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Hydrochemical Regime of the Kiliya Delta of the Danube River in Retrospective and Modern Conditions: I. Main Indicators of Water Chemical Composition

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Abstract—The article focuses on the changes in the hydrochemical regime of the Kiliya delta of the Danube River, which have occurred during many years of research. It is established that after damming of the Danube River, supersaturation of the river water with dissolved oxygen is observed in the upper and middle river course, which results from an increase in the photosynthetic activity of the algae, a reduction in the content of suspended solids, and pollution of the water with inorganic nitrogen and phosphorus compounds. It is shown that since the 1970s the water mineralization level has increased by approximately 30%. The concentration of Na^+, K^+, SO_4^{2-}, and Cl^- ions has increased. Cases of saltwater penetration into the waters of the Prorva, the Gneushev, and the Bystryi branches have been observed. In modern conditions, the concentrations of nitrate ions and inorganic phosphorus remain high, whereas the concentration of ammonium nitrogen, on the contrary, has decreased almost thrice. It is found that there is an increase in the concentration of dissolved organic substances, especially in spring and summer, which is due to the intensification of bioproduction processes. Among dissolved organic substances in the water of the Kiliya delta of the Danube River, the dominating position is occupied by humic substances, the relative content of which reaches 54.8–85.6%.

Keywords: dissolved oxygen, water mineralization, inorganic forms of nitrogen, inorganic phosphorus, dissolved organic substances, humic substances, the Kiliya delta of the Danube River

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INTRODUCTION

The Danube River is the second longest (2860 km) river in Europe, after the Volga, passing through or bordering the following ten states: Germany, Austria, Slovakia, Hungary, Croatia, Serbia, Bulgaria, Romania, Ukraine, and Moldova. The Danube flows into the Black Sea, forming a delta at the Romania–Ukraine border.

The hydrochemical regime of the Danube River is formed due to the processes, occurring along the entire length of the river itself, as well as under the influence of the wastewaters from the industry, agriculture, and residential areas of the Danube countries. The key factors forming the hydrochemical regime can be divided into natural (aqueous runoff dynamics, meteorological conditions, in particular, precipitation quantity and quality, vital activities of aquatic organisms etc.) and anthropogenic, primarily attributable to the nature and quantities of the wastewater. The Danube River is characterized by a high content of suspended solids, predominantly, of mineral nature; pollution by metals, nutrients, and other specific chemical compounds; damming of the river; and the seawater penetration into the delta arms [1–5].

The Danube delta is the third largest river delta in Europe (4200 km^2), after the Volga delta and the Terek delta. A part of the delta located on the territory of Ukraine (the Kiliya branch) accounts for 20% of the total delta area. The Danube delta includes the Kiliya and the Tul'chinskii branches, with the latter forking into the Sulinskii and the Georgievskii branches, flowing through the Romanian territory [1]. The annual average river runoff amounts to 216 km^3; however, in high-water years this figure can reach 313 km^3 and be as low as 134 km^3 in low-water years. The maximum water flow rate in the lower part of the Danube River is 20 000 m^3/s, whereas the minimum is 1,800 m^3/s [3, 4, 6, 7]. The water flow distribution between the above-mentioned delta branches changed during the observation period (1856–2003). Within this time, the share of the average water runoff in the Kiliya arm decreased from 72 to 52%, whereas in the Tul'chinskii branch, on the contrary, it increased from 27.2 to 48%. Such radical changes occurred in the late 1980's—early 1990's and were associated with hydraulic and engineering works in the Sulinskii and the Georgievskii branches, which also caused seasonal changes in the flow redistribution, in particular, to its increase in the Georgievskii branch during low-water periods [1]. The intra-annual distribution of the water runoff is characterized by a spring-summer high-water season (March–July) and summer-autumn (August–October) and winter low-water periods. In addition, autumn and winter floods are observed [1, 3, 6]. The river water sources include melt, rain, and ground waters. The dominance of any of the sources depends on the season. As a rule, in spring meltwater feeding predominates, whereas in summer the main water sources are rain and meltwater [4].

The Kiliya delta of the Danube River consists of two inner and one outer (marine) deltas. The first inner delta is located between the cities of Izmail and Kiliya, while the second is to be found between the cities of Kiliya and Vilkovo. The outer delta of the Kiliya arm is formed downstream of Vilkovo and consists of the two main branches: the Ochakovskii and the Starostambul'skii [1]. In turn, smaller streams branch off from the Ochakovskii and the Starostambul'skii branches. According to the hydraulic and morphometric characteristics, the Starostambul'skii branch should be considered as the mainstream. It is 23 km long, 150–400 m wide, and 4–8 m deep. The Ochakovskii branch has a slightly winding riverbed with persistent banks, its width and depth ranging within the limits of 180–400 m and 5.2–15 m, respectively. Upstream of the branching point of these two streams, but downstream of the city of Vilkovo, the Belgorodskii branch turns off to the left of the Kiliya arm. It has a winding riverbed, the width and depth of which reach 10–40 and 1.5–4.0 m, respectively [8].

