

Hydrological, Hydrochemical Conditions of Lake Donuzlav (Western Crimea, Black Sea) Based on the Results of Expeditions in 2019

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Abstract

Industrial sand extraction and wastewater discharge are among the main anthropogenic factors affecting the state of the ecosystem of Lake Donuzlav (Crimea, Black Sea). Sand mining primarily significantly changes the seabed and can cause the formation of an oxygen-deficient zone. In this regard, it is necessary to continue the up-to-date hydrochemical and hydrobiological monitoring in the areas of mussel-and-oyster farms, sand mining zones, cargo port, and in the area affected by the release of the Donuzlav sewerage treatment plant. The purpose of this work is to study the hydrological and hydrochemical structure of the southwestern region of Lake Donuzlav, which is subject to anthropogenic influence and includes a zone of industrial sand mining. In April, May and September 2019, studies of the hydrological and hydrochemical structure of lake waters were carried out, including measurements of temperature, salinity, content of dissolved oxygen, five-day biochemical oxygen demand (BOD₅), alkaline permanganate oxidizability, content of silicate, mineral and organic nitrogen and phosphorus. It is shown that the spatial distribution of water temperature and salinity is characterized by great heterogeneity and temporal variability. The hydrochemical studies indicate high oxygen supply in the lake; no cases of oxygen deficiency were detected during the research period. The minimum concentrations of dissolved oxygen did not drop to the minimum allowable levels. All BOD₅ values were below the maximum allowable levels. Local anthropogenic impact on the lake waters was registered in the increased concentrations of nutrients and oxidizability values in the sand mining areas, near the sewerage outlet, in the port area and in the area affected by the domestic wastewater release.

Keywords: hydrological and hydrochemical structure, biogenic elements, Lake Donuzlav, Crimea, Black Sea

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Гидролого-гидрохимический режим вод озера Донузлав (Западный Крым, Черное море) по результатам экспедиций 2019 года

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Аннотация

Промышленная добыча песка и сброс сточных вод относятся к основным антропогенным факторам, влияющим на состояние экосистемы озера Донузлав (Крым, Черное море). Добыча песка, прежде всего, существенно меняет рельеф дна и может стать причиной возникновения зон с дефицитом кислорода. В связи с этим в районах мидийно-устричных ферм, зонах добычи песка, грузового порта, а также в районе влияния выпуска КОС «Донузлав» необходимо продолжение мониторинговых гидрохимических и гидробиологических работ в современных условиях. Цель настоящей работы – исследование гидролого-гидрохимической структуры юго-западного района озера Донузлав, подверженного антропогенному влиянию и включающего зону промышленной добычи песка. В апреле, мае и сентябре 2019 г. проведены исследования гидролого-гидрохимической структуры вод озера, включающие измерения температуры, солености, а также определения содержания растворенного кислорода, биохимического потребления кислорода за пять суток (БПК₅), перманганатной окисляемости в щелочной среде, содержания кремния, минеральных и органических форм азота и фосфора. Показано, что распределение температуры и солености воды отличается большой пространственной неоднородностью. Материалы гидрохимических исследований свидетельствуют о высокой концентрации кислорода в воде; случаев дефицита кислорода за период исследований не обнаружено. Минимальные концентрации растворенного кислорода не снижались до значений предельно допустимых концентраций (ПДК). Все значения БПК₅ не превышали ПДК. Локальное антропогенное воздействие на воды озера заключается в повышении концентраций биогенных веществ, органического азота и фосфора, а также значений окисляемости в районе добычи песка, вблизи выпуска сточных вод КОС «Донузлав» и в районе порта.

Ключевые слова: гидролого-гидрохимическая структура, биогенные элементы, озеро Донузлав, Крым, Черное море

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Introduction

Lake Donuzlav is a unique semi-enclosed man-made sea bay located on the western coast of Crimea. Until 1961, the lake had no connection with the sea and was the second largest saline lake in Crimea with high salinity values (90–95 PSU); however, its traditional denomination as “lake” has still been preserved. The earliest detailed information about the hydrochemical structure of Lake Donuzlav and the field of currents in it are given in [1, 2]. Industrial sand mining in the lake began in 1962 and continues in the present. Papers [3–6] were focused on various aspects of the impact of this activity on the ecosystem of the bay. First of all, sand mining significantly alters the seabed and can cause the formation of oxygen-deficient zones.

