9]. This perimeter is on the western border of the Transylvanian basin, in a diapiric zone that appears in the form of salt masses [10].

"Ocnei" lake is one of the most important and representative lacustrine units of the existing nine lakes in Turda area (Cluj County), Romania, mainly because of its considerable depth (around 33 m) and volume (around 26,000 m³ by 2001) [11]. The ionic composition of Ocnei Lake is similar to seawater [12].

Previous analyzes have shown that the limit values of certain physico-chemical and microbiological parameters of lakes water are exceeded. This is due to the exploitation of lakes in an unorganized setting [13].

In order to establishing the measurement periods, it was considered the behavior of the two lakes under different natural condition. For comparisons there are the results of the studies carried out in previous years.

RESULTS AND DISCUSSION

Experimental research on "Rotund" lake

The experimental research was developed between 2 measurements campaigns.

Following the analyzes carried out on April 14th, 2016 (first campaign), on the "Rotund" lake, were found the following:

The climatological data identified: 33.1% atmospheric humidity; 26.5 °C air temperature; 3.8 ÷ 5.6 m/s air currents; 26 °C air temperature at the level of the water; 37% water humidity at the level of the water; clear sky.

Since the equipment is dedicated for measuring at different depths, on the sensor immersion cable, were made 5 signs corresponding to each depth of measurement.

The lake water has a neutral character with a pH value of 8.14 at a depth of - 0.3 meters and 6.43 at a depth of - 4 meters, therefore the variation of the parameter is within the neutrality range of water.

The water conductivity exceeds 200 mS/cm at a depth of - 4 meters and on other deep segments it increases slightly.

The water temperature on the water mirror is 21.73 °C, having an increase up to a depth of - 2 meters followed by a slight decrease up to a depth of - 4 meters where was recorded 18.71 °C.

The salinity of the lake exceeds 70 units of PSU in all segments of depth.

The total solids dissolved (TDS) into the water of the lake increases with the depth, so at the level of the water mirror was identified the amount of 61.29 g/l and at the depth of - 4 meters it was identified 116 g/l dissolved solids.

From the results of the analyzes carried out on 11 August 2005 by the specialists of the S.C. Salina Turda S.A., it was found a basic pH with a limit value of 8.5 [14]. The analyzes resulted from the pH monitoring during April 2016 are confirmed in the literature by S.C. Salina Turda S.A. in August 2005, and in both cases, it was found that the pH is slightly basic, having the tendency to decrease the basicity, which requires a constant monitoring of this indicator.

Following the analyzes carried out on June 08th, 2016 (second campaign), on the "Rotund" lake, were found the following:

The lake water is slightly basic with a pH value of 8.79 at a depth of - 0.2 meters and 6.78 with a neutral character at a depth of - 4 meters, therefore the variation of the parameter lies in the field of water neutrality; water conductivity exceeds 200 mS/cm at a depth of - 4 meters and on other deep segments it increases slightly.

The water temperature at a depth of - 0.2 meters is 25.39 °C with a first increase up to a depth of - 1 meter followed by a slight decrease up to a depth of - 3 meters, where was recorded 29.07 °C and at - 4 meters was determined a temperature of 22.84 °C.

The salinity of the lake exceeds 70 units of PSU (Maximum Sensor Limit) on most deep segments, except for the water mirror level where was recorded 44.11 units of PSU.

The total dissolved solids (TDS) in the lake water are growing with the increasing of the depth, so it was found 32.99 g/l at the water mirror level and at a depth of - 4 meters a quantity of 117.76 g/l solids dissolved.

The pH determined, in the second measurement campaign had a higher value, across all the segments of depth, than the value determined in the first measurement campaign.

At S.C. Salina Turda S.A., it was found the results of the analyzes carried out during the period of August 2005, prior to the touristic arrangement of the lakes. At that time, water was neutral at the upper permissible limit (pH = 8.5).

As a result of the analyzes in the second campaign it was found that the water has a slightly basic character (pH = 8.79).

