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9. Gradual Changes in Water Quality Parameters in Razim-Sinoe Aquatic Complex in the Period 1991-2017

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Abstract: This paper discusses the evolution in time of water quality parameters in Razim-Sinoe aquatic complex, the largest surface water in the natural system in Romania, situated in the southern part of the Danube Delta Biosphere Reserve. For this purpose, data regarding mean values of nutrients concentrations (nitrogen from ammonium, nitrogen from nitrite, nitrogen from nitrate, phosphorus from orthophosphates) and salinity (chloride, sulphates, calcium, magnesium and sodium) were collected between 1991 and 2017 from Razim and Golovita lakes.
Our results revealed a gradual increase in nutrients concentrations by the year 2010, followed by a significant decreasing trend after this year. In the same time, a decreasing tendency in salts content was remarked throughout the study period. Still, over the monitored period 1991-2017, exceeding were reported of the reference value for good ecological status (second quality class) for chlorides, sulphates, calcium, magnesium and sodium, in accordance with Water Framework Directive (2000/60/EC), transposed into Romanian legislation through the Order 161/2006 for the approval of the Normative concerning the classification of surface water quality in order to establish the ecological status of water bodies.
Keywords: Razim-Sinoe, nutrients, salinity, aquatic ecosystem

INTRODUCTION

Razim-Sinoie Lagoonal Complex is the largest lagoon in Romania, occupying 1145 km^2 which represents 19.74% from the entire area of the Danube Delta Biosphere Reserve (Oţel, 2007).
Located in northeastern Dobrogea, south of the Danube Delta and on the Black Sea coast, this lacustrine complex' geographic coordinates lies between 44°20' and 45°02' northern latitude and 28º40' and 29°09' eastern longitude.

In terms of evolution, this area, appeared and evolved in an ancient, branched marine gulf, Halmyris. This lagoon, first occupied by the sea, started gradually 2000 years ago to separate from the Black Sea (Gâştescu *et al.*, 2016), by a series of offshore bars, created by the sediment deposition coming from the interactions between the Sea and the Danube River, which isolated the Razim-Sinoe lagoon complex. The communication with the sea was extremely important in terms of hydrochemical point of view.

This aquatic complex is now connected in the north to one of the Danube River branch, Sfantu Gheorghe, the source of water alimentation, through the channels Dunavat and Dranov.
The first stage, occurred at the beginning of the last century at the proposal of the biologist Grigore Antipa, refers to the improvement of the hydrological conditions for a better valorization of the existing fish resources, mainly by the reduction of the salinity differences in Razim Lake. In that period Dunavat, Dranov and Enisala canals were achieved, which allowed the penetration of important quantities of sweet water into Razim Lake.

After 1970, the main concern regarding this complex was to transform these lakes, especially those from the northern compartment (e.g lakes Razim, Babadag, Goloviţa, Zmeica) into a hydrotechnic system used for irrigations. Therefore, by the closure of the narrow strip of sand called Gura Portitei after 1970 and the influence of the sweet water coming from the Danube that gradually became more and more visible conducted to the stabilization in water salinity and the total salts concentrations, especially in northern compartment (Razim-Golovita) (Breţcan *et al*., 2008).

Nowadays, the complex surface per component units at a medium level of 50 cmrMN is 86770 ha after Gastescu, 1971, cited by Staras 1995 and comprise as the main lakes, Razim lake (41400 ha), Sinoe lake (17150 ha), Goloviţa lake (11870 ha), Babadag lake (2470 ha), Zmeica lake (5460 ha) but also several other lakes such as Istria (560 ha), Nuntaşi-Tuzla (1050 ha), etc.

Today, Razim lake is the biggest freshwater basin in Romania (Catianis *et al*., 2018) and together with the other lakes Sinoie, Golovita, due to its environmental conditions, play a significant role in the supply of water for, fishery exploitation, flood prevention, irrigation and also recreation and water tourism. Golovita lake is fed from the Razelm lake, which receives 30-90 m^3/s from the channels, Dunavatu and Dranov, and 0.47 m^3/s from the rivers Taita and Telita through the lake Babadag (Tudorancea and Tudorancea, 2006).

