ABSTRACT: The main objective of the present hydrochemical study is aimed at establishing the water pollution trends for the Shabla and Ezerets Lakes along the Bulgarian Black Sea coast, as well as to determine the reasons for this pollution. The previous studies have been reviewed in detail. Systematic sampling has been made of the lake water during one-year period. The comparative analysis of the historical information has proved a considerable increase in the amounts of the inorganic forms of nitrogen and phosphorus in the lakes, and accelerated eutrophication. This is due to the disturbed natural water balance of the basins resulting from intensive water pumping and to the catchment area pollution by fertilizers. Recommendations for particular activities are made in conformity with the conclusions about the hydrochemical state with the aim of protection and sustainable development of the wetlands. The present study could be used as the basis for a future monitoring with respect to the methodology and database.

KEYWORDS: Eutrophication, seasonal dynamics, water pollution, wetlands.

Introduction
The importance of wetlands as ecosystem types consists in the stable maintenance of high biodiversity in the limited space of the ecotone. For this reason the system can be relatively easily studied and managed, and a great number of plant and animal species can be easily protected. The Shabla and Ezerets Lakes situated in close proximity to the Black Sea are one of the few natural wetlands preserved in Bulgaria. They are of unique environmental value. Almost the whole population of the globally threatened Red-breasted Goose species (Branta ruficollis) winters in the wetland area. The lakes are remote from big industrial centers. They are located in North Dobroudzha - an arid region with developed agriculture. The negative anthropogenic impact is due mainly to intensive water pumping and to pollution of the catchment by dung and household waste, and is expressed in enhanced eutrophication process. This leads to the need of systematic studies and implementation of corresponding activities for wetland protection. The present study consists in analyzing of water quality parameters for both lakes and in establishing their seasonal dynamics. The trends in the water chemical composition due to the anthropogenic activities in the region are established after comparison with the results from previous studies. Complex monitoring, technical, technological and other measures for the lake ecosystem protection have been suggested.

Characteristics of the Shabla and Ezerets Lakes

Hydrographic Characteristics. The Shabla and Ezerets Lakes are situated in the immediate proximity to the northwestern Black Sea coast in the southeastern part of Dobroudzha Plain. They represent closed firths separated from the sea by a 50-100 m wide sandspit. They are situated next to each other in deep dry gullies formed during the process of limestone erosion by the water torrents.
The water basins are fed by karst springs. The lakes drain the Sarmatian aquifer horizon. Their underground catchment area includes 266 km$^2$. The lakeshores are low and densely covered by reed massifs. A 5-6 m wide and about 1 m deep channel connects the two water basins. They were connected by overflows before digging the channel. An artificial channel leading to the Black Sea existed in the northern part of the Ezerets Lake till the end of the 50-ies. The excess lake water was emptied in it during the years of high winter or spring water and marine deposits then again silted it. At present no channel digging is performed and there is no direct water exchange between the lake and the sea (Figure 1).

The free water area of the Shabla Lake is 0.79 km$^2$ and of the Ezerets Lake - 0.72 km$^2$, their volume being 3.6x10$^6$ m$^3$ and 2.5x10$^6$ m$^3$ respectively.