The results of the studies carried out in Lake Donuzlav in recent years (2015–2021) are included in the monograph *Modern Hydrometeorological and Hydrochemical Regimes of the Donuzlav Bay*, 2021, where the main focus is on the thermohaline and hydrochemical conditions and water dynamics [7]. The analysis of the materials obtained from the results of expeditions in 2018 [8] gives an idea of the current state of the thermohaline and hydrochemical structure of the bay. These works show the need for regular monitoring of the environmental state of the lake in order to prevent possible negative effects of economic activity on the industrial and recreational potential of the lake.

The purpose of this work is to study the thermohaline and hydrochemical structure of the southwestern area of Lake Donuzlav, which is subject to anthropogenic influence and includes an area of modern industrial sand mining. The main focus is on the results of the 2019 expeditions obtained in the areas of sand mining, cargo port, mussel-and-oyster farm, as well as in the area affected by the domestic wastewater discharge of the Donuzlav sewage treatment plant.

Material and Methods

Studies of the southwestern part of Lake Donuzlav were carried out in April, May, and September 2019. A total of three surveys were performed; samples were taken at 51 stations (Fig. 1) in the surface layer and near the bottom using a type of the Nansen bottle BM-48M. The water temperature in April was measured using a deep-sea reversing thermometer *TG* and, in May and September,



Fig. 1. Sampling scheme in Lake Donuzlav in 2019: April (green squares), May (blue squares), September (red squares); I – mussel-and-oyster farm; II – discharge of domestic water; III – sand production site; IC – input channel

using an optical biophysical sounding probe *Condor* (available at: <http://ecodevice.com.ru/ecodevice-catalogue/multit>). In total, 79 water samples were taken, in which salinity (using an electric salinometer GM-65), pH value, dissolved oxygen, five-day biochemical oxygen demand (BOD₅), alkaline permanganate oxidizability and concentrations of silicate, mineral and organic nitrogen and phosphorus were determined.

Sample analysis was carried out in accordance with the Russian regulatory documents (RD)¹⁾. The dissolved oxygen concentration was determined by the standard Winkler method. The quantitation range is from 0.1 mL/dm³ to oversaturation. The measurement error (ME) is 3.4 %. The determination of the concentration of dissolved inorganic phosphorus was carried out according to the Murphy–Riley method. The quantitation range is 5÷1000 µg/dm³, and the ME is 4.6 %.

¹⁾ RD 52.24.420-2019, RD 52.24.383-2018, RD 52.24.380-2017, RD 52.24.381-2017, RD 52.24.382-2019, RD 52.24.432-2018, RD 52.10.805-2013, RD 52.24.387-2019.

The dissolved inorganic silicon was determined by Koroleff's colorimetric method. The quantitation range is $10\div 2000\ \mu\text{g}/\text{dm}^3$, and the ME is $5.8\div 4.7\%$. Nitrite nitrogen was determined using the method based on the azo dye formation by reacting nitrite with hydrochloric sulfanilamide and α -naphthylethylenediamine. The quantitation range is $0.5\div 100\ \mu\text{g}/\text{dm}^3$, and the ME is $18.0\div 1.5\%$. Nitrate nitrogen was determined after its reduction to nitrite nitrogen on cadmium columns. The range is $5\div 500\ \mu\text{g}/\text{dm}^3$, and the ME is $7\div 2.7\%$. Ammonium nitrogen was determined using the modified Sagi–Solórzano method. The quantifiable ammonium nitrogen concentration range is $15\div 1500\ \mu\text{g}/\text{dm}^3$, and the ME is $11.4\div 1.7\%$.

Results and Discussion

Survey dated April 08, 2019. No sand mining took place during the survey. According to the data of Yevpatoria marine hydrometeorological station (available at: https://tr5.ru/Архив_погоды_в_Евпатории), in the first decade of April. The air temperature dropped to $6\ ^\circ\text{C}$ in the morning and rose to $21\ ^\circ\text{C}$ in the afternoon. During the survey period, the easterly and northeasterly winds with the speed of $2\text{--}5\ \text{m/s}$ prevailed.

Temperature and Salinity. The water temperature in the surface layer was characterized by insignificant spatial variation in the range of $10.6\text{--}10.8\ ^\circ\text{C}$, and only by $15:00$ in the shallow area of the sand mining site, the water warmed up to $12.6\ ^\circ\text{C}$. The water temperature decreased slightly with depth. For example, at the stations along the fairway, at depths greater than $10\ \text{m}$, the water temperature was $9.6\text{--}10.0\ ^\circ\text{C}$. The salinity in the surface water layer varied from $17.85\ \text{PSU}$ in the farm area to $18.05\ \text{PSU}$ in the areas of the sand mining site and lake entrance channel. The salinity varied slightly with depth.