All these characteristics, along with several important arrangements works and significant researches conducted during the time in this aquatic complex have been modified the dynamical, hydrological, hydrochemical and hydrobiological features of this lacuster ecosystems.

This paper aims to present an overview of the researches regarding water characteristics and the gradually changes that occurred in Razim–Sinoe lacustric complex in the period 1991-2017 in terms of the water quality parameters.

MATERIAL AND METHODS

Due to the great diversity of this aquatic ecosystem and its environmental conditions, Razim-Sinoe this unique coastal lakes complex has been systematically studied by the Danube Delta National Institute for Research and Development Tulcea since 1991.

To investigate the gradual changes in water quality parameters, data for Razim and Golovita lakes have been selected in this study, in order to observe the evolution in time of the environment characteristics during the last 26 years of research (1991-2017) (Figure 1).

Generally, sampling campaigns were conducted three times per year, in spring, summer, and autumn. Sampling methods of the surface water samples, including handling, preservation and storage were done in accordance with current legislation, each sample is considered to be representative only in the time and in the place of sampling (Teodorof *et al.*, 2015).

Analytical determinations were performed, according to European standards, in the Chemistry Laboratory of DDNI Tulcea, laboratory certified by the Romanian Association of Standardization Renar since 2006.

Figure 1 Map of the sampling points

The quality indicators selected from the Tabel 6, Appendix C, Elements and chemical and physical-chemical quality standards from Romanian Order 161/2006 (*****, 2006) are:

- Nutrients - ammonium nitrogen, nitrite nitrogen, nitrate nitrogen, dissolved phosphorus
- Salts – chlorides, suphates, calcium, magnesium, sodium

The results were framed into quality classes according to the Romanian Order 161/ 2006 (*****, 2006), for the approval of the Normative concerning the classification of surface water quality in order to establish the ecological status of water bodies, which represent the Water Framework Directive (WFD; 2000/60/EC; European Parliament and Council 2000) transposition into national legislation. The porpose of the surface water classification is to establish the ecological conditions of the water bodies and consist in five quality classes: first quality class (very good ecological status), second quality class (good ecological status), third quality class (moderate ecological status), forth quality class (poor ecological status) and fifth quality class (bad ecological status).

For surface water quality assessment different techniques were used during the study, like titrimetric methods in the case of chloride, sulphates, calcium and magnesium. Molecular spectrometry was the method used for the quantification of inorganic indicators such as nitrogen ammonium, nitrogen nitrite, nitrogen nitrate and orthophosphates, with Perkin Elmer Lambda 10 UVVIS spectrometer and specific equipment for the water samples pretreatment phase. The concentration of sodium was determined using Perkin Elmer inductively coupled plasma mass spectrometer (ICP-MS).

Results, expressed in mg/L, represent 10 years average values, respectively the periods 1991-2000, 2001-2010 and 7 years average values for the period 2011-2017.
The graphs were made for each quality parameter in the two selected sampling points, Razim and Golovita lakes.

RESULTS AND DISCUSSIONS

As important indicators of the surface water quality, the primary inorganic forms of nitrogen, like ammonium, nitrites, nitrates along with phosphorus control the growth of the aquatic plants.
The evolution of the nutrients concentrations found in the surface water samples in Razim-Sinoe aquatic complex, during the last 26 years, were widely heterogenous as it can be seen in the figures 2-5.