Like in many deltas of other rivers, in the Danube delta there is a possibility of saltwater penetration. This fact can be associated both with deepening of the delta branches for navigation purposes and with reduced river runoff volumes, as well as surges and tides in the river and seawater mixing zone. In the Kiliya delta of the Danube River, a saltwater wedge penetrates the Prorva and the Gneushev branches at reduced water flow rates of 300–400 m^3/s. A similar situation is observed in the Sulinskii arm. The maximum penetration range of the saltwater wedge in the Prorva branch reaches 16.8 km, whereas in the Sulinskii branch the figure is 16.5 km. In 50% of cases, the saltwater in the Prorva moves only as far as 5 km or less along the stream [1, 9, 10]. After the consruction of the first stage of the navigation channel along the Bystryi branch in 2004, it became possible for the saltwater wedge to penetrate this branch as well. The saltwater penetration range was calculated based on a hydraulic model and a three-dimensional "tritox" model. The resulting figure was 4–5 km, which indicates the formation of the saltwater wedge within the boundaries of the branch. The researchers conducting the simulation believed that under natural conditions there was a probability of the saltwater penetration even beyond the limits of the Bystryi branch. As the simulation shows, the penetration of the saltwater wedge can occur at water flow rates below 800–900 m^3/s [11]. The field research results for 2004–2010 point at the seawater penetration during low-water seasons along the entire length of the Bystryi branch in case of north and east winds [12].

In the Kiliya delta of the Danube River, the ice cover is formed in its upper region in early January and persists until the end of February–early March. The thickness of the ice cover does not exceed 25–35 cm. Due to intensive turbulent mixing of the water, the temperature difference between the surface and the bottom layers does not exceed 0.3°C [3, 6].

The formation of the river delta depends on the effluent of suspended solids. Many years of observations have shown that on average this parameter has ranged from 42 to 84 million t/year. Changes in the effluent of suspended solids in the lower Danube have become noticeable starting from the middle of the 20th century, which is associated with sedimentation of the solids in the upstream reservoirs. During the entire observation time, it is possible to distinguish the following periods in the formation of the flow of suspended substances: a period of conditionally natural regime (1840–1920), a period of slightly modified regime (1921–1960), and a period of radically modified regime (1961–2002). The effluent of suspended solids was significantly altered by the commissioning of the Iron Gate–I reservoir starting in 1971, as well as the Iron Gate–II reservoir, a little later. In addition, the effluent of suspended substances was affected by the construction of low-pressure dams and numerous reservoirs on the tributaries. Whereas before 1920 the average content of suspended solids was 324 mg/L, the respective figures for the periods of 1921–1960, 1961–1970, 1971–1984, and 1985–2002 were 263, 217, 210, and

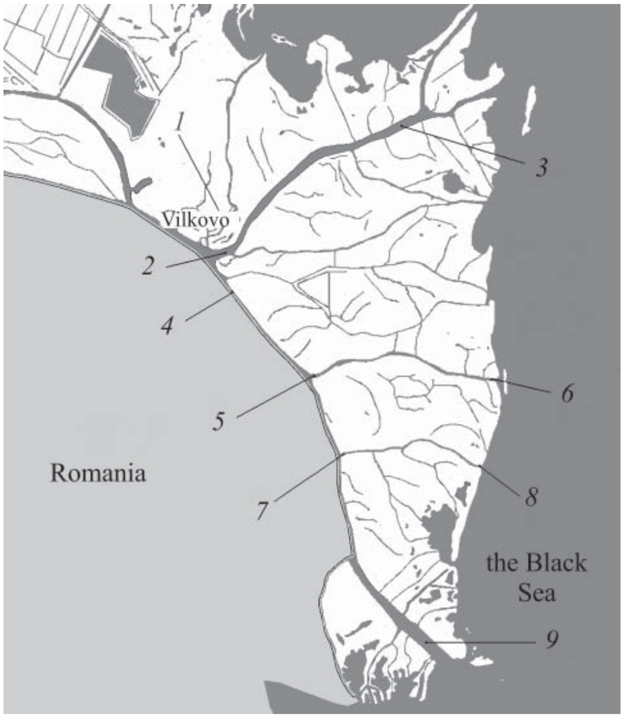

Fig. 1. Chart map of the Kiliya delta of the Danube River. Water sampling stations: (*1*) Belgorodskii branch (Vilkovo), (*2*) Ochakovskii branch (17th km), (*3*) Ochakovskii branch (6th km), (*4*) Starostambul'skii branch (outflow), (*5*) Bystryi branch (outflow), (*6*) Bystryi branch (mouth), (*7*) Vostochnyi branch (outflow), (*8*) Vostochnyi branch (mouth), and (*9*) Starostambul'skii branch (mouth).

