QUALITY ANALYSIS OF OCNA SIBIULUI'S LAKES I. PHYSICAL-CHEMICAL AND BACTERIOLOGICAL DESCRIPTION OF WATERS

MARIA POPLĂCEAN[1]

S.C. Apă-Canal S.A. Sibiu, Laborator analize apă potabilă

Abstract: This paper present the results obtained at the physical-chemical and microbiological analysis of thirteen hypersaline lakes in the Ocna Sibiului region in Romania. Three of these lakes (Cloşca Lake, Crişan Lake and Horia Lake) have a low mineralization degree, low concentration of chlorides and calcium and a reduced amount of organic matter, whereas the Black Lake is characterized by a high mineralization degree, maximum amount of chlorides and organic matter, a reduced concentration of dissolved oxygen, minimum pH. Brâncoveanu Lake is characterized by hight mineralization of water, high concentration of chlorides and calcium, high hardness and dissolved oxygen. Ocnița Lake, Bottomless Lake, The Mine's Mouth Lake, Swallow Lake, The Lake with insland, The Mud Lake present moderate degree of mineralisation, moderate concentration of chlorides and calcium

Cloşca Lake, Linnen Lake and Cats Lake present maximum values of faecal indicators. Most of the other lakes show a lower number of colonies and faecal coliform organisms. The low value of bacteriological parameters reflects that the faecal contamination was reduced in those periods when the bathing season was closed.

Keywords: water, microbiological analysis, chemical analysis, hhypersaline lake, Ocna Sibiului

INTRODUCTION

Ocna Sibiului hypersaline lakes show a high curative potential, both through the waters and the mud that have therapeutic property. The risk of falling ill or of infection associated to the swimming pools and to the balneary water is connected with the water's contamination with faecal impurities. The faecal contamination may be caused by the people who take a bath or by the sources of contaminated water (Oprean and Poplacean, 2005).

In this study we present researches regarding the physic-chemical and bacteriological monitoring, comparing the results obtained from waters in the

[1] Corresponding author: Maria Poplăcean, S.C. Apă-Canal S.A. Sibiu, Laborator analize apă potabilă, E-mail: oplaceanmaria@yahoo.com

thirteen salty lakes of Ocna Sibiului.

MATERIALS AND METHODS

Materials

These researches were done in three campaigns during the cold season (November 2006, January and March 2007).
The analysis were done on the samples taken from thirteen lakes: Fără fund Lake, Cloşca Lake, Horia Lake, Crişan Lake, Ocna Pustie Lake, Ocnița Lake, Cu nămol Lake, Mâțelor Lake, Rândunica Lake, Brâncoveanu Lake, Pânzelor Lake, Negru Lake, With island Lake, Mine's Mouth Lake. Their general characteristics are presented in (Alinei et al., 2006).
The equipments and the chemical used for analyses are presented in Tables 1 and 2.

Table 1. Equipments used to determine bacteriological and chemical parameters and technical characteristics

No	The name of the equipment	The producer, country	Measuring range / accuracy
1.	Autoclave STERIMATE	ASTELL-SCIENTIFIC, U.K.	-temperature: 0^0..150^0, pressure: 0..4 bar, time: 0..60 min
2.	Thermostat MEMMERT BE 400	MEMMERT GmbH+ CO.KG Germany	- temperature range: $0,5^0$..70^0C - accuracy: $\pm$0,1^{o}C
3.	Spectrophotometer with molecular absorption Jenway 6100	JENWAY, England	- spectral range: 320...920 nm - photometric accuracy 0,005 Abs. , $\pm$0,1%T
4.	Multi-parameter instrument MULTILINE P4-SET 3 - pH / redox sensor	WTW , Germany	pH : 0..14 unit pH, accuracy 0,01$\pm$1 digit, reference system Ag /AgCl gel, redox: accuracy 1 mV$\pm$1 digit
	- dissolved oxygen sensor		Oxygen saturation - measuring range 0..199,9% - accuracy: $\pm$0,5% oxygen concetration - measuring range 0..19,9mg/ l - accuracy: 0,1mg/l
	- conductivity sensor		- measuring range 0..1999μS/cm