**Figure 1.** A scheme of the Shabla and Ezerets Lakes

**Hydrological characteristics.** The water balance data of the Shabla-Ezerets lake complex (inflow and outflow) under natural conditions without water pumping are summarized by Danchev et al. (1997). The origin of the main inflow into the lakes is from the karst-spring feeding. The total inflow in the Shabla-Ezerets amounts to 21.702x10$^6$ m$^3$/yr, including precipitation, surface and underground outflow. The water of the Sarmatian aquifer reaches the western lakeshores and is poured in a scattered or concentrated manner along the entire shorelines, as well as through well formed sub-aquatic springs inside the water area. The outflow component of the water balance consists mainly by the filtration of lake
water towards the Black Sea. The total outflow is 21.60x10^6 m^3/year including evaporation, transpiration and filtration towards the sea. Since 1954 the underground water of the Sarmatian aquifer in the region of the Shabla and Ezerets Lakes has been the object of exploitation for potable and agricultural water supply and for irrigation. A great number of catchment facilities have been constructed in the course of 20 years on a relatively small area in proximity to the western lake shores - shaft and borehole wells as well as drainage channels. They drain underground and lake water. Water pumping continues for already more than 40 years, its volume being increased in parallel with the needs of potable water supply (including that of the town of Dobrich) and with enlargement of the irrigated areas. The water pumping is intensive and irregular and disturbs the water balance, taking away a great part of the underground water feeding the lakes. The negative consequences are expressed in abrupt fluctuations and decrease of the water stay and volume in the basins, in the drying of shore-line shallows and in the hazard of salty marine water intrusion in the aquifer (Danchev et al., 1997).

**Hydrochemical characteristics.** The first brief data about the total solids in the Shabla and Ezerets Lakes were given by Valkanov (1957) and later by Rozhdestvenski (1962). Rozhdestvenski (1964, 1967) made the thorough hydrochemical description resulting from the investigations during the periods 1949-1962 and 1965-1966. It included interpretation of data about the mineral composition, the oxygen regime, nutrients and organic substances (COD_{K_MnO_4} and COD_{K_2Cr_2O_7}). The author characterizes the Shabla and Ezerets Lakes as oligohalinic eutrophic lakes. Botev (1998) performed detailed hydrochemical investigations during the period 1992-1994 and established enhancement of the eutrophication processes. Danchev et al. (1997) provided summarized information about the chemical composition of the water from the underground watershed area of the lakes as well as about the pollution sources. The present hydrochemical study was made during the period 1995-1996 as the first attempt to systematically follow the changes in temperature and oxygen regime, mineral composition, nutrients and organic matter in the Shabla and Ezerets Lakes.

**Sampling methods and analyses**

The present study of the Shabla and Ezerets Lakes was carried out in the period August 1995 - October 1996. Eight systematic samplings were made with the aim of establishing the seasonal dynamics of the water chemical parameters. The samples were collected at 4 stations. Taking under consideration the small area of the two water basins, this number was considered as the minimal sufficient one for describing the hydrochemical state and for recording the spatial differences. The situation of the stations was selected in representative parts of the lakes: station 5 - “Shabla Lake - south” and station 8 - “Ezerets Lake - west” as areas of average depths in proximity to the karst springs; station 6 - “Shabla Lake - north” and station 7 - “Ezerets Lake - east” as areas of maximal depths in proximity to the seacoast (Fig. 1). This situation allowed the comparison with the preceding investigations and facilitated the interpretation of the performed in parallel hydrobiological analyses. The water samples collected from the lake surface were analyzed according to 18 parameters in order to establish the temperature and oxygen regime, the mineral composition, the quantity and dynamics of the nutrients and organic matter using conventional methods. The analyses were performed in Water Quality Laboratory at the IWP - BAS and on the Field using Hach DR/2000 equipment.
Results and discussion

1. Temperature regime

The maximum summer temperatures of surface water in the Shabla and Ezerets Lakes in the period July-August were about 25-26°C. The winter minimum was in January-February (about 0°C) when freezing of the greater part of the lake surface was observed. Considerable temperature differences were recorded in vertical direction during the spring-summer season because of the great depth of the two lakes. The typical state of summer stratification was observed during the period June-August 1996. The maximal temperature difference between the surface and the bottom layer was 7.8°C for the Shabla Lake and 8.8°C - for the Ezerets Lake. The distribution of the layers was stable and the vertical wind mixing affected only the surface water. The temperature stability was disturbed in September-October when conditions occurred for the full mixing due to wind action and for equalizing the gradients, i.e. homothermic effect. The seasonal temperature dynamics of the Shabla and Ezerets Lake water follows the typical pattern for the dynamic stagnant water basins situated at moderate latitudes. Rozhdestvenski has described the same type of thermal characteristics. Botev has reported the summer temperature gradient. The seasonal dynamics of the average monthly temperature of surface water in the Shabla Lake proves that no significant changes in the lake thermal characteristics have taken place during a 45-year period (1949-1996). The maximum temperatures are within the range 24.0-28.0°C and the minimum temperature is about 0°C. The maximum temperature difference between the surface and the bottom is in the range 2.5-19.1°C.