142 mg/L. Consequently, the content of suspended solids for the entire observation period decreased 2.3-fold [1]. According to V. M. Timchenko [3], the average annual content of suspended solids in the 1980s–1990s was 170 mg/L, and in some cases it could reach 500–1500 mg/L. In the seasonal aspect, the maximum values of the suspended matter content are observed in summer, with mineral particles accounting for 95–98% of the total [3–5]. The research results for the period of 1958–1963 indicate an uneven distribution of both the water runoff and the effluent of suspended solids in the Kiliya delta of the Danube River. The largest amount of the suspended matter, accounting for 40.1% of the total, was transported along the Starostambul'skii arm, whereas the figures for the Ochakovskii, the Potapovskii, the Bystryi, and the Prorva branches were 37.4, 19.2, 17.3, and 12.1%, respectively [1].

The present work summarizes the data on the hydrochemical regime of the Kiliya delta of the Danube River in retrospect and in modern conditions, using the results of many years of research carried out by various authors, as well as our own studies, performed in different years. Special attention is paid to the salt composition of water, nutrients, organic substances, and metal migration forms at the current stage of the delta operation.

EXPERIMENTAL

Field research works of the Kiliya delta of the Danube were carried out in 2013–2014 and 2018. The chart map of the area under study and the sampling stations are shown in Fig. 1. Water samples were taken from the surface layer using a Ruttner's bathometer. The water mineralization was determined at the sampling site using AZ-86031multifunction device, which also makes it possible to measure the water temperature, pH values, concentration and saturation of the water with dissolved oxygen. In laboratory conditions, the water sample was passed through Synpor (Czech Republic) nitrocellulose filter with a pore diameter of 0.4 μm in order to separate the suspended solids. Later, values of the hydrochemical parameters under study were measured in the water filtrates. The content of inorganic forms of nitrogen and phosphorus in the water was determined using the photometric analysis techniques. To measure the concentration of ammonium nitrogen, Segnette's salt (potassium sodium tartrate) with Nessler's reagent were used, the Greiss reagent was applied in case of nitrite ions, sodium salicylate in case of nitrate ions, and ammonium molybdate with ascorbic acid were used to measure the concentration of inorganic phosphorus. The chemical oxygen demand values (COD_{Mn}, COD_{Cr}) were determined according to the standard techniques [13]. The water colority was measured on the basis of the photometric method, using the dichromate-cobalt simulation scale [13]. The concentration of humic substances (HS) was determined according to the calibration chart: Water colority, degrees of Cr-Co-scale – humic substances concentration, mg/L. The calibration chart was developed using purified dry preparations of fulvic acids and humic acids, isolated from the water of the Kanev Reservoir. Humic substances were isolated from the water, using a column filled with diethylaminoethyl cellulose (DEAE) produced by SERVA. The ratio of fulvic and humic acids in the composition of these substances was studied. In order to isolate the humic acids fraction from the composition of the humic substances, the solution of the latter was acidified to pH ≈ 1.0, heated to ~60°C, and left for 24 h until total precipitation. The molecular-weight distribution of fulvic and humic acids was studied using the gel chromatography method. For this purpose, a column filled with TOYOPEARL HW-50 gel (Japan) was used. The isolation of humic substances on a column with diethylaminoethyl cellulose, as well as the separation of fulvic and humic acids into fractions on the column with the above-mentioned gel are described in our previous works in detail [14, 15]. The concentration of humic substances and their constituent fractions was also determined photometrically at $\lambda = 254$ nm, as described in the article [14].

RESULTS AND DISCUSSIONS

Oxygen regime and water pH. A self-purification ability and redox processes in surface water objects largely depend on the content of dissolved oxygen in the water. Its deficiency leads to secondary water pollution with nutrients, metals, and organic substances, which, in turn, negatively affects the life activity of hydrobionts. In water objects designated for commercial fishing, the content of dissolved oxygen should not be lower than 4 mg/L [16].

For many years following the damming of the Danube River, the concentration of dissolved oxygen has tended to decrease in wastewater discharge sites and increase in water bloom areas (saturation degree exceeding 100%) [17–19]. In the lower reaches of the Danube in the 1950s there was practically no dissolved oxygen deficiency throughout the year, its concentration ranging from 8 to 12 mg/L. The degree of the water saturation with oxygen was not less than 75–95%. The absence of oversaturation with oxygen indicated a low photosynthetic activity of phytoplankton, which could not actively develop due to the high content of suspended solids. This fact was confirmed by the narrow range of pH values, lying within the limits of 7.6–8.4 [20]. With a decrease in the suspended matter content, there is an increase in the number of water bloom cases, resulting in the water oversaturation with oxygen and its alkalization. In the autumn of 1990, the concentration of dissolved oxygen and the water saturation with oxygen were within the range of 5.8–10.8 mg/L and 78–112%, respectively, and the pH value amounted to 7.5–8.6 [17]. According to many years of studies in the Danube countries, during the period of 1996–2000, the dissolved oxygen concentration along the entire length of the Danube River was 4.3–10.3 mg/L, whereas in the Kiliya delta of the Danube the figure was 6.1–8.2 mg/L [21]. The concentration of dissolved oxygen in the Kiliya delta of the Danube between 1995 and 2006 lied within a wider range of values (5.2–13.8 mg/L), with the pH values of 7.1–8.6 [22]. During the period of 2003–2012, a wide range of the dissolved oxygen content and pH values was observed in the mouths of the Bystryi and the Vostochnyi branches, the specified parameters varying within the limits of 5.1–13.0 mg/L and 7.23–9.85, respectively. The high