			- accuracy: ±1%
	- integrated temperature sensor		- measuring range 5^0..99,9°C - accuracy: 0,1K±1 digit
5.	Analytical balance PRECISA 205 A SCS	METTLER TOLEDO, Switzerland	- measuring range 0...200 g
6.	Mono-distiller GFL 2104	GFL, Germany	Distillation volume 4 l / h
7.	Drying oven 100 dm^3	ITM, Romania	Chamber volume : 100 dm^3 - measuring range 40^0…220^0C
8.	Thermo reactor CR 2010 WTW,8 loc	WTW, Germany	Working temperatures 100^0C ; 120^0C ; 148^0C
9.	Water baths WB14	WTW Germany	volume : 14 l range : 10^0….95^0C
10.	Magnetic stirrer Oxi-Stirrer 300	WTW, Germany	
11.	Calcination oven ZB/2	ASAL S.R.L. Italy	

Table 2. Reagents and materials used for bacteriological and chemical determination

Parameters	**Reagents**	**Materials**
Oxidability	- distilled water - Sulfuric acid p.a .(d = 1,84 kg/ dm^3) - Potassium permanganate	- Flasks Erlenmayer 300 cm^3 and 1000 cm^3
	0,1 V: weighted and wrapped in ampoulle - Potassium permanganate 0,01N - Oxalic acid 0,1 N: weighted and wrapped in ampoulle - Oxalic acid 0,01 N Titrisol - Merck	- Automatic burette according to Pellet, with lateral stopcook, class A, 50 ml, with 0,1 ml gradation and maximum tolerated error ± 0,05 ml - Flasks volumetric 1000 ml , class A, the uncertainty of measuring ± 0,4 ml - Pipette transfer with one mark 100 ml, class A, maximum tolerated error ± 0,08 ml
Fixed residuum		- Crucible 50 … 100 ml - Graduated pipette 10 … 100 ml - Filter paper with low porosity
pH	- Technical buffer pH :4,01 - Technical buffer pH :7,00 - Electrolyte solution KCl	- Beokers -thermometer with divided scale at $0,5^0$C

Total hardness	- Distilled water - Chloric acid (d:1,9 kg/ dm^3) - Ammonium chloride - Titriplex III solution for metal titration c(Na_2- EDTA·2 H_2O) -Calcium carbonate -Black eryochrom T, murexid, naphthol green B, sodic chloride	- Flasks volumetric 500 ml, 1000 ml , class A - Pipette transfer with one mark 100 ml, class A, - Burette with straight bore stopcock, Schellbach line, class A, 25 ml, with 0,05 ml gradation and maximum tolerated error ± 0,03 ml
Calcium	- Distilled water - Chloric acid (d: 1,9 kg/ l) – Sodium hydroxide - Titriplex III solution for metal titration c(Na_2- EDTA·2 H_2O) -Calcium carbonate -Black eryochrom T, murexid, naphthol green B, sodic chloride	- Flasks volumetric 1000 ml, class A, maximum tolerated error ± 0,4 ml - Burette with straight bore stopcock, Schellbach line, class A, 25 ml, with 0,05 ml ml gradation and maximum tolerated error ± 0,03 ml -Pipette transfer with one mark 100 ml, class A, maximum tolerated error ± 0,08 ml
Chlorides	- Distilled water - Nitric acid (d: 1,4 kg/ dm^3) - Nitric acid conc. 0,05 n - Diphenyl carbazonum - Bromophenol blue ind. - Ethylic alcohol 96 % - Mercury II nitrate solution, 0,1 n - Mercury II nitrate solution 0,01 n - Sodic chloride - Sodium hydroxide	- Flasks volumetric 100, 200 ml, class A, - Graduated pipette 1, 5, 10, 20 ml class AS - Burette 10 ml, Schellbach line, class AS with 0,02 ml gradation and maximum tolerated error ± 0,02 ml .
Coliforms bacteria	- Lauryl Sulfate Tryptose Broth - simple - Lauryl Sulfate Tryptose Broth - concentrate - Eozine Blue Metylene Lactose Agar (GEAM Levine) - Buffered water sterile solution in use	- Sterile test tubes 16 x 160 mm - Durham tubes - Petri dishes with 10 cm diameters - Sterile graduated pipette $1cm^3$ and $10cm^3$ - Sterile bottle $250cm^3$ - Bacteriological acus
Thermotolerant coliforms bacteria	-B.C.P. Bromocresol Purple-Lactose Broth (Mac Conkey Broth)	- Sterile test tubes 16 x 160 mm, sterile - Durham tubes - Pasteur sterile pipette