2. Mineral composition

The total solids in the water of the Shabla Lake during the period August-December 1995 amounted to the average of 0.840 g/l. Slight freshening was observed in 1996 - 0.779 g/l on the average. The same process was more clearly expressed in the Ezerets Lake: the total solids were on the average 0.915 g/l in 1995 and 0.724 g/l in 1996. Slight fluctuations in the total solids were established in seasonal respect for the two lakes. The lowest values were observed in June. The highest values were recorded in the beginning of the autumn (September-October). This dynamics was related with the fluctuations in bicarbonate concentration. No substantial differences in total solids were observed in horizontal direction in the lakes. Compared to the results from the period 1949-1962, the total solids were reduced almost twice in the Ezerets Lake and 1.5 times - in the Shabla Lake. This change is at the expense of the reduced share of chlorides and was observed first by Rozhdestvenski (1967). This was the result from the ceased in-rush of marine water in the Ezerets Lake through the channel connecting it with the sea (Table 1, Figure 2).

According to the analyses the bicarbonates \( \text{HCO}_3^- \) have the greatest share in the total solids of the Shabla and Ezerets Lakes. Their average value is 441 mg/l for the Shabla Lake and 434 mg/l - for the Ezerets Lake. No considerable differences were observed in horizontal direction during the investigated period. The bicarbonates are introduced with the karst-spring water of the Sarmatian aquifer. The close values for the two lakes as well as the dominating bicarbonate content in the total solids prove that the relative share of the karst-spring feeding of the water balance is similar and most important for the two water basins.
The presence of the chlorides (Cl-) is found to be at the second place in the water content of both lakes. The average values established for the Shabla and Ezerets lakes are 255 mg/l and 230 mg/l respectively (0.49 %o and 0.44 %o chloride salinity according to Knudsen). The chlorides are slightly increased to the northern part of the Shabla Lake and to the eastern part of the Ezerets Lake in horizontal plan. These are the sections in contact with the seacoast where marine water is filtrated. The karst-spring fresh water is found in the opposite direction (Fig. 1).

Table 1. Average ion content of the water for four periods of investigation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Shabla Lake</th>
<th>Ezerets Lake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids, g/l</td>
<td>1.120</td>
<td>0.59</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>mg/l</td>
<td>387</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>mg/l</td>
<td>19</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>mg/l</td>
<td>501</td>
</tr>
<tr>
<td>S</td>
<td>%</td>
<td>0.93</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>mg/l</td>
<td>72</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>mg/l</td>
<td>87</td>
</tr>
<tr>
<td>Hardness</td>
<td>mgeq/l</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Figure 2. Total solids trends for four periods
According to the Venice system the Shabla and Ezerets water is considered fresh according to its chloride salinity. According to the classification of Alekin (1970) the water is with hydrocarbonate-chloride one with a high degree of mineralization. The average values of water hardness recorded during the investigation period are 7.35 mgeq/l for the Shabla Lake and 6.70 mgeq/l for the Ezerets Lake. The seasonal fluctuations are negligible. According to the classification of Alekin the lake water is hard and is of the hydrogen-carbonate-chloride-magnesium-calcium type ($\text{HCO}_3^-, \text{Cl}^-, \text{Mg}^{2+}, \text{Ca}^{2+}$). The characteristic of the main water-balance inflow component - the water from the Sarmatian aquifer is similar (Danchev et al., 1997). Compared to the results from previous studies the water hardness in the Shabla and Ezerets Lakes has been slightly decreased together with the decrease in the calcium and magnesium ion content (Table 1).