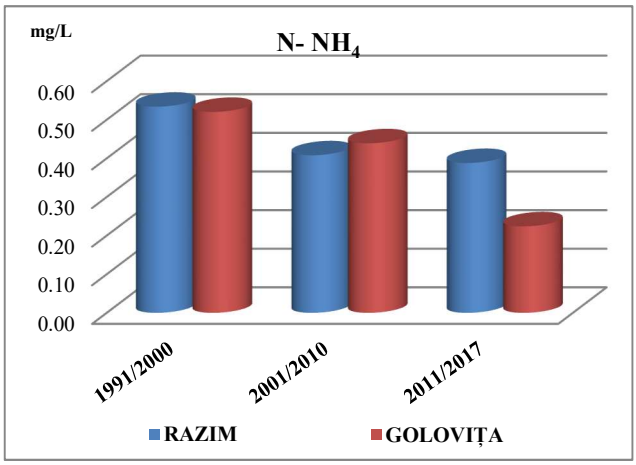

Figure 2 Evolution of N-NH_4 concentrations

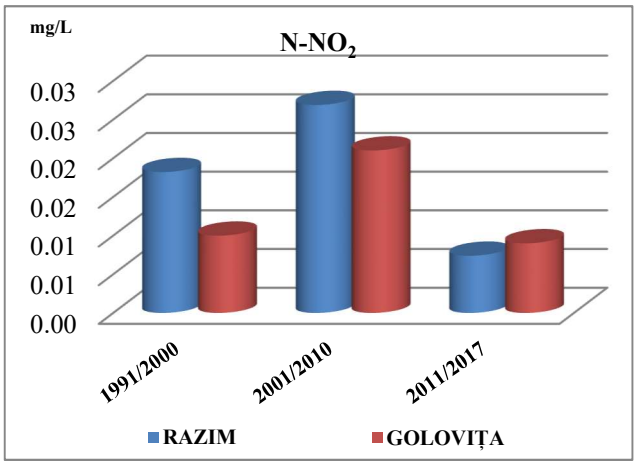

Figure 3 Evolution of N-NO_2 concentrations

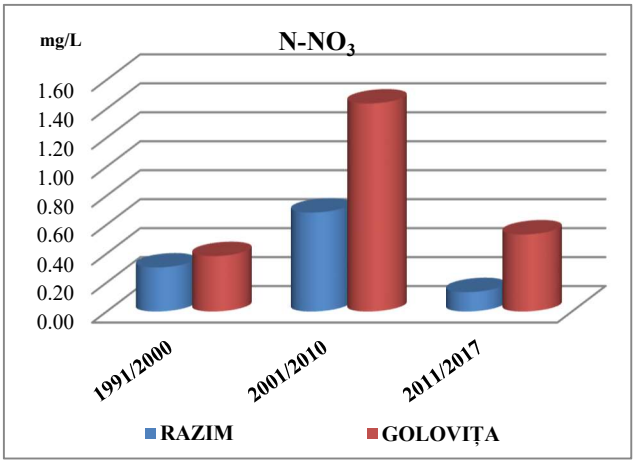

Figure 4 Evolution of N-NO_3 concentrations

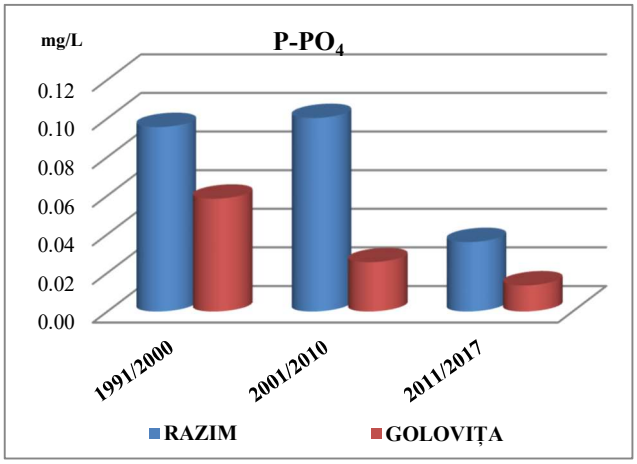

Figure 5 Evolution of P-PO_4 concentrations

Ammonium nitrogen have the highest values in the first investigated period, 1991-2000, similar in both sampling points, with concentrations values varying between 0.534 mg/L Razim lake and 0.520 mg/L in Golovița lake. After that period, a slightly decreasing trend can be observed in ammonium nitrogen concentrations in the next ten years (2001-2010), followed by significant variations occurred in the last studied period 2001-2017, when the values fluctuated in the range of 0.388 mg/L Razim lake and 0.152 mg/L in Golovița lake; in the case of Golovita lake the values recorded in the last period are with almost 30% lower compared to the first analyzed period (Figure 2).

The maximum allowed concentration corresponding to second quality class in accordance with Order 161/2006 (WFD transposed into National legislation) for ammonium nitrogen is 0.8 mg N/L. The results have shown that no value exceeds the reference value in any sampling point, and have concentrations that can be framed into good ecological status.
The admissible value for nitrite nitrogen, corresponding to second quality class according to Order 161/ 2006 is 0.03 mg N/L.