Enterococi	- Azide Broth - simple - Azide Broth - concentrate -Azide Broth with bromo cresol purple -Buffered water sterile solution	- Sterile test tubes 16 x 160 mm -Sterile graduated pipette 1cm³ and 10cm³ - Pasteur sterile pipette - Sterile bottle 250cm³
Escherichia coli	- Triptone water - Erlich – Kovacs reagent	- Sterile test tubes 16 x 160 mm - Pasteur sterile pipette

Methods

In order to establish the level of bacteriological pollution and that of constitution of potential risk for health, bacteriological parameters were determined: the most probable number of coliforms bacteria, the most probable number of thermotolerant coliformic bacteria, most probable number of enterococi. The bacteriological analysis of water in cold season reflects low values of faecal pollution parameters (Oprean and Poplacean, 2006a) (Oprean and Poplacean, 2006b). The physical-chemical parameters determined during the investigation of salty lakes' water were temperature, pH, total hardness, the organic substances, calcium, the chlorines and the fixed residue. The bacteriological and the physical-chemical parameters were determined using standard methods (Table 3).

Table 3. Determined parameters and analysis methods used

Parameters determined	**Analysis methods**
Coliforms bacteria	STAS 3001-1991
Thermotolerant coliforms bacteria	STAS 3001-1991
Enterococi	STAS 3001-1991
Chlorides	STAS 3049-1988
Total hardness	STAS 3026 -1976
Calcium	STAS 3662 - 1990
Fixed residuum	STAS 9187 - 1984
Oxidability	STAS 3002 -1985
pH	SR ISO 10523-1997
Temperature	STAS 6324-1961

RESULTS AND DISCUSSION

The physical-chemical parameters determined in those three campaigns varied according to the figures 1 – 7.

As Figure 1 shows, the temperature in the analysed lakes varies from 7^0 C – 12^0 C in November, 4^0 C – $9{,}5^0$ C in January and $5{,}5^0$ C – $13{,}5^0$ C in March.