3. Oxygen regime

Seasonal oxygen oversaturation is observed for the surface water of the Shabla and Ezerets Lakes in the period from March till August. The highest values established for the Shabla Lake are 155 % and for the Ezerets Lake - 186 %. This situation is the chemical representation of the abundant phytoplankton blooming in the spring-summer period and the related with it intensive photosynthesis (Stoyneva, 1997). The fluctuations in the oxygen saturation during these months are due to the climatic changes (temperature, wind) as well as to the changes in the phytoplankton cenosis. In the autumn considerable decrease (up to 54 %) in surface water oxygen saturation is established due to the inflow of bottom water with low oxygen content towards the surface layers as a result of the autumn circulation. The oxygen saturation is increased in winter to 80-85 % due to higher gas solubility at low water temperatures. Oxygen deficit is observed in bottom water during the period of summer stratification in vertical plan. The lowest values are 0.0 mgO$_2$/l and 0 % of oxygen saturation. As already mentioned, stable thermal stratification is formed in summer in such deep lakes. The bottom layers have no hydrodynamic contact with the surface ones. The low oxygen-content karst-spring water flows also at the bottom. Moreover, intensive processes of bacterial destruction of the abundant organic matter occur in the hypolimnion. The oxygen influx from the surface is insufficient to compensate the consumption during biodegradation. The result is oxygen exhaustion and oxygen deficit. The anaerobic decay processes with release of hydrogen sulfide have been only subjectively established from the typical silt odor. The continuous state of oxygen deficit is hazardous for the stagnant and difficult-moving zoobenthos and for the ground fish. Hydrogen sulfide exerts direct toxic effect on living organisms. The bottom layers are enriched with oxygen during the autumn circulation, reaching rapidly 40-50 % of saturation. The described specific features of the oxygen regime in the Shabla and Ezerets Lakes were established during the first studies of Rozhdestvenski. The water basins were eutrophic as early as 40 years ago. The studies of Botev provided evidence for this too.

4. Nutrients

Ammonium nitrogen ($\text{NH}_4^+$-$\text{N}$). The established concentrations in the lake water are high all the year round - on the average 1.3 mgN/l for the Shabla Lake and 1.5 mgN/l for the Ezerets Lake. No seasonable changes in ammonium content have been observed depending on the phytoplankton development. The concentration is high even during the warm months characterized by the greatest blooming of the blue-green algae
Water pollution in the Shabla and Ezerets lakes, Bulgaria

Hence, the conclusion could be made that the ammonium circulating in the lakes does not restrict the phytoplankton development and is a typical parameter for the big productivity of the two water basins. The trend of increasing the ammonium amount is delineated when making a comparison with the data from previous studies. This confirms the supposition of Danchev et al. (1997) that the lakes have been the recipients of polluted water with natural and artificial fertilizers during the last 30 years. The authors have established that at present the water of the Sarmatian aquifer contains ammonium that does not meet the norms of the Bulgarian State Standard (BDS) “Drinking water” due to intensive fertilizing and solid waste disposal.

Nitrite and nitrate nitrogen ($NO_2^-$-N, $NO_3^-$-N). The average nitrite and nitrate concentrations observed in the Shabla Lake during the present study are 0.042 mgN/l and 0.64 mgN/l respectively. The concentrations in the Ezerets Lake are higher - about 0.045 mgN/l for nitrites and 1.50 mgN/l for nitrates. In seasonal aspect, the high values in spring prove the inflow of rich in nutrients bottom water during the spring circulation. The nitrite and nitrate content in the epilimnion is progressively reduced in summer due to the consumption by the phytoplankton and to the deposition in the bottom layers in the course of the dead organic matter settlement. Considerable increase in the content is established in surface water in autumn. The established nitrates in the groundwater feeding the lakes do not meet the norms according to BDS for drinking water. This is due to fertilizer and wastewater pollution (Danchev et al., 1997). Compared to the reference data, the recorded by Botev (1998) decrease in the nitrate content of the lakes during the 1965-1966 period is not confirmed (Table 2). The nitrites are first analyzed in the present study and the trends in their changes cannot be commented too.