Hydrochemical Parameters. The studies showed high oxygen concentration in the entire water column (saturation above 100%) and its fairly even horizontal distribution. The minimum oxygen content (100.4%) observed in the bottom layer, was more than 2.5 times above the minimum allowable level (40%) according to the water quality standards for water bodies of fishery importance²⁾. *BOD₅ and oxidizability* in the surface layer demonstrated low values, which varied within $0.91\text{--}1.36\ \text{mgO}_2/\text{dm}^3$ and $2.56\text{--}3.53\ \text{mgO}_2/\text{dm}^3$ and were below the maximum allowable levels ($2.0\ \text{mgO}_2/\text{dm}^3$ and $4.0\ \text{mgO}_2/\text{dm}^3$, respectively). From the *BOD₅* and oxidizability values, the water area under study can be characterized as unpolluted.

In the sand mining area in the near-bottom water layer, the lowest oxygen concentration and the highest concentrations of organic phosphorus and silicate were observed. The concentrations of *mineral nitrogen and phosphorus* in the surface water were as follows: the nitrite nitrogen and mineral phosphorus concentrations in the layer ($0.3\text{--}1.1\ \mu\text{g}/\text{dm}^3$ and $0.6\text{--}2.5\ \mu\text{g}/\text{dm}^3$) did not exceed the maximum

²⁾ *On the Approval of Water Quality Standards for Water Bodies of Commercial Fishing Importance, Including Standards for Maximum Permissible Concentrations of Harmful Substances in the Waters of Water Bodies of Commercial Fishing Importance*: Order of the Ministry of Agriculture of Russia dated December 13, 2016, No. 552. URL: <http://publication.pravo.gov.ru/Document/View/0001201701160006> [Accessed: 11 March 2023].]

allowable levels. The concentrations of nitrate nitrogen varied from 9.2 to 19.1 $\mu\text{g}/\text{dm}^3$ and those of ammonium nitrogen from 0.6 to 191.8 $\mu\text{g}/\text{dm}^3$. In the mussel-and-oyster farm area, the decrease in the nitrate and increase in the ammonium concentrations with depth were observed.

The distribution of the silicate and ammonium nitrogen concentrations in the surface and bottom layers was uneven (Fig. 2). The ranges of the silicate fluctuations were 49.7–137.4 $\mu\text{g}/\text{dm}^3$ in the surface layer and 38.4–130 $\mu\text{g}/\text{dm}^3$ in the bottom layer. The highest concentration of silicon in the bottom layer coincided with the maximum concentration of ammonium nitrogen (Station 4), and the highest concentration of silicon (137.4 $\mu\text{g}/\text{dm}^3$) in the surface layer was observed in the sand mining site area.

Organic nitrogen and phosphorus were determined only in the surface water layer, and their concentrations varied from 6.1 to 9.5 $\mu\text{g}/\text{dm}^3$ and from 875 to 1104 $\mu\text{g}/\text{dm}^3$, respectively. In the farm area and in the areas adjacent to it, increased organic nitrogen concentrations were observed, and in the sand mining site area, the highest concentration of organic phosphorus was noted.