As figure 3 shows, nitrite nitrogen concentrations registered an increasing trend in the period 2001-2010, compared to the first investigated period 1991-2000. The peak values, recorded in the second period, have comparable values in both sampling points, reaching up to 0.027 mg/L in Razim and 0.026 mg/L in Golovița lakes. Minimum values were recorded in the last studied period, 2011-2017, with similar values, 0.007 mg/L in Razim lake and 0.005 mg/L in Golovița lake.
Even the nitrite nitrogen concentrations present significant variations, the recorded values have never exceeded the limit of the second quality class.
Similar to the case of nitrite nitrogen, nitrate nitrogen have the higest values in the second period of the investigation, 2001-2010, as figure 4 shows. The concentrations varied, in that period, between 0.683 mg/L in Razim lake and 1.436 mg/L in Golovița lake. Low levels of nitrogen from nitrate were

detected in the first period between 1991-2000 and the last period, 2011-2017, with values from 0.134 mg/L in Razim lake and 0.532 mg/L in Golovița lake. The reference value of 3 mg N/L corresponding to the second quality class, was not exceeded in the investigated period.

In the case of orthophosphates, both sampling points have the same decreasing tendacy in the 26 years of investigation (Fig. 5). Althought, the maximum concentration of 0.1 mg/L in Razim lake, was recorded in the period 2001-2010, a decreasing tendancy is observed in this lake in the next period, 2011-2017, when the level of orthophosphates decrese with almost 36%. The lowest value of 0.014 mg/L was detected in Golovita lake in the last monitored period. As in the case of nitrogen compounds, orthophosphates concentrations did not exceed the reference value of 0.2 mg P/L for second quality class.

In the case of salinity, an important measurement, mainly due to its previous connection with Black Sea, was carrefully investigated in this study over 26 years, in order to reveal the changes that occured in this lagoon complex where freshwater coming from Sfantu Gheorghe branch and salty sea water mixed in this former lagoon.

Knowing the fact that in the past, the salinity of the water in Razim lake use to be closer of the conditions in the Black Sea or even higher in some periods, this research provides important informations regarding hydrochemical regime of the lakes water that have gradually changed since that time.