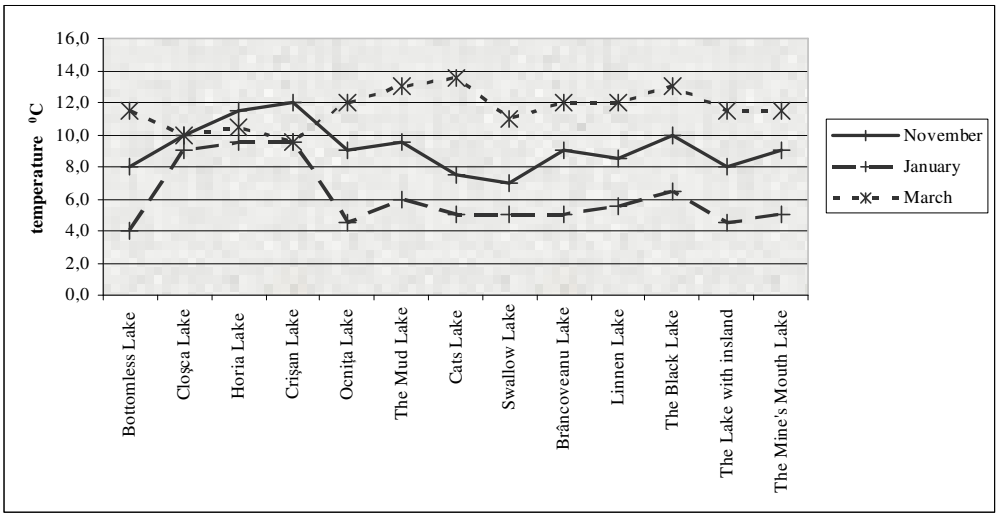

Figure 1. Variation diagram for water's temperature in Ocna Sibiului lakes

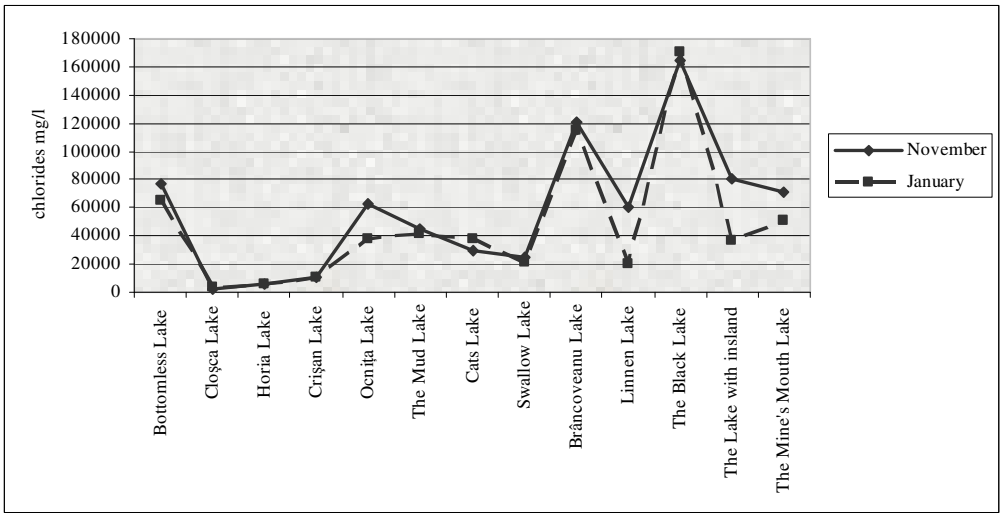

Figure 2. Variation diagram for water's chlorides in Ocna Sibiului lakes

Chlorides concentration varies in a large domain, from minimum: 2864 mg/l in Cloşca Lake to maximum: 170422 mg/l in The Black Lake. The variations during seasons appear only for some lakes, as Linnen Lake and the Mine's Mouth Lake.