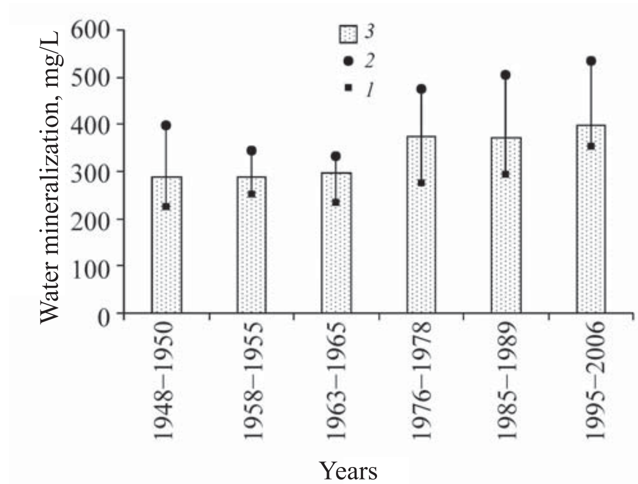

Fig. 2. Limit (*1*, *2*) and average (*3*) values of water mineralization in the Kiliya arm of the Danube River in different years of research [6, 22].

oxygen concentrations and the water alkalization in these areas indirectly indicate recurring cases of intensification of the phytoplankton photosynthetic activity [23]. The phenomena of the water undersaturation with oxygen (70–55% saturation in the surface horizon and 17% saturation in the bottom layer) have become evident. Most probably, these phenomena are caused by the consumption of oxygen for oxidation of organic substances of the autochthonous origin, the concentration of which in the delta water has increased. However, in places of the phytoplankton active vegetation, the water is oversaturated with oxygen (120–150%) [2, 19].

At the end of October 2018, the concentration of dissolved oxygen was 7.8–8.1 mg/L, and the water saturation with oxygen in the Bystryi, the Kiliya, and the Ochakovskii branches lied within the range of 75.9–80.7%, which indicates a sufficient oxygen content in the water for self–purification processes to dominate. The pH value varied within the range of 8.03–8.09.

Water mineralization and major ions. Since the middle of the 20th century, the mineralization of the Danube River water has been changing (Fig. 2). While in the 1950s–1960s the average indicators of the water mineralization lied within the range of 287–296 mg/L, starting from the second half of the 1970s and in the early 2000s, it reached 372–398 mg/L, which means an increase of approximately 30%.

Among the major ions, accounting for the water mineralization, over time there has been a significant increase, mainly involving such ions as Na^+, K^+, SO_4^{2-}, and Cl^-.

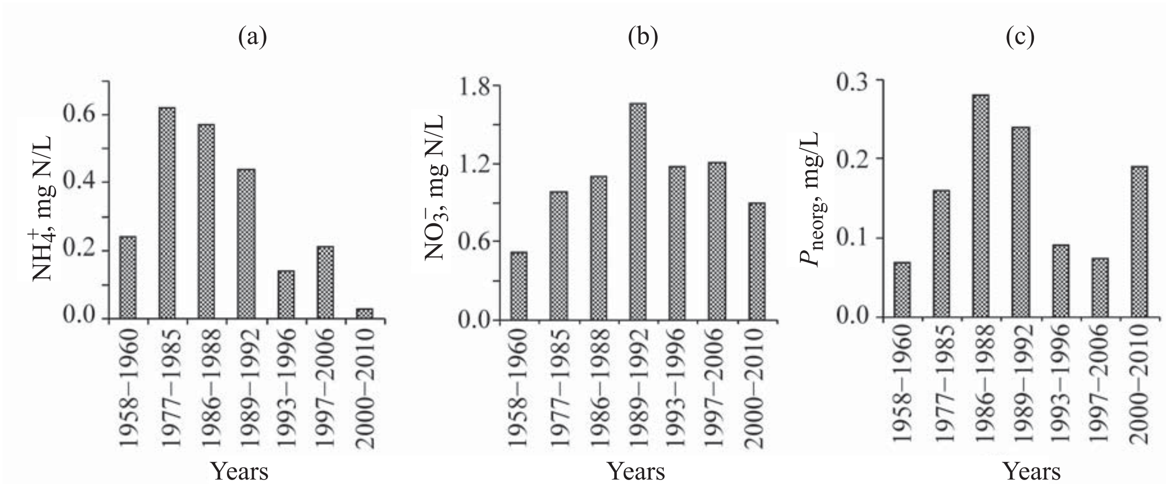

Fig. 3. Averaged values of concentration of ammonium (a) and nitrate nitrogen (b), and inorganic phosphorus (c) in the water of the Kiliya delta of the Danube in different research periods [12, 18, 19, and 22].