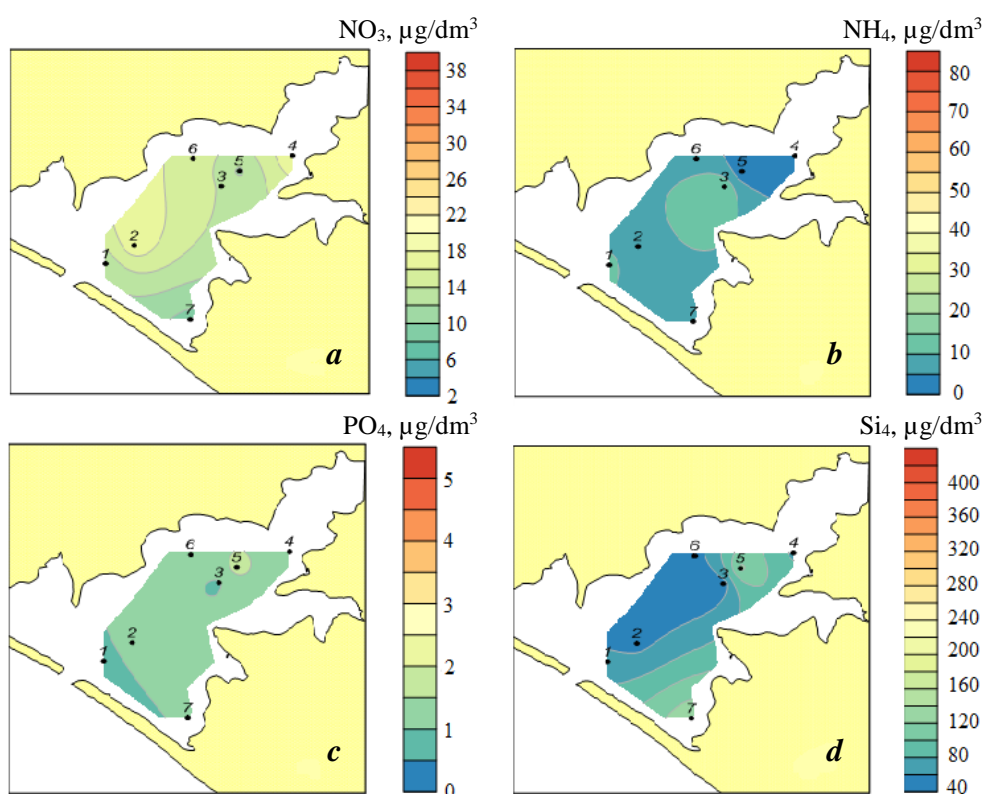


Fig. 2. Distribution of nutrient concentrations in the surface layer: nitrates (a), ammonium nitrogen (b), phosphates (c), silicon (d); April 2019. Numbers denote stations

Survey dated May 27, 2019 was conducted during the sand mining. The survey was preceded (on May 26) by blowing of a westerly wind of 5–8 m/s (and blasts up to 10 m/s). Simultaneously with the water sampling, a scheme of frequent station locations was worked out using the multi-parameter probe *Condor*. The survey yielded data on the water temperature and parameters related to pollution in the area. This made it possible to choose the location of water sampling stations. In the sand mining site area with the depths of less than 2 m, the suspended matter pollution area was stretched downwind, with its horizontal spread about 600 m [9].

Temperature and Salinity. At the end of the spring period, intense warming of the waters and formation of a thermocline took place in the lake. There was no temperature stratification in areas shallower than 4 m (including the sand mining site area) (Fig. 3). The water column was homogeneous and warmed up to 22.9–23.3 °C. At stations with depths greater than 8 m, the temperature distribution was characterized by a presence of a 4–8-m-thick upper quasi-homogeneous layer with a temperature of 22.3–22.7 °C and a 3–5-m-thick transient layer with the vertical gradient of no greater than 0.6°C/m. Under the transient layer at a depth of 12–16 m, the temperature was the lowest, 18.8–19.5 °C (Fig. 4).

The salinity of the surface layer varied in the range of 18.29–18.45 PSU, increasing to the northeast and reaching its maximum in the shallow Shchelkunov Bay. At depths over 10 m, along the channel fairway transect, the vertical salinity gradient was insignificant and the maximum salinity values did not exceed 18.32 PSU.

Hydrochemical Parameters. The *dissolved oxygen* saturation was high. In the surface layer, the saturation reached as much as 121.7 % with the average value of 109.7 %. In the bottom layer, the oxygen saturation was slightly lower: the average value was 103.2 % and the lowest one was 95.7 % (near the lake