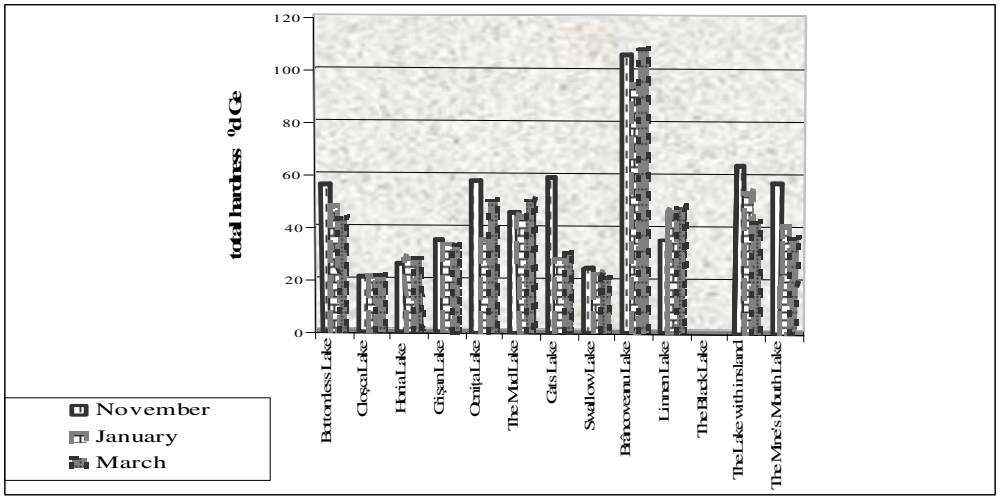

Figure 3 Variation diagram for water's total hardness in Ocna Sibiului lakes

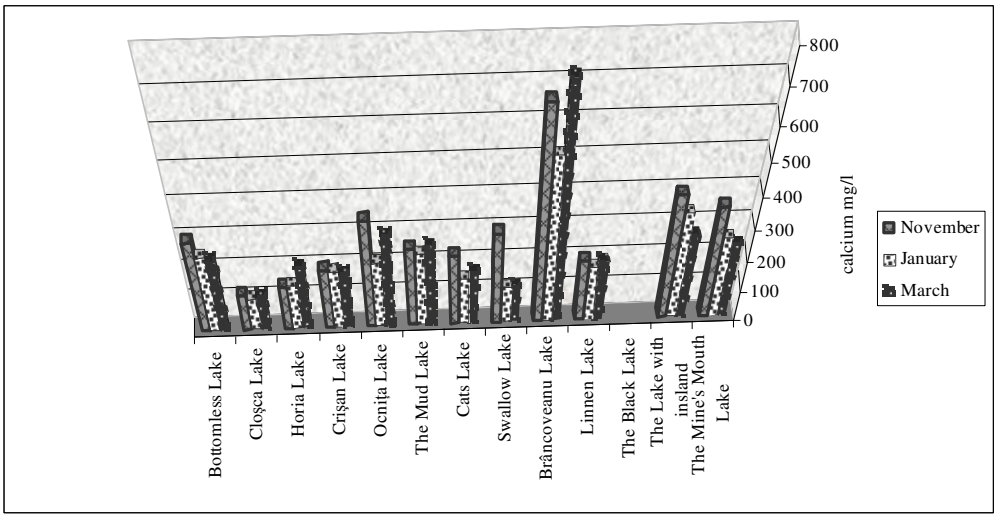

Figure 4. Variation diagram for water's calcium in Ocna Sibiului lakes

Total hardness (figure 3) varies from minimum: $20,76^0$dGe in the Cloşca and Swallow lakes to maximum: $107,99^0$dGe in the Brâncoveanu Lake. No significant variations during seasons are observed.
In the case of calcium concentration the extreme values are obtained:

- Minimum: 105,15 mg/l– Cloşca Lake
- Maximum: 723,44 mg/l – Brâncoveanu Lake (figure 4)

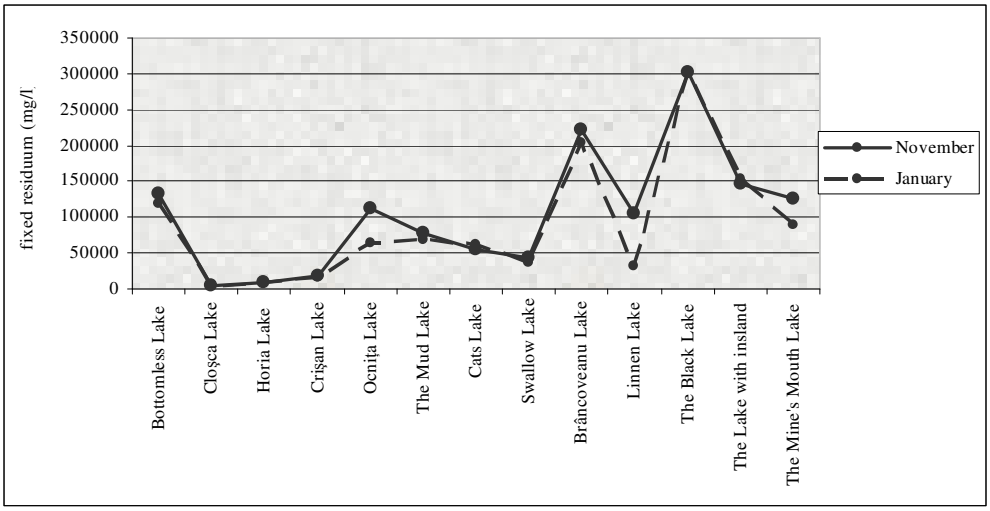

Figure 5. Water's fixed residuum in Ocna Sibiului lakes

Fixed residue varies between a minimal value (3700 - 5000 mg/l in the Cloşca Lake, Horia Lake, Crişan Lake) and a maximal value (301700 mg/l in The Black Lake, Brâncoveanu Lake), as Figure 5 shows. It can be observed that for this characteristic, no significant differences between seasons appear.