For example, the total content of Na^+ and K^+ ions in the 1950s averaged to 10 mg/L, whereas in the late 1980s it increased up to 31 mg/L. A similar increase was typical for anions as well. Thus, the average content of sulfate ions increased from 25 to 52 mg/L and the content of chloride ions rose from 14 to 32 mg/L. These data convincingly indicate the influence of the anthropogenic factor on the water mineralization in the Kiliya delta of the Danube River. It is not unlikely that this fact is associated with an increase in the water withdrawal for economic needs and irrigation, accompanied by constantly growing amounts of wastewater released into the river [17].

There is a tendency towards widening of the mineralization limit value range, as well as towards an increase in the mineralization average indicators. While in the middle of the 20th century, the difference between the boundary values amounted to 100 mg/L, in the 1990s it reached 200 mg/L [17]. In the lower part of the Danube River, the water mineralization level in 1948–1950 and 1958–1959 was equal to 230–400 mg/L [20]. According to the results of the Blue Danube–90 international expedition in September–October of 1990, the mineralization level of the Danube River water from Vienna to Vilkovo ranged within the limits of 325–520 mg/L. As a rule, the mineralization increased downstream of industrial effluent discharge sites, as well as downstream of the Danube's confluence with the Tisza, the Sava, the Morava, and the Prut rivers [17]. From 1995 to 2006, the water mineralization level in the lower part of the Danube (the Kiliya branch) was 270–536 mg/L with the average value of 398 mg/L for the period [22]. In the 1990s there was an increase in the water mineralization range in the course of the year. According to the major ions ratio, the Danube water belongs to the hydrocarbonat class, the calcium group, type II [17].

In addition to saltwater desalination on the Danube seashore, the phenomenon of periodic saltwater penetration has become characteristic for some of the Danube distributaries [1], which was confirmed during our expedition (27.10–03.11.2018). The mineralization level of the surface layer water in the Kiliya (upstream of Vilkovo) and the Ochakovsky (17th km) arms was within the range of 227–255 mg/L, while in the Bystry branch (6th km) it reached 540 mg/L.

Nutrients. This group of chemical elements includes nitrogen, phosphorus, silicon, and iron compounds. Nitrogen and phosphorus compounds determine the degree of the water object pollution with household effluents, also affecting the trophic status of the water body. High concentrations of these compounds lead to eutrophication of surface waters with the resulting negative consequences, such as the water bloom, dissolved oxygen deficiency, and mass fish mortality. As for many other chemical elements, maximum permissible concentration levels have been established for nitrogen and phosphorus compounds. For example, according to the methodology for water quality environmental assessment [24], the concentration of ammonium nitrogen, nitrite, nitrate ions, and inorganic phosphorus in water should not exceed 0.3, 0.01, 0.5 mg N/L, and 0.05 mg P/L. Similar concentration limits for inorganic forms of nitrogen and phosphorus in the European Union countries, used to assess the water quality of the Danube River, are as follows: 0.3, 0.06, 3.0 mg N/L, and 0.1 mg P/L [21]. According to the results of many years of studies, it has been found that the highest concentrations of ammonium nitrogen, nitrate ions, and inorganic phosphorus were observed within the period from the late 1970s to the early 1990s (Fig. 3).

A similar situation was typical for nitrite ions as well. During the period of 1958–1960, their concentration averaged to 0.012 mg N/L, and from 1977 to 1996, this parameter ranged from 0.044 to 0.074 mg N/L. During the period of 1997–2000, the concentration of nitrite ions returned to the original values and averaged to 0.015 mg N/L [18]. However, according to the results of Yu. I. Bogatova research works [12], the concentrations of nitrite ions in the periods of 1990–2000 and 2000–2010 were higher and amounted to 0.045 and 0.056 mg N/L, respectively. The increase in the concentration of nutrients in the 1970s–1990s was associated with intensification in the use of fertilizers and detergents, as well as with dumping of partially treated wastewater into the river. This phenomenon manifested itself most evidently in such river parts as the Borcha arm (340 km from the mouth), Silistra–Calarasi (367 km), Nikopol–Turnu Magurele (592 km), Oryahovo – Beket (680 km), and Vidin – Calafat regions (788 km), and downstream of Budapest (1630 km from the mouth) [17]. Since the beginning of the 1990s, there has been a decrease in the concentrations of ammonium nitrogen and inorganic phosphorus (almost 3-fold), while the concentration of nitrate ions has remained almost unchanged. During the period of 2000–2010, the concentration of inorganic phosphorus returned to the values of the 1970s–1990s (Fig. 3). As the results of our studies show, the concentration of ammonium nitrogen, nitrite and nitrate ions in the water of the Kiliya branch upstream of Vilkovo in August of 2014 reached 0.010, 0.003, and 0.560 mg N/L, respectively. Thus, recently there has been a tendency towards a decrease in concentrations of ammonium nitrogen and nitrite ions, while the concentration of nitrate ions remains high.