Table 2. Average nutrient values for three periods of study

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<tbody>
<tr>
<td></td>
<td>Shabla</td>
<td>Ezerets</td>
<td>Shabla</td>
</tr>
<tr>
<td>$NH_4^+$-N mg/l</td>
<td>0.18</td>
<td>0.20</td>
<td>0.31</td>
</tr>
<tr>
<td>$NO_3^-$N mg/l</td>
<td>0.85</td>
<td>0.67</td>
<td>0.23</td>
</tr>
<tr>
<td>$PO_4^{3-}$P mg/l</td>
<td>0.02</td>
<td>0.03</td>
<td>0.54</td>
</tr>
<tr>
<td>Si mg/l</td>
<td>1.10</td>
<td>2.04</td>
<td>3.78</td>
</tr>
<tr>
<td>Fe mg/l</td>
<td>0.20</td>
<td>0.03</td>
<td>0.05</td>
</tr>
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</table>

Orthophosphate phosphorus ($PO_4^{3-}$-P). The average value of orthophosphates in the Shabla Lake is 0.52 mgP/l and in the Ezerets Lake - 0.37 mgP/l for the period 1995-1996. Gradual seasonal decrease of the concentration is observed at the end of summer and more sharp increase - in October.

The phosphates in the epilimnion are exhausted during the growth of phytoplankton in spring and summer. They are recovered from bottom water during the autumn circulation. Rozhdestvenski (1967) draws special attention to the low phosphate quantity in the lakes - 0.02-0.03 mgP/l on the average. Considerable increase is found by Botev and in the present study (Table 2). This is explained by the applied great amounts of phosphorus fertilizers on
the soils in the catchment since the 60-ies till now. No season could be determined with distinct inflow of polluted water in the lakes at present. The phosphate content in the Shabla and Ezerets Lake catchment area meets the BDS norms for drinking water (Danchev et al., 1997). Although the heavy fertilizer loading during the last years is ceased, the phosphates carried by surface and underground water during the last 30 years are accumulated in the lakes. The quantities circulating now in the water basins are sufficient to ensure phytoplankton superproductivity from April till November. Several conclusions could be drawn on the basis of the results for the quantities and dynamics of the inorganic nitrogen forms in the

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**Figure 3.** Trends in the nutrient changes for the Ezerets Lake

**Figure 4.** Trends in the nutrient changes for the Shabla Lake
Shabla and Ezerets Lakes. The amounts of the total inorganic nitrogen and phosphorus are high, they do not restrict the phytoplankton development and characterize the water basins as eutrophic and even hypertrophic ones (Wetzel, 1983). Ammonium nitrogen is the main form of nitrogen exchange during the warm months when the greatest algae’ blooming occurs. This is an evidence for rapid circumrotation of matter in the trophogenic volume of the basins without reaching full mineralization. A great part of the nutrients leaves the epilimnion in the form of the non-mineralized production that is deposited at the bottom. The surface layers are enriched with nutrients from the bottom layers during the autumn circulation. The trends in the nutrient changes are shown in Table 2 and Figures 3 and 4.

5. Organic matter

The organic matter quantity in the Shabla and Ezerets Lakes determined in the present study as COD\textsubscript{K2Cr2O7} is considerable - about 120 mgO/l for the Shabla Lake and 105 mgO/l for the Ezerets Lake. The seasonal dynamics proves clearly the autochthonous origin of the organic matter. The most general trend is increasing from spring to summer and then decreasing from autumn to winter (Table 3). This follows the phytoplankton growth (the primary product formation). The highest COD\textsubscript{K2Cr2O7} values and the greatest differences between the two lakes are related with the abundant algae blooming (Stoyneva, 1997). According to the COD\textsubscript{K2Cr2O7} values the Shabla and Ezerets Lakes could be classified as hypertrophic water basins.