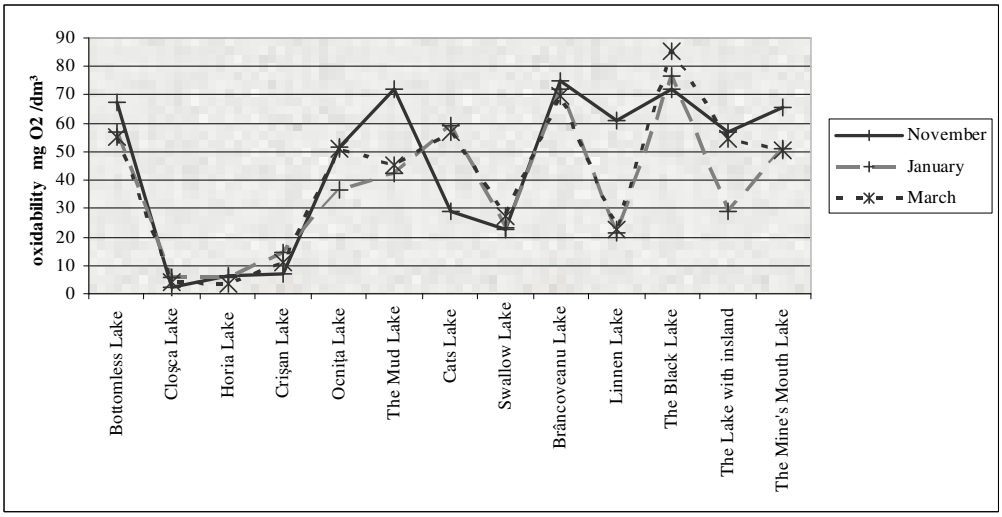

Figure 6. Variation diagram for water's oxidability in Ocna Sibiului lakes

Figure 6 presents the results obtained at the analysis of oxidability. This characteristic is directly correlated with the content in oxidable matters, as

the organic compounds. Beside natural causes, these compounds arrive in lakes with people, because some of them (excepting Brâncoveanu Lake, With Island Lake, Mine's Mouth Lake and Black Lake) are open for swimming.
For this parameter, the minimal values varies between 2,39 and 5 mg O_2/l in Cloşca Lake, Horia Lake, Crişan Lake and the maximal value is 75,15 mg O_2/l in The Black Lake and Brâncoveanu Lake. The seasonal analysis of this characteristic shows a variation between November and the other two months (January and March).

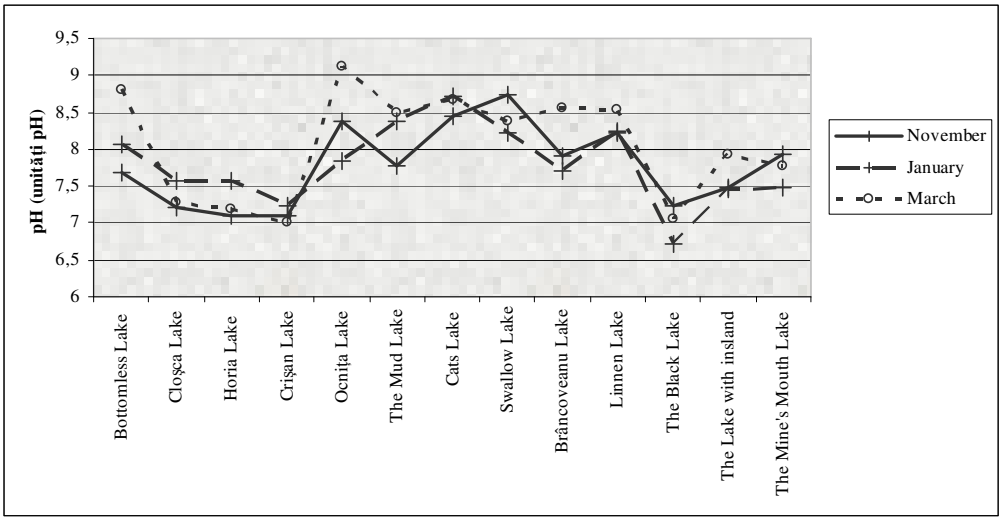

Figure 7. Variation diagram for water's pH in Ocna Sibiului lakes

pH varies in the neutral region, between minimum: 6,71-7,1pH units – The Black Lake, Cloşca Lake, Horia Lake, Crişan Lake and maximum: 8,71-9,12 pH units – Swallow Lake, Cats Lake, Linnen Lake, Ocniţa Lake. Variations between seasons are observed, also (figure 7).

The bacteriological parameters determined varied according to the figures 8 - 11. Coliforms bacteria are found in very different amounts (figure 8), from very low concentrations (0 or near 0 in The Black Lake, Brâncoveanu Lake, Bottomless Lake, Ocniţa Lake, The Mine's Mouth Lake) to very high contents in Cloşca Lake, Cats Lake. The bacteria come, most probably, from humans.