Considering the tendency to decrease basicity, is required to monitor the pH of the lake once a year, possibly, in the same period.

Table 1. The evolution of the physico-chemical parameters on depth for the "Rotund" lake

Depth (m)	pH		Temperature (°C)		TDS (mg/l)		Conductivity (mS/cm ^A)	
	First campaign	Second campaign	First campaign	Second campaign	First campaign	Second campaign	First campaign	Second campaign
-0.2		8.79		25.39		32.99		72.18
-0.3	8.14	8.31	28.29	38.36	61.29	58.24	130.44	145.62
-1	8.07	8.26	28.57	39.17	63.5	61.1	135.25	151.02
-2	8.07	8.34	25.71	35.76	65	65.68	131.94	158.4
-3	7.62	7.58	22.1	29.07	84.08	91.19	158.83	196.65
-4	6.43	6.78	18.71	22.84	116	117.76	204.45	226.46

In 2016, in terms of thermal regime for the first campaign, it was recorded the temperature of, approximately 28 °C at the level of the water mirror (- 0.3 meters) with a slight increase of 0.3 °C up to a depth of - 1 meter. It was noticed that the temperature is dropping up to 22 °C at a depth of - 3 meters and 18 °C at a depth of - 4 meters.

In the second research determination, it was recorded the temperature of 25.39 °C at the water mirror level (- 0.2 meters) with a significant increase up to a depth of - 0.3 meters where the temperature was 38.36 °C. As for the depth of - 1 meter, the temperature recorded a slight increase up to 39.17 °C. On the other segments of depth, the temperature is in a slight decrease, at a depth of - 3 meters, recording 29.07 °C and at a depth of - 4 meters, the temperature dropped sharply up to 22.84 °C.

The water conductivity of the lake has an increasing value starting with the first segment of depth studied.

For the first campaign, it was recorded a value of 130.44 mS/cm^A at the water mirror level, followed by a steady increase up to the level of the last segment of depth where the conductivity exceeded the value of 200 mS/cm^A.

In the second campaign it was recorded a value of 72.18 mS/cm^A at the water mirror level, followed by a steady increase up to the last segment of depth where the conductivity was 226.46 mS/cm^A.

The total of solids dissolved in the water of the "Rotund" lake increase with the increasing of the depth. From the measurements made in April, 14th, at the water mirror level was determined a value of 61.29 mg/l TDS and at a depth of - 4 meters 116 mg/l TDS. In June, 08th, it was found at the water mirror level a value of 32.99 mg/l TDS and at the depth of - 4 m 117.76 mg/l TDS.

The salinity determined in the water of the "Rotund" lake exceeds 70 units of PSU.

Analyzing the results obtained, it was observed that with the increasing of the depth, the conductivity of the water also increases.

The amount of dissolved oxygen is maintained constant (0 mg/l) throughout the depth due to a long period of stagnation of the lake because of the interruption of the spa activity due to the unfavorable climatic conditions for bathing.

The results are compared with the analyzes conducted during the warm season of the year, namely August 2005, where was recorded a value of 9.21 mg/l dissolved oxygen [14]. The value of dissolved oxygen is directly influenced by the water disorder due by the balnear treatment.

Experimental research on "Ocnei" lake

In order to determine the values of the quality parameters of the "Ocnei" lake, a number of 17 sampling points have been established as a result of its sketching.

By following the analyzes carried out on April 14th, 2016 (first campaign), on "Ocnei" lake, it was found:

The climatological data identified: 42% atmospheric humidity; 24.2 °C air temperature; 0.7 ÷ 3.1 m/s air currents; 23.8 °C air temperature at the water level; 46% water humidity at the water level; clear sky.

The lake water has a neutral character with a pH value of 8.38 at a depth of - 0.3 meters and 6.45 at a depth of - 4 meters, therefore the variation of the parameter is in the neutral range of water.

The water conductivity exceeds 200 mS/cm at a depth of - 4 m and on other deep segments it slightly increases.