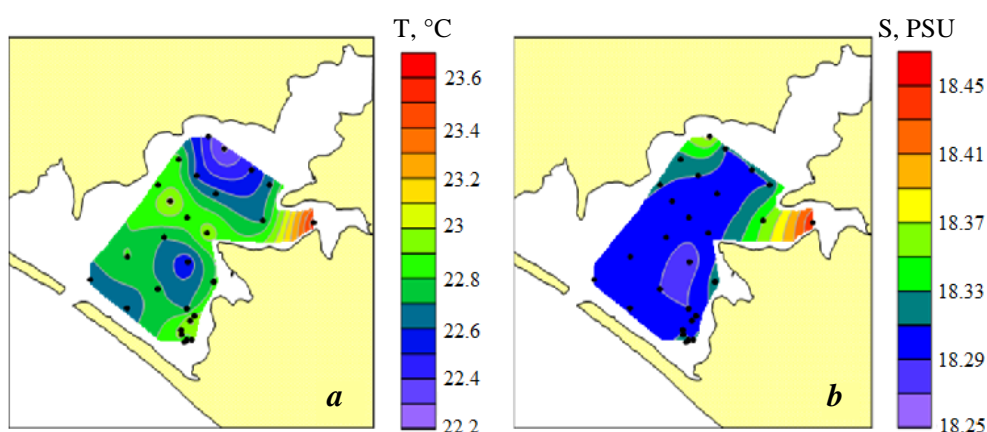


Fig. 3. Distribution of temperature (a) and salinity (b) in the surface layer, May 2019. Points are station locations

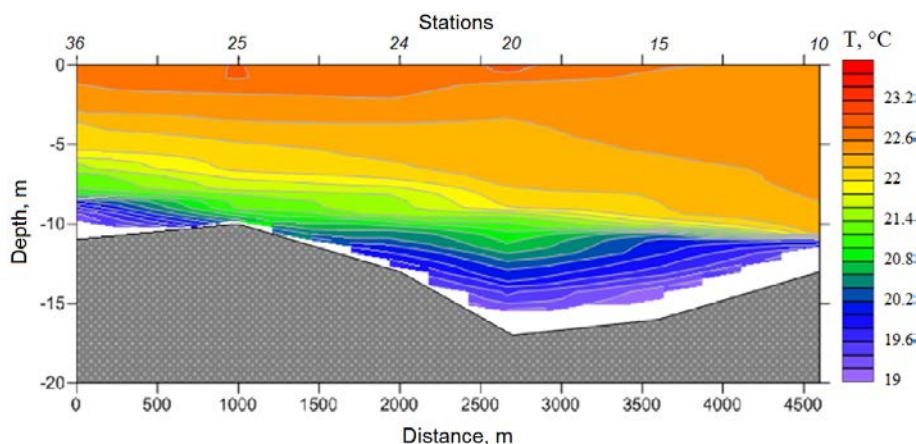


Fig. 4. Temperature distribution at the channel transect; May 2019

entrance channel). In addition, at Stations 10 and 15 along the channel fairway transect, the oxygen saturation in the near-bottom layer was 97.8 % and 97.5 %.

BOD₅ demonstrated low values with insignificant spatial variability: they did not exceed the maximum allowable levels (MAL) according to fishery standards and varied from 1.12 to 1.97 mgO₂/dm³ with the average equal to 1.54 mgO₂/dm³. The oxidizability values, like BOD₅, did not exceed MAL. The only exception was the measurement in the sand mining site area, where the value of oxidizability was 4.24 mgO₂/dm³ and exceeded the corresponding MAL by 0.24 mgO₂/dm³. In general, the low BOD₅ and oxidizability values registered in the May survey indicate that the area under study was not polluted.

The concentrations of *mineral nitrogen and phosphorus* were low and evenly distributed over the water area under study. The concentrations of nitrate nitrogen in the surface layer varied from 2.7 to 20.0 µg/dm³ and those of ammonium nitrogen from 8.9 to 48.4 µg/dm³, with the average values equal to 8.1 and 26.2 µg/dm³, respectively. The highest concentrations of nitrate and ammonium nitrogen were observed in the sand mining site area. The concentrations of mineral phosphorus and mineral nitrogen were low (from 0.1 to 5.4 µg/dm³) with the average value of 2.2 µg/dm³ for the surface layer. The maximum values were observed in the areas of the mussel-and-oyster farm and the sand mining site.

Figure 5 shows the distribution of concentrations of mineral nitrogen, phosphorus, and silicon in the surface layer of the lake. The phosphate concentrations in May were almost twice as high as in April. The concentrations of mineral forms of nitrogen in the surface layer of Lake Donuzlav in 2019 and 2018 did not differ. The silicate concentration distribution in the survey was uneven; the fluctuation range in the surface layer was 44.1–409.8 µg/dm³ with the average value of 111.3 µg/dm³. The highest silicate concentration was found in the area affected by the domestic wastewater discharge. The average silicate concentrations in May were almost 1.5-fold higher than in April. The concentrations of organic nitrogen