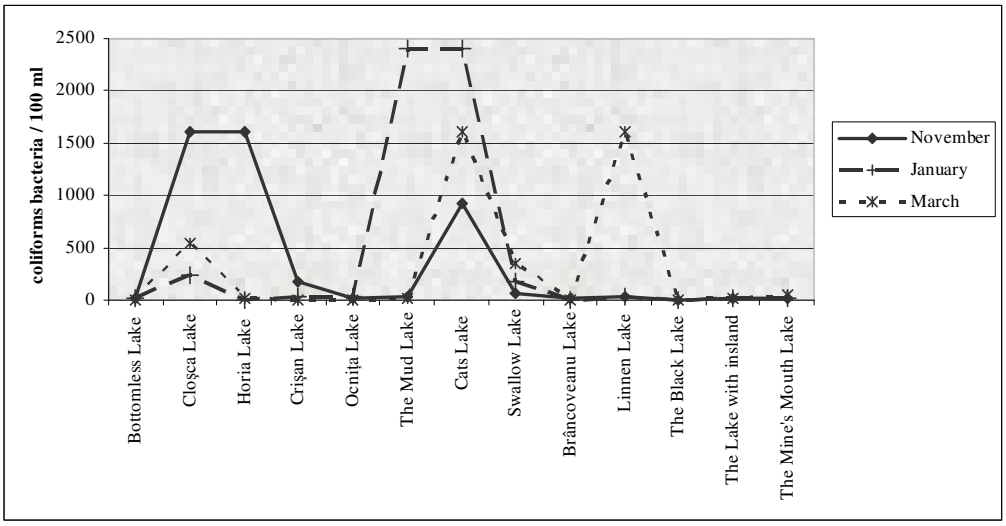

Figure 8 Water's coliforms bacteria in Ocna Sibiului lakes

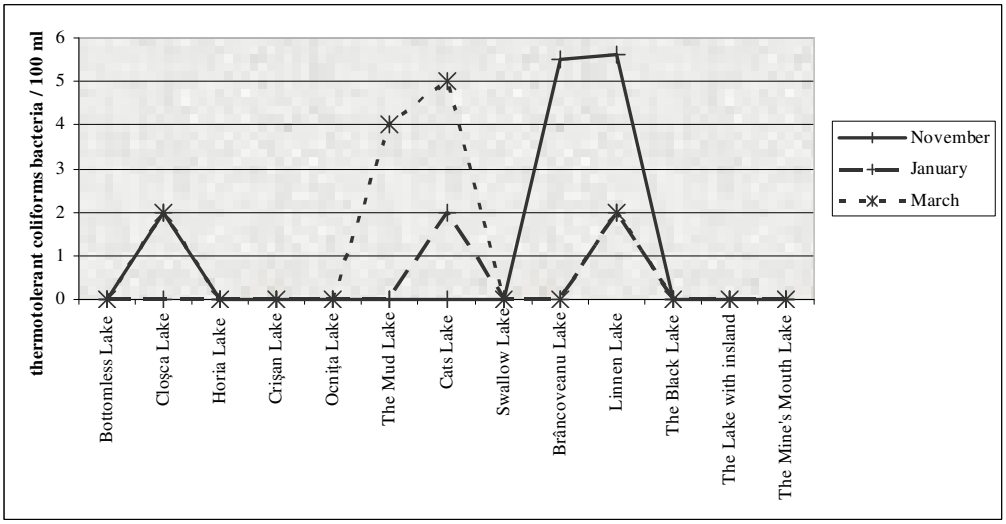

Figure 9. Water's thermotolerant coliforms bacteria in Ocna Sibiului lakes

As figure 8 shows, in the lakes where they are found, it seems that coliforms not only survive, nut they even multiply during winter at low temperatures (figure 1). At the beginning of spring, together with the temperature increase, the population of coliforms becomes higher.
Thermotolerant coliforms bacteria are found in low concentrations in the Linnen Lake, Cloşca Lake, Cats Lake (figure 9).

From the faecal bacteria, the maximal concentrations of *Escherichia coli* is found in Cloşca Lake, Linnen Lake, Cats Lake (figure 10). These are the most visited lakes in summer, the results showing the necessity of implementing and maintaining of very strict hygienic rules in these lakes. Enterococci are most abundant in Cts Lake and Linnen Lake (figure 11).