The water temperature on the mirror is 21.73 °C, having an increase up to a depth of - 2 meters followed by a slight decrease up to a depth of - 4 m where the temperature recorded was 25.14 °C.

The salinity of the lake exceeds 70 units of PSU in all segments of depth.

The total dissolved solids (TDS) in the water of the lake grow with the increasing of the depth, so at the water mirror level it was found 61.29 g/l TDS and at a depth of - 4 m it was recorded 116.51 g/l TDS.

The second determination was carried out in June 08th, 2016 (second campaign), for the "Ocnei" lake and it was observed the following issues:

The lake water has a neutral character with a pH value of 8.63 at a depth of - 0.2 meters and 6.56 at a depth of - 4 meters, therefore the variation of the parameter is in the neutral range of water.

The water conductivity exceeds 200 mS/cm at a depth of - 4 meters and on other deep segments the conductivity increases.

The water temperature, at a depth of - 0.2 meters, was 22.66 °C, having a first increase up to - 1 meter, followed by a slight decrease up to - 3 meters, where was recorded a temperature of 33 - 34 °C. At a depth of - 4 meters it was recorded 30.95 °C.

The salinity of the lake exceeds 70 units of PSU in most deep segments, except for the water mirror level where was recorded 62.29 units of PSU.

The total dissolved solids (TDS) in the water of the lake increases with the depth, so at the water mirror level was identified a quantity of 61.29 g/l TDS and at a depth of - 4 meters 118.72 g/l TDS.

By following the analyzes performed on April 14th, on "Ocnei" lake, it was found a basic pH between 8.38 in the water mirror level and a near neutral pH with a value of 6.45 at a depth of - 4 meters. For the second campaign it was determined a basic pH with a value of 8.63 on the water mirror and a neutral pH with a value of 6.56 at a depth of - 4 meters.

From the results of the analyzes carried out on 11.08.2005, by the specialists of the S.C. Salina Turda S.A., it was found a pH of 8.8 [14].

Table 2. The evolution of the physico-chemical parameters on depth for the "Ocnei" lake

Depth (m)	pH		Temperature (°C)		TDS (mg/l)		Conductivity (mS/cm ^A)	
	First campaign	Second campaign	First campaign	Second campaign	First campaign	Second campaign	First campaign	Second campaign
-0.2		8.63		22.66		61.29		85.8
-0.3	8.38	8.39	21.73	33.48	61.29	54.26	94.62	124
-1	8.16	8.25	26.03	35.49	64.96	64.3	132.36	132.36
-2	8.15	8.23	26.06	33.2	65.32	64.39	133.26	148.85
-3	7.28	7.3	25.59	33.93	99.04	105.7	199.65	246.72
-4	6.45	6.56	25.14	30.95	116.51	118.72	233.41	264.1

The analyzes resulted from the pH monitoring during April 2016 are confirmed in the literature by S.C. Salina Turda S.A. carried out in August 2005, and in both cases it was found that the pH is slightly basic, having the tendency to decrease the basicity of the lake.

In the first campaign, in terms of thermal regime, the temperature of 21.73 °C was found at the water mirror level, with a significant increase up to a depth of - 2 meters where was recorded a temperature of 26.06 °C. In June, 2016, it was recorded 22.66 °C at the water mirror level, at a depth of - 0.2 meters, with a significant increase up to a depth of - 0.3 meters where the temperature determined was 33.48 °C. As for the depth of - 1 meter, in the second campaign, the temperature was slightly increased up to 35.49 °C. As far as the temperatures on the other segments of depth are concerned, they are in a slight decrease, at a depth of - 4 meters being recorded 30.95 °C. For the depth of - 3 and - 4 meters, the temperature recorded a slight decrease up to 25.59 °C at a depth of - 3 meters and 25.14 °C at a depth of - 4 meters.

The salinity determined in the water of Lake "Ocnei" exceeds 70 units of PSU.

The water conductivity has an increasing process starting with the first segment of depth up to the last one.