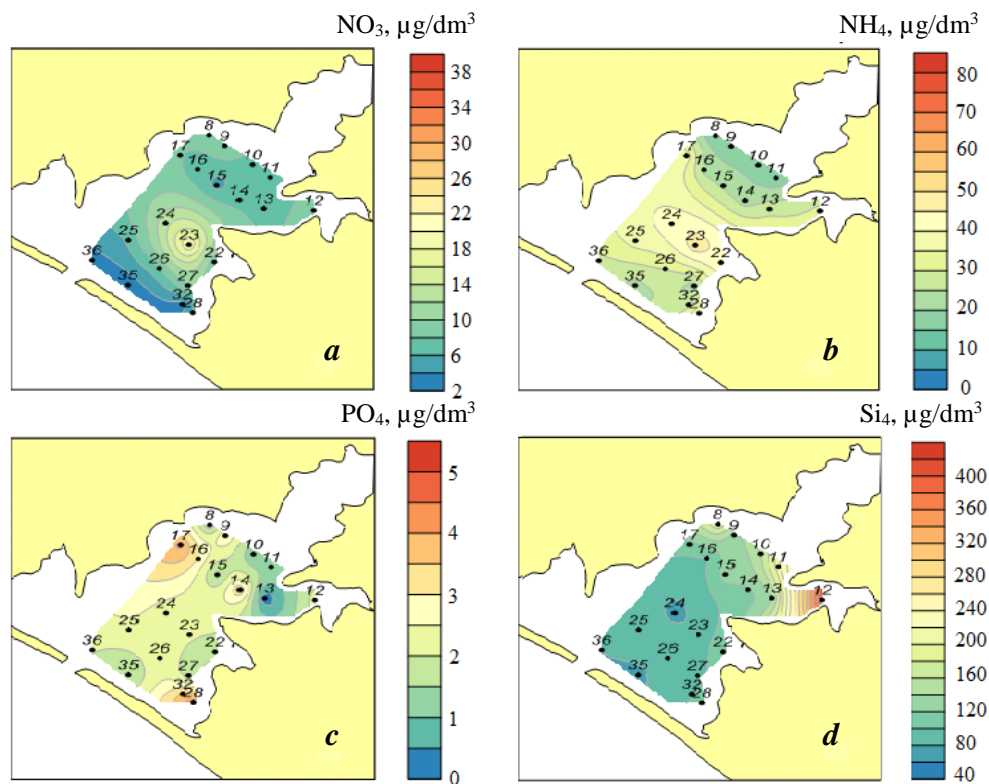


Fig. 5. Distribution of concentrations of biogenic elements in the surface layer: nitrates (a), ammonium nitrogen (b), phosphates (c), silicon (d); May 2019. Numbers denote stations

and phosphorus varied in the surface layer from 643 to 1426 $\mu\text{g}/\text{dm}^3$ and from 11.4 to 20.1 $\mu\text{g}/\text{dm}^3$, respectively. In the sand mining site area, an increase in the contents of both organic nitrogen and phosphorus was observed.

The permanganate oxidizability method allows indirectly obtaining an approximate estimate of dissolved organic carbon content in water. According to Skopintsev³⁾, the value 0.34 is the mean ratio of the oxidizability oxygen in the 0–50 m layer (1.22 mg/dm^3) to organic carbon (3.6 mg/dm^3). Using the permanganate oxidizability values measured by us and the coefficient 0.34, we calculated the content of dissolved organic carbon (C_{DOC}) in the surface layer. The range of the C_{DOC} variations was 8.09–12.47 mgC/dm^3 . The maximum was recorded in the sand mining site area (Station 28) and the minimum was in the mussel-and-oyster farm area.

³⁾ Skopintsev, B.A., 1975. [Formation of the Modern Chemical Composition of the Black Sea Waters]. Leningrad: Gidrometeoizdat, 335 p. (in Russian).

Survey dated September 16, 2019. According to the data of Yevpatoria marine hydrometeorological station, the air temperature on September 15–16 varied from 13 to 23.8 °C. On September 15, northeasterly winds at a speed of 3–6 m/s prevailed, and within one day they changed to westerly and southwesterly winds with the speed of 3–5 m/s. The amounts of sand mining were reduced that day, the wastewater discharge occurred intermittently and with different intensities. Therefore, the size of the area of increased concentration of suspended solids was smaller than on May 27, 2019. The suspension patch was elongated along the coast to the northeast.