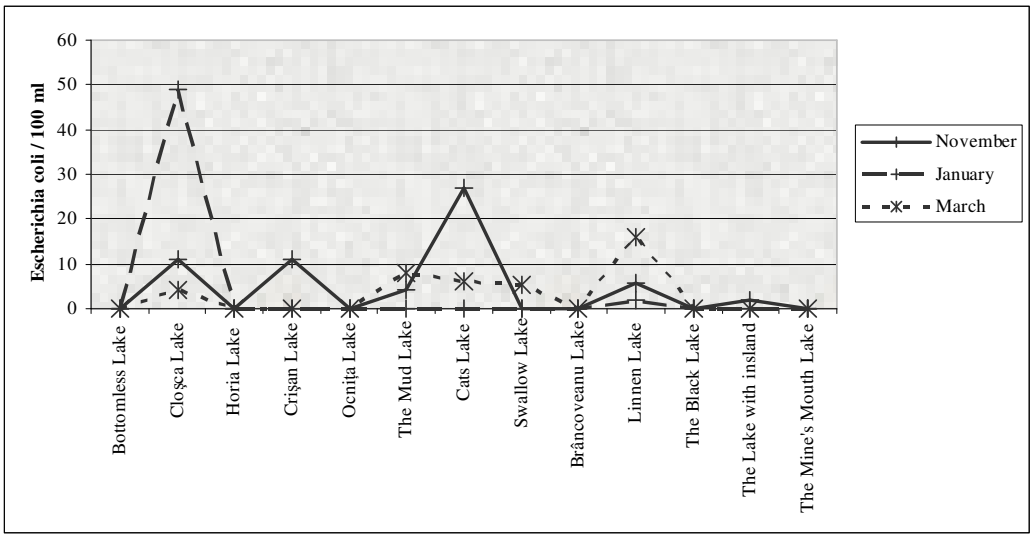

Figure 10 Variation diagram for water's Escherichia coli in Ocna Sibiului lakes

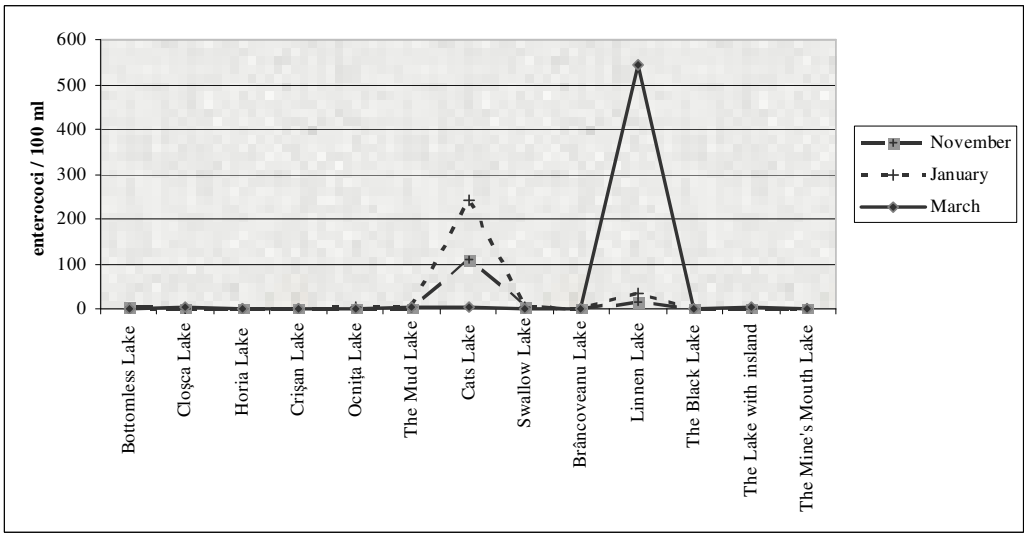

Figure 11 Variation diagram for water's enterococi in Ocna Sibiului lakes

CONCLUSIONS

Cloşca Lake, Crişan Lake and Horia Lakes are characterized by low mineralization degree, low concentration of chlorides and calcium, reduced amount of organic matter. The Black Lake is characterized by high mineralization degree, maximum amount of chlorides and organic matter, a reduced concentration of dissolved oxygen, minimum pH.
Brâncoveanu Lake is characterized by hight mineralization of water, high concentration of chlorides and calcium, high hardness and dissolved oxygen.
Ocnița Lake, Bottomless Lake, The Mine's Mouth Lake, Swallow Lake, The Lake with insland, The Mud Lake present moderate degree of mineralisation, moderate concentration of chlorides and calcium
Cloşca Lake, Linnen Lake and Cats Lake present maximum values of faecal indicators. Most of the other lakes show a low number of colonies and faecal coliform organisms. The low value of bacteriological parameters reflects that the faecal contamination was reduced in those periods when the bathing season was closed. However the results suggest that the bathing conditions in some lakes may be unsatisfactory and investigations and possible remediation of water's quality are required (*, 2005) (**, 2000).

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