The conductivity of the lake, determined on April 14th, 2016, recorded a value of 94.62 mS/cm^A at the water mirror level, followed by a steady increase up to the last segment of depth, where the conductivity exceeded 200 mS/cm^A. On the other hand, on June 08th, 2016, has an increasing value starting with the first depth segment studied. A value of 85.8 mS/cm^A was recorded at the water mirror level, followed by a steady rise up to a depth of - 2 meters, where was recorded a slight decrease in conductivity.

The total dissolved solids in the water of the "Ocnei" lake increases with the increasing of the depth.

From the measurements developed in April 2016 at the level of the water mirror was determined 55.53 mg/l and at a depth of - 4 meters was recorded a value of 116.51 mg/l.

In June, 2016, the total dissolved solids in the water of "Ocnei" lake grow with the increasing of the depth, so the measurements made at the water mirror level determined a value of 43.93 mg/l and at the depth of - 4 m was recorded the value of 118.72 mg/l.

The amount of dissolved oxygen in April 2016 is maintained constant, 0 mg/l, throughout the depth of the water due to a long period of stagnation of the lake because the spa activity was interrupted due to the unfavorable climatic conditions for bathing. Compared with the results of the analysis performed during the warm season of the year, namely August 2005, where a dissolved oxygen value of 11.22 mg/l was recorded [14]. This value being directly influenced by the water disorder followed by the balnear treatment.

CONCLUSIONS

The pH determined in the two measurement campaigns was lower compared to the measurements made in 2005, but is in the neutral pH range (6.5 ÷ 8.5). From these determinations it was found that lakes tend to lose basicity.

There is a high influence on the temperature of the water caused by the climatic conditions. The temperature of the lakes is steadily increasing up to the half of the depth of the study, following a gradual decrease with the increasing of the depth.

This temperature variation is observed in both measurement campaigns. Temperature is strictly influenced by the weather conditions and the heliotherm phenomenon. In the second campaign, the temperature of the water mirror level was lower compared to the one determined in the first campaign, due to a rainy period. Measurements made in 2005 do not influence the findings of the 2016 analysis, climatic issues being variable.

Conductivity of the lake increases progressively with increasing of the depth in both measurement campaigns.

The water salinity exceeds the detection limit of the sensor. The determination of the parameter value was achieved only at the level of the water mirror, at the depth of - 0.2 meters.

EXPERIMENTAL SECTION

In order to carry out physico-chemical analyzes of the water lakes from the "Salina Turda" area, the water samples were taken from different depths, namely: from the level of the water mirror (- 0.3 meters), -1 meter, - 2 meters, - 3 meters and as well as - 4 meters.



Figure 1. Location of the salt lakes from the protected area "Salina Turda"

This environment is called meromictic because the water is stratified and the water column is clearly divided into distinct water masses that mix slowly or do not intermix at all [15].

The measurement campaign took place in April 2016 (the first measurement campaign), as well as in June 2016 (the second measurement campaign). The second measurement campaign was based on the results obtained from the first analysis campaign.

To determine the quality parameters of the lakes, the following are set:

- the maximum depth of analysis is - 4 meters, depth at which changes may occur from bathing pads;
- depth sampling - 0.3 meters, - 1 meter, - 2 meters, - 3 meters, - 4 meters;
- collecting samples on the lake water mirror.

General Work Steps:

- the sketch of the analysis lake;
- making the grid for establishing the sampling points;
- preparation of registration forms;
 - instrument calibration and ground preparation for sampling;
 - analysis of microclimate parameters (air temperature, atmospheric humidity, wind speed and water temperature);
- boat movement at the originally set points and in-situ depth analysis;
- registration of values;
- the interpretation of the results.

For the “Rotund” lake, the first research was accomplished in April, 14th, 2016, and the second one in June, 08th, same year. In the first measurement campaign, a number of 9 cropping points per diameter were chosen depending on the surface of the lake (figure 2).