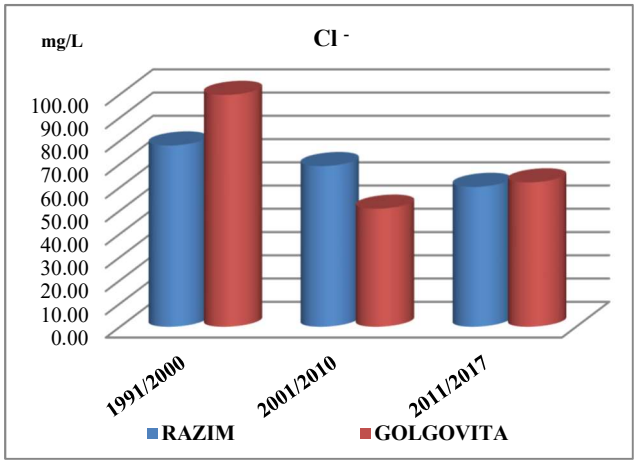

Figure 6 Evolution of Cl^- concentrations

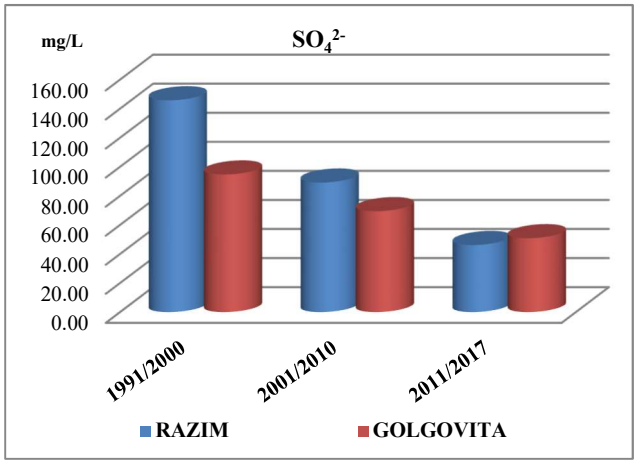

Figure 7 Evolution of SO_4^{2-} concentrations

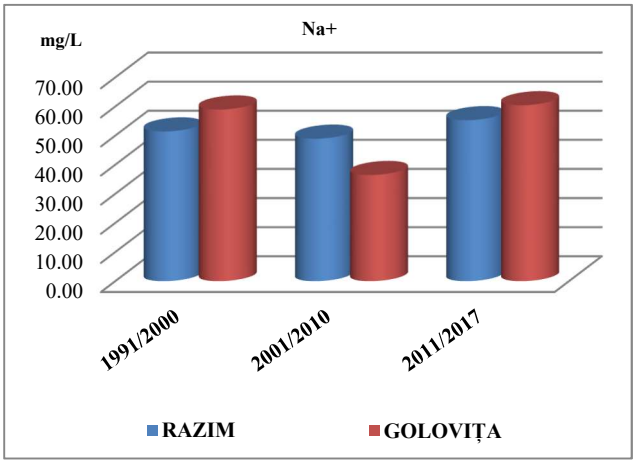

Figure 8 Evolution of Na^+ concentrations

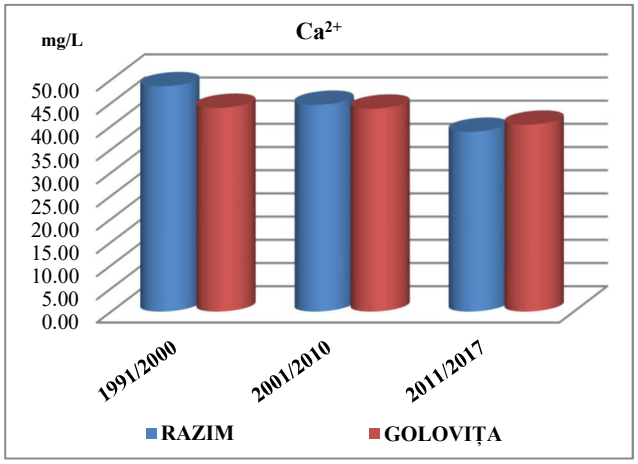

Figure 9 Evolution of Ca^{2+} concentrations

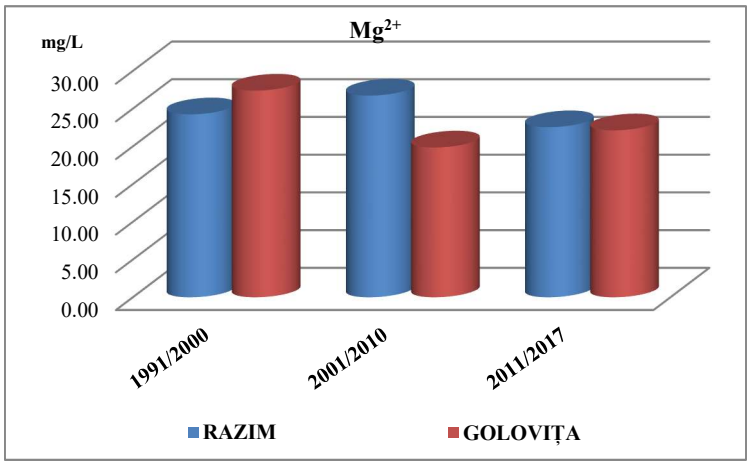

Figure 10 Evolution of Mg^{2+} concentrations

The amount of chlorides in Razim-Sinoe aquatic complex is influenced both by the Danube waters and also sea waters, depending on the Danube flow and also wind direction at the Gura Portitei mouth.
Previous studies (Diaconul *et. al*, 1963) offer an overview on chloride levels, in different conditions, such as those between 1950-1952, when high levels of chloride was mainly due to the clogging of the Dranov and Dunavat channels, which feed the Razim-Sinoe complex; in that period mean chloride concentration reached up to 4.5 g/L in Razelm and 9 g/L in Golovita lake. After that, the dredging of the channels and the masive sweet water input reduced the level of NaCl to 0.5 g/L during 1956.