Temperature and Salinity. In September, the autumn cooling of the waters begins and the temperature is equalized throughout the entire water column. On September 15–16, the air temperature dropped to 13 °C at night and rose to 24 °C in the daytime. The local temperature minimum (19 °C) was observed in the sand mining site area, while in most of the area under study the temperature was about 21 °C (Fig. 6). Up to the depth of 17 m, the water temperature was almost uniform. The salinity varied in the range of 18.4–18.8 PSU, increasing from the lake entrance channel to the middle part of the lake. The maximum salinity values (18.8 PSU) were recorded in the shallow area of the sand mining site.

Hydrochemical Parameters. The oxygen distribution in the water area in the late summer was quite uniform. In terms of saturation, its content varied from 89.9 to 108.7 % in the surface water layer and from 89.9 to 108.7 % in the near-bottom layer. The lowest values were recorded on the border of the sand mining site area and the adjacent water area; the highest values were recorded in the area along the channel fairway transect.

The values of BOD_5 varied in the surface layer from 0.73 to 1.95 mg/dm³ and did not exceed MAL. The highest BOD_5 value was observed in the sand mining site area. The oxidizability varied from 3.29 to 5.37 mgO/dm³. The lowest value was observed in the port area at a depth of 9 m, and the highest value, exceeding MAL by 1.37 mgO/dm³, was observed in the surface layer of the same station. In the sand mining site area, the oxidizability values exceeded MAL due to the return water discharge.

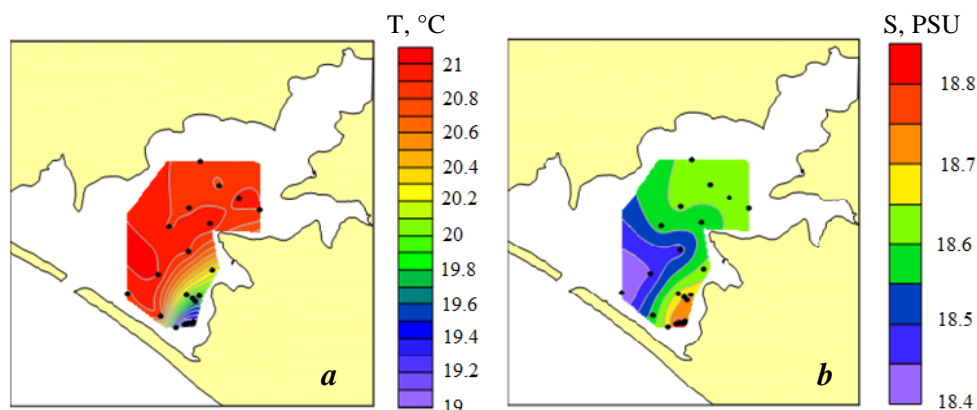


Fig. 6. Distribution of temperature (a) and salinity (b) in the surface layer September 2019. Points are station locations

The dissolved organic carbon concentration C_{DOC} calculated from oxidizability changed during the survey from 9.68 to 15.79 mgC/dm³ and approached the ranges of C_{DOC} obtained in May (8.09–12.47 mgC/dm³) in Lake Donuzlav.

Similarly to the previous survey, the concentrations of *nitrite nitrogen and mineral phosphorus* demonstrated low values and uniform distribution over the area (Fig. 7). The concentrations of nitrite nitrogen in the surface and bottom layers varied from 0.2 to 1.2 µg/dm³ and those of mineral phosphorus from 1.5 to 4.6 µg/dm³. The distribution of the nitrate nitrogen, ammonium nitrogen, and silicon concentrations was uneven both horizontally and vertically. The highest concentrations of nitrate in the surface (38.0 µg/dm³) and bottom layers (42.4 µg/dm³) were recorded in the port and sand mining site areas. The concentrations of nitrate nitrogen at other stations were fairly even, with their average values being 13.4 µg/dm³ in the surface layer and 12.6 µg/dm³ in the bottom layer. The concentrations of ammonium nitrogen in the surface layer varied from 3.2 to 78.8 µg/dm³ with the average of 24.5 µg/dm³. The highest ammonium nitrogen concentration was noted in the surface layer at the sand mining site.