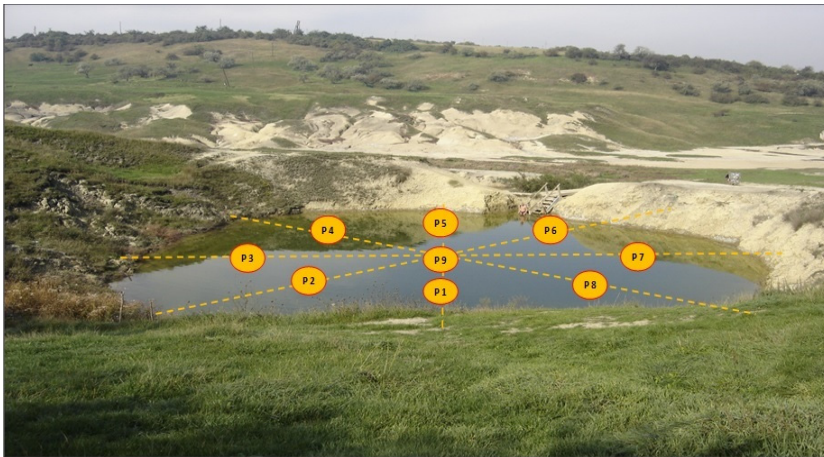


Figure 2. Distribution of the sampling points for “Rotund” lake

At each point, 5 samples were collected on depths of - 0.2 meters, - 0.3 meters, - 1 meter, - 2 meters, - 3 meters and - 4 meters. In the vicinity of the banks, where the depth of the lake is smaller, the measurement took place at the bottom of the lake.

As for the “Ocnei” lake, a number of 17 picking points per diameter were chosen depending on the surface of the lake (figure 3). The research was carried out at the same depths as for the “Rotund” lake.

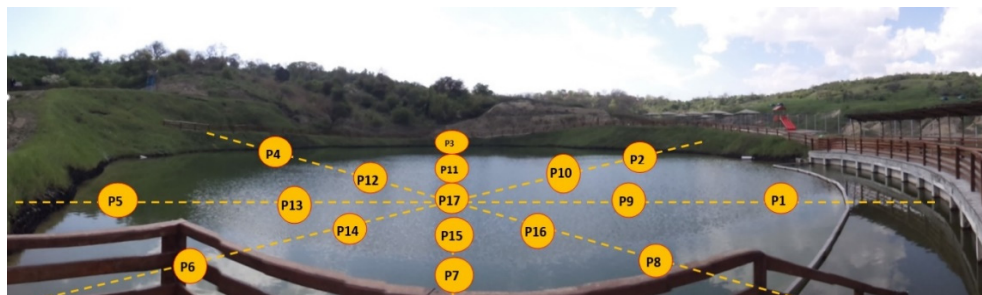


Figure 3. Distribution of the sampling points for "Ocnei" lake

From the physical point of view, samples were taken and analyzed to determine the following properties: pH, turbidity, conductivity, resistivity, sea water density, temperature and TDS, and from the chemical point of view samples were also taken and analyzed in order to determine the chemical properties characteristic of the lakes studied, namely: dissolved oxygen and salinity.

These analyzes were performed using the Hanna HI 9829 multiparameter instrument with which determinations were performed on site.

Research on the distribution of physico-chemical water quality parameters in the two lakes took place in April and June, 2016, when measurements were made using the Hanna HI 9829 multi-parameter instrument on 5 deep segments.

Hanna HI 9829 is a multi-parameter instrument which monitors 14 essential water quality parameters (7 measured and 7 calculated). The device is portable and is equipped with a multi-sensor probe that makes possible the measurement of the following parameters: pH, ORP, turbidity, dissolved oxygen, conductivity, chlorine, nitrate, ammonia and temperature. The Hanna turbidity sensor conforms to ISO 7027.

In order to determine the microclimate parameters (on-site determinations) during the deployment of the measurement campaigns, it was used the *Almemo 2390-5* multifunctional instrument.

The *Almemo 2390-5* multifunctional measuring instrument is a device for measuring microclimate parameters.

This instrument comprises 3 detection sensors:

- Sensor for measuring the light intensity;
- Air speed sensor;
- Humidity and temperature sensor.

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