In our study, figure 6 shows a clear decreasing tendency of chloride levels in both lakes, Razim and Golovita, during all the investigated period. Although the minimum concentration of 50.768 mg/L, was recorded in the period 2001-2010 in Golovita lake, chlorides levels decrease in this lake from 99.715 mg/L in the first period 1991-2000 to 62.080 mg/L in the last period 2011-2017, representing a percentage of 37%. Maximum allowed concentration for chloride, according to Romanian Order 161/2006, the second quality class is 50 mg /L. The results of the analyses showed that all the obtained concentrations are higher than reference value of the second quality class, framing, generally into the third quality class.

Together with chlorides, sulphates give informations regarding the water salinity. In the case of sulphates, the maximum allowed concentrations for the second quality class according to Romanian Order 161/ 2006 is 120 mg/L. In all investigated period a gradually decreasing trend was remarked concerning the sulphates in both lakes, Razim and Golovita. The highest value was recorded in the period 1991-2000 (145.718 mg/L) in Razim lake and decreases up to 89.117 mg/L in the period 2001-2010, that means 50%, followed by other decreasing tendency to the mean value of 46.127 mg/L during 2011-2017. In Golovita lake, the mean concentrations of sulphates continuously decrease from 94.663 mg/L in the first investigated period (1991-2000) to 69.390 mg/L in the period 2001-2010, reaching up to a mean values of 50.803 mg/L in the period 2011-2017, that represent almost 50% from the sulphates levels in the first period. This decreasing tendency is due to sweet water input.

With the same behavior as in the case of chloride, sulphates levels in the Razim-Sinoe aquatic complex is mainly influenced by the Danube flow and the wind direction at the mouth of Gura Portitei. In accordance with the current legislation, the sulphates concentrations in the studied period, framed into first, second and third quality class.

In water, sodium is generally bound to chloride or sulphates. The evolution of chloride and sodium concentrations, presented in figures 6 and 8 show similarities and give information regarding water salinity. A decreasing trend was recorded in the second period (2001-2010) compared to the first period of the study, followed by a slightly increasing treng in the last period. As figure 8 presents, the minimum (36.467 mg/L – in the period 2001-2010) and the maximum (60.431 mg/L in the period 2011-2017) values were recorded in Golovita lake. The sodium concentrations were higher than the reference value of 50 mg/L, corresponding to the second quality class and framed into the third quality

class in the first and the last investigated period and in the second quality class for the period 2001-2010 for both lakes Razim and Golovita.
As figure 9 shows, the level of calcium is relatively constant during the 26 years of investigations, with values ranging between 38.744 mg/L and 48.574 mg/L, values that show minor modifications in this complex from the hardness point of view. Calcium is generally bound to bicarbonates and along with magnesium is responsible for water hardness. All the recorded values for calcium are lower than the reference value of 100 mg/L corresponding to second quality class, in accordance with the Order 161/ 2006.

As in the case of calcium, there are no large variations of magnesium in the Razim-Sinoe aquatic complex during the investigated period. In Razim lake values ranged from 22.537 to 24.386 mg/L and in Golovita lake the values varied between 27.386 mg/L in the period 1991-2000 and 22.120 mg/L in the period 2011-2017. For this indicator, the reference value of 50 mg/L corresponding to second quality class, has never been exceeded.

CONCLUSIONS

A retrospective of the data sets containing an analysis of nutrients and salts concentrations in Razim-Sinoe lagoon complex was performed.
Our investigations were carried out in the last 26 years and the results of surface water quality in two important lakes Razim and Sinoe, were interpreted and compared in three different periods, 1991-2000, 2001-2010, 2011-2017.

In terms of nutrients compounds, like inorganic forms of nitrogen (ammonium nitrogen, nitrite nitrogen, nitrate nitrogen) along with orthophosphates, our research revealed an ascending trend in the first periods, until the year 2010, with a considerable descending tendency in the last years.

From the salinity point of view, even if exceedings of the reference limit for second quality class (in accordance with Romanian Order 161/ 2006) were recorded in the investigated period, this can be attributed to the wind direction on Gura Portitei mouth and also to the remobilization of the bottom sediment in these lakes.

Man-induced significant interventions occurred in Razim-Sinoe aquatic complex during the time in order to change its use, modified this lacuster ecosystem and its hydrochemical and implicitly its hydrobiological characteristics.

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