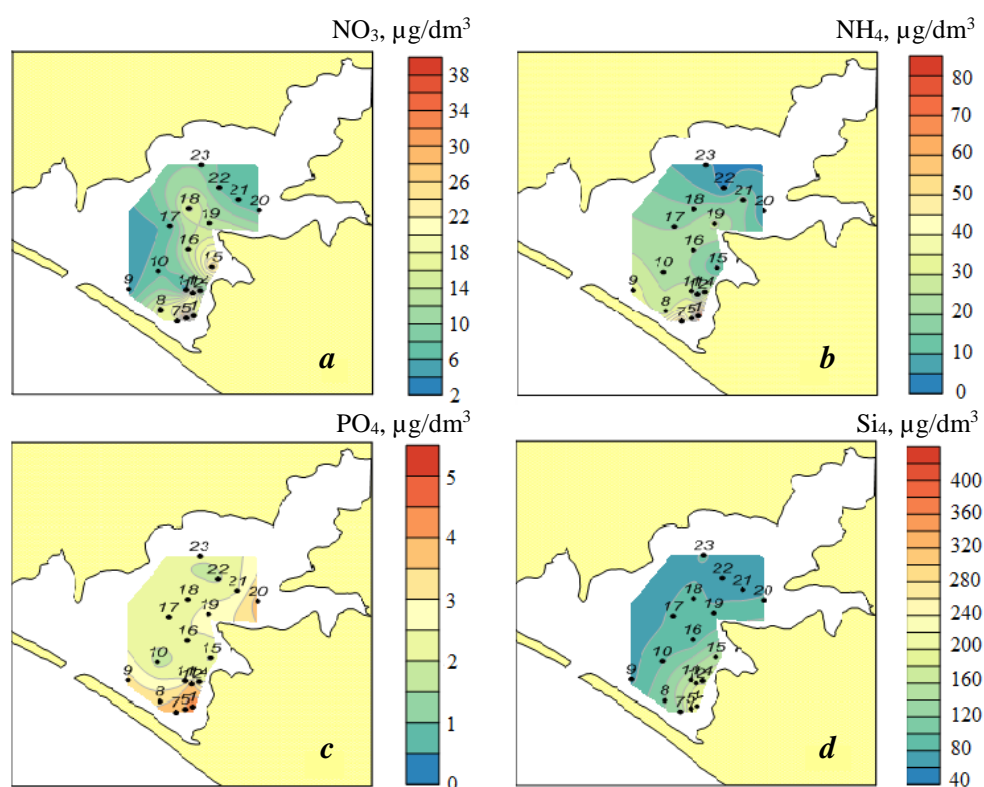


Fig. 7. Distribution of concentrations of biogenic elements in the surface layer: nitrates (a), ammonium nitrogen (b), phosphates (c), silicon (d); September 2019. Numbers denote stations

The distribution of *silicon* concentrations in the surface layer varied from 73.3 to 211.5 $\mu\text{g}/\text{dm}^3$ with the average of 119.7 $\mu\text{g}/\text{dm}^3$. Increased values were observed both in the sand mining site area (Stations 1, 5–8) and in the suspension patch, which was observed up to Stations 11–15. In the rest of the water area, the concentration of silicon was low.

The concentrations of *organic nitrogen and organic phosphorus* were distributed as follows: in the areas affected by the domestic wastewater discharge and sand mining, increased organic nitrogen concentrations (from 1033 to 1297 $\mu\text{g}/\text{dm}^3$) were noted. In the rest of the water area, the respective values were significantly lower and varied from 703 to 885 $\mu\text{g}/\text{dm}^3$. The organic phosphorus distribution was similar to the distribution of organic nitrogen: the increased values (from 18.6 to 30.9 $\mu\text{g}/\text{dm}^3$) were observed in the areas where the organic nitrogen increase was observed, and lower values (from 17.6 to 26.9 $\mu\text{g}/\text{dm}^3$) were in the areas of the organic nitrogen decrease.

Conclusion

The spatial distribution of the thermohaline characteristics in waters of Lake Donuzlav is highly heterogeneous. In spring, there is intensive warming of water and formation of thermal stratification in the lake. In the second half of September, the autumn cooling of waters begins and the vertical distribution of temperature is uniform throughout the entire water column. The hydrochemical studies performed indicate high oxygen concentration in waters of the lake. The lowest concentrations of dissolved oxygen never reached the minimum allowable values. No cases of oxygen deficiency were found over the period under study. All BOD₅ values were lower than MAL. The anthropogenic impact on Lake Donuzlav in the areas of sand mining, port and domestic wastewater discharge results in the local increase in oxidizability and concentration of nutrients, as well as organic phosphorus and nitrogen. The highest values of the mineral and organic nitrogen and phosphorus concentrations were observed in the sand mining site area.

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