Table 3. Seasonal dynamics of COD\textsubscript{K2Cr2O7} for the period 1995-1996

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<tbody>
<tr>
<td>COD\textsubscript{K2Cr2O7}</td>
<td>Shabla</td>
<td>31.08</td>
<td>250</td>
<td>120</td>
<td>75</td>
<td>84</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Ezerets</td>
<td>12.10</td>
<td>91</td>
<td>91</td>
<td>93</td>
<td>72</td>
<td>155</td>
<td>140</td>
<td>84</td>
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<td></td>
<td></td>
<td>21.12</td>
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<td></td>
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<td>31.07</td>
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<td></td>
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<td>15.10</td>
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The organic matter quantity in the Shabla and Ezerets Lakes has been determined as COD\textsubscript{KMnO4} during all the previous studies. The average values are high and typical for eutrophic water basins. Maximums of up to 10 mgO/l have been observed during blooming periods. In a comparative plan the trend is towards the increase of the organic matter amount in the lakes (Table 4).

Table 4. Average values of COD\textsubscript{KMnO4} for three periods of investigation

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<tbody>
<tr>
<td>COD\textsubscript{KMnO4}</td>
<td>Shabla 6</td>
<td>4.5</td>
<td>4.50</td>
<td>6.07</td>
</tr>
<tr>
<td>mgO/l</td>
<td>Ezerets 7</td>
<td>4.13</td>
<td>5.32</td>
<td></td>
</tr>
</tbody>
</table>

Conclusions

The following general conclusions are made on the basis of the present study:

1. The surface and underground water flowing into the Shabla and Ezerets lakes have transferred considerable quantities of nutrients in the course of the last 40 years due to intensive fertilizing of the soils in the region and waste water discharge from the settlements and stock-breeding farms.
2. The natural water balance of the lakes has been disturbed due to intensive water pumping from the aquifer and to the stopped direct water exchange between the Ezerets Lake and the Black Sea. The lack of channel connection prevents the discharge of the lake water enriched in nutrients and organic matter and the inflow of karst-spring and marine water. The two lakes have been converted to “a trap” for the nutrient and organic matter.

3. The evidences for the intensive production processes in the lakes are: great amounts and rapid circumrotation of nitrogen and phosphorus all the year round; high values of oxygen saturation in the surface layer and oxygen deficit in the bottom layers during the summer stratification period; considerable organic matter concentration and thick organogenic silt layer at the bottom.

4. The eutrophication process in the lake ecosystem has been enhanced as a result of the anthropogenic activity in the region. Heavy algae blooming of long duration is recorded each year. The primary production is not assimilated in nutrient paths and is accumulated in the lakes.

5. The control on the primary productivity can be achieved by the simultaneous reduction of the nutrient influx and purification by increasing the water exchange in the lakes through a channel.

It is necessary to develop an action plan for the wetland management in order to recreate the equilibrium in the lake ecosystem, including the following activities:

- Establishing of the hydrographic, hydrological, hydrophysical, hydrochemical and hydrobiological characteristics of the lakes.
- Identification of the pollution sources in the catchment area.
- Development of a program for the monitoring of the lake ecosystem.
- Development of a regime for exploiting the water from the Sarmatian aquifer and from the lakes with the aim of stabilizing the water balance of the wetland.
- Development of technical and technological activities for protecting of the catchment area from pollution (for storage and application of the fertilizers, wastewater treatment and solid waste disposal).
- Development of technical and technological activities for the removal of the biological production from the lakes (spring discharge of the high water from the Ezerets Lake toward the sea, scraping the silt from the lake bottom, digging of reed massifs, cutting and burning of reed).
- Development of a program for performing the technical and technological activities in time.

Acknowledgements

This study was carried out thanks to the financial support of the Bulgarian-Swiss Biodiversity Program: Northern Coastal Wetlands Project.
References


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