According to the results of comprehensive international studies of the Danube River, it turns out that the greatest pollution of the river with inorganic nitrogen and phosphorus compounds is typical for the Romanian and Bulgarian river sections. This phenomenon was observed both in 1990 and in the period of 1996–2000. Thus, the concentrations of ammonium nitrogen, nitrite and nitrate ions, and inorganic phosphorus in the low-water period of 1990 were in the range of 0.2–22.4, 0.02–0.17, 0.8–6.5 N/L, and 0.16–1.0 mg P/L, respectively. It should be noted that the upper values of the listed ingredients content are typical for wastewater discharge sites, which indicates the necessity for the construction of water treatment facilities. During the period of 1996–2000, the content of the specified forms of nitrogen and phosphorus was 0.1–1.42, 0.017–0.233, 1.5– 4.8 mg N/L, and 0.030–0.62 mg P/L [17, 21].

In the course of research focusing on the hydrochemical regime of the Danube River, special attention should be given to the fresh and sea water mixing area (the seaside), where complex physicochemical and biochemical processes of the nutrients transformation take place. The seaside serves as a geochemical barrier, where inorganic forms of nitrogen and phosphorus, silicon, and organic substances are deposited in the bottom sediments. It is found that at the Danube estuary seaside at the salinity of 2–8PSU, the maximum decrease in the content of suspended substances and inorganic nitrogen forms as a result of physicochemical processes is observed. The concentration of inorganic phosphorus begins to decrease already at the salinity of < 2PSU, whereas at 2–8PSU there is a slight increase in its content due to the desorption of phosphorus from the composition of suspended solids. At the water salinity of >8PSU, the decrease in the concentration of nutrients mainly results from biochemical consumption of these substances by hydrobionts [12].

Dissolved organic matter. An important indicator of the ecological state of any water body is the content of dissolved organic substances in the water. It should be noted that surface waters contain a wide range of dissolved organic matter, in particular, humic substances, carbohydrates, proteinaceous compounds, carboxylic acids, amines, phenols, surfactants, and other specific organic compounds [25]. In the practice of hydrochemical monitoring studies, the concentration of dissolved organic substances is estimated based on determination of chemical oxygen demand (COD) indicators, using potassium permanganate (COD_{Mn}) and potassium bichromate (COD_{Cr}) as oxidants. The value of COD_{Mn} indirectly reflects the content of easily oxidizable dissolved organic matter, whereas COD_{Cr} is associated with the total content of such substances. Among numerous organic compounds found in surface water objects, humic substances are prevalent, and only in summer there can be an increase in the content of carbohydrates, phenols, and protein compounds, which are byproducts of the algae life activity [14, 15, 25–27]. However, this applies mostly to water

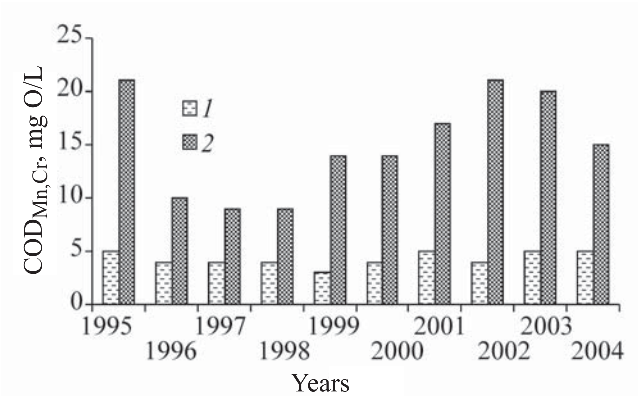

Fig . 4. Changes in annual average values of chemical oxygen demand [(*1*) COD_{Mn}, (*2*) COD_{Cr}] in the water of the Kiliya delta of the Danube [22].

bodies with a high biological productivity. Apparently, the specified fact can be also attributed to the branches of the Kiliya delta of the Danube River, where the water bloom phenomenon takes place.

During many years of studies, starting from 1958, the values of COD_{Mn} for the water in the Kiliya delta of the Danube River have not exceeded 10 mg O/L with rare exceptions, which indicates a relatively low content of easily oxidized organic substances. However, an increase in the values of this indicator has been noted over time. While in the periods of 1958–1959 and 1986–1990 the values of COD_{Mn} were within the range of 2.0–6.0 and 2.3–6.6 mg O/L, between 1996 and 2000 the figures reached 4.2–9.6 mg O/L [19–21]. According to other authors [28–29], the values of COD_{Mn} in the 1970s–1980s averaged to 4.36 mg O/L, but already in the 1990s they increased to 12.54 mg O/L, which is almost thrice. In the delta branches, the maximum COD_{Mn} values can even reach 15.2–18.3 mg O/L. G.P. Garkavaya et al. [19] associate the increase in the values of COD_{Mn} from 4.36 to 18.3 mg O/L during the period of 1977–1996 with an increase in the intensity of production processes in the Kiliya delta and note the phytoplankton development intensification. Consequently, a significant increase in the amount of organic substances is directly associated with bioproduction processes, which were not so strong in the 1950s–1960s. At the same time, the role of the anthropogenic factor in the increased concentration of labile organic compounds should not be underestimated as well. These favorable conditions for the phytoplankton development were formed, on the one hand, due to the increased concentrations of inorganic nitrogen and phosphorus compounds, and, on the other hand, they were associated with the decrease in the content of suspended solids.

According to the results of monitoring studies in the period of 1995–2004, the averaged values of COD_{Mn} changed little and amounted to 3–5 mg O/L (Fig. 4), while the limit values fluctuated within a wider range from 1 to 17 mg O/L, which indicated their seasonal variability [22].

During the period of 1996–2000, the values of COD_{Cr} were within the range of 9–50 and 14–38 mg O/L, respectively, for the Danube River as a whole and its Kiliya delta in particular. In the mouth of the Sulinskii and the Georgievskii branches, the values of COD_{Cr} amounted to 9–50 and 20–36 mg O/L [21]. As with nutrients, the maximum values of this indicator are typical for the Romanian and Bulgarian sections of the river, which points at the anthropogenic component in the inflow of organic substances into the river water. In the upper and middle sections of the Danube, the values of COD_{Cr} did not exceed 20 and 30 mg O/L, respectively [21]. The averaged COD_{Cr} values in 1995–2004 ranged from 9 to 21 mg O/L (Fig. 4), while the variability of this indicator was much wider, i.e. 3–66 mg O/L [22]. Thus, the content of dissolved organic substances in the Danube water undergoes spatial and temporal changes, associated with various rates of the anthropogenic impact and with the seasonal characteristics of the inflow of organic substances into the water. It is found that the maximum values of COD_{Mn} and COD_{Cr} are observed in the spring–summer period, which is related to bioproduction processes and the runoff of organic substances from the catchment area [19].

In September 2013, the values of COD_{Mn} and COD_{Cr} in the water of the Kiliya delta were within the range of 1.4–2.4 and 6.2–12.2 mg O/L, respectively, which corresponds to the average values of these indicators for many years. According to our calculations, the content of dissolved organic substances ranged from 4.65 to 9.15 mg/L. The calculations have been performed, using the following equation: $C_{DOM} = COD_{Cr} \cdot 0.75$ [31].

The concentration of humic substances, as the dominant group in the dissolved organic matter in the water of the Kiliya delta of the Danube River, is 3.1–7.7 mg/L, while their relative content in the total balance of dissolved organic substances reaches 54.8–85.6%, which is within the limits typical for surface water objects [30]. It is detected that the absolute and relative content of humic substances in the branches of the Kiliya delta of the Danube River has decreased downstream. For example,

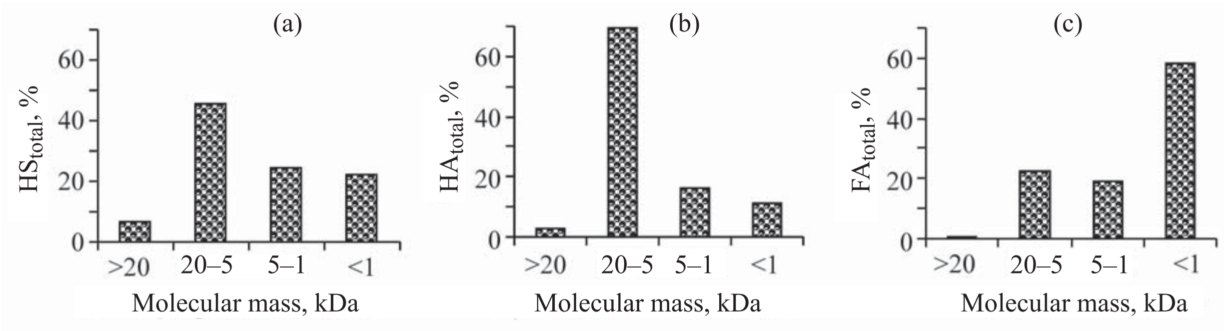

Fig. 5. Molecular weight distribution of undivided humic substances HS (a), humic acids HA (b), and fulvic acids FA (c), contained in the water of the Kiliya delta of the Danube; (a) May 2012 (C_{HS} = 2.7 mg/L), (b, c) November 2012 (C_{HA} = 0.4 mg/L, C_{FA} = 5.6 mg/L).

in the Ochakovskii branch, the concentration of humic substances and their share have varied, respectively, from 7.7 to 5.1 mg/L and from 85.6 to 55.7%, whereas the figures for the Starostambul'skii branch have ranged from 5.7 to 3.1 mg/L and from 69.1 to 66.7%. Due to the fact that humic substances predominates in the composition of dissolved organic matter, we have conducted a more detailed study focusing on humic substances. As a result, it has been established that they are mainly represented by the fulvic acid fraction (>90%), which is typical for the majority of surface waters in Ukraine [14, 15].

The study of the molecular weight distribution of undivided humic substances indicates the dominance of compounds with a molecular weight of 20–5 kDa in their composition (Fig. 5). The relative content of this fraction in the composition of humic acids has been even higher and has almost reached 70%, whereas fulvic acids are characterized by the predominance of compounds with a molecular mass of < 1 kDa in their composition (Fig. 5).

Thus, the predominance of fulvic acids in the composition of humic substances should be considered as a factor playing an important role in the migration mobility of metals. The content of metals in compounds with a molecular mass of < 5 kDa should be considered as a form in which they are potentially available for assimilation by living organisms due to their ability to penetrate the cell membrane [32].

CONCLUSIONS

Under the impact of anthropogenic factors, there have been changes in the hydrochemical regime of the Kiliya delta of the Danube River, related to the increase in the content of the main indicators of the water chemical composition (oxygen, pH, mineralization, major ions, nutrients, and organic substances). The Danube water at wastewater discharge sites is characterized by a high level of eutrophication, especially in summer.

The analysis of the results obtained in recent years has shown that damming of the Danube River in the upper and middle sections has led to a decrease in the content of suspended solids in the water and an increase in its transparency. This phenomenon, together with an increase in the concentration of nutrients, leads to intensification of the phytoplankton development and the primary production of organic substances. The latter has been reflected in the content of dissolved oxygen, the range of which has expanded to reach 5.2–13.8 mg/L. The phenomena of the water undersaturation with oxygen (70–55% saturation in the surface horizon and 17% saturation in the bottom layer) have become noticeable. Most probably, these phenomena are caused by the consumption of oxygen for oxidation of organic substances of the autochthonous origin, the concentration of which in the delta water has increased. However, places of the phytoplankton active vegetation are characterized by oversaturation with oxygen (120–150%).

The maximum content of ammonium nitrogen in the water of the Kiliya delta of the Danube River dates back to the 1970s–1980s, whereas at present the concentration of this form of nitrogen has decreased almost thrice. At the same time, the content of nitrate ions has not undergone such noticeable changes and averages from 0.9 to 1.2 mg N/L. The concentration of inorganic phosphorus has decreased as compared to the 1970s–1990s. However, recently this parameter has increased again to an average of 0.2 mg/L.

In the modern period, there has been a significant increase in the indicators of the organic matter content, especially in the branches of the Kiliya delta, which, in turn, has a negative impact on the oxygen regime status. In this area, the maximum values of COD_{Mn} and COD_{Cr} reach 15.2–18.3 mg O/L and 14–

38 mg O/L, respectively. In terms of the organic matter content in the water of the branches near their confluence with the Black Sea, they can be characterized as eutrophic.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

1. *Gidrologiya Del'ty Dunaya* (The Danube Delta Hydrology), Mikhailov, V.N., Ed., Moscow: GEOS, 2004.
2. Kharchenko, T.A., Liashenko, A.V., and Bashmakova, I.Kh., *Hydrobiol. J.*, 2000, vol. 36, no. 2, p. 3. https://doi.org/10.1615/HydrobJ.v36.i2.10
3. Timchenko, V.M., *Gidrobiologiya Dunaya i Limanov Severo-Zapadnogo Prichernomor'ya* (Hydrobiology of the Danube and the Northwest Black Sea Coast Salt Lakes), Kiev: Naukova Dumka, 1986, p. 3.
4. Timchenko, V.M., *Ekologichni problemy baseinu Dunayu v mezhakh Ukrainy* (Environmental Problems of the Danube Basin within Ukraine), Kiev, 1996, p. 67.
5. Timchenko, V.M., *Gidrobiologicheskie issledovaniya Dunaya i pridunaiskikh vodoemov* (Hydrobiological Studies of the Danube and the Adjacent Water Bodies), Kiev: Naukova Dumka, 1987, p. 3.
6. Kharchenko, T.A., Timchenko, V.M., Koval'chuk, A.A., Novikov, B.I., Yenaki, I.G., Zhuravleva, L.A., Klokov, V.M., D'yachenko, T.N., Ivanov, A.I., Karpezo, Yu.I., Bashmakova, I.Kh., Parchuk, G.V., Kurandina, D.P., Ovcharenko, N.A., Braginskii, L.P., Linnik, P.N., Nabivanets, Yu.B., Yevtushenko, N.Yu., Sytnik, Yu.M., Komarovskii, F.Ya., Maslova, O.V., Smirnova, N.N., and Taran, O.N., *Gidroekologiya ukrainskogo uchastka Dunaya i sopredel'nykh vodoemov* (Hydroecology of the Ukrainian Part of the Danube and the Adjacent Water Bodies), Kiev: Naukova Dumka 1993.
7. Romanenko, V.D., *Ekologichni problemy baseinu Dunayu v mezhakh Ukrainy* (Environmental Problems of the Danube Basin within Ukraine), Kiev, 1996, p. 7.
8. Kharchenko, T.A., Timchenko, V.M., and Ivanov, V.I., *Ekologichni problemy ponyzz'ya Dunayu, bioriznomanittya ta bioresursy ozerno-bolotnogo landshaftu Del'ty* (Environmental Problems of the Lower Danube, Biodiversity and Bioresources of the Delta Lake and Marsh Landscapes), Kiev: Interekotsentr, 1998.
9. Bondar, C., *Hydrol. Studies*, 1972, vol. XXXII, Bucharest.
10. Bondar, C., *Proc. XI Conference of the Danube Countries on Hydrological Forecasting*, Bucharest, 1982, vol. 2, 1986.
11. Maderich, V., Morgunov, M., and Koshebutskii, V., *Prikl. Gidromekhan*., 2006, vol. 8, no. 1, p. 31.
12. Bogatova, Yu.I., *Vod. Res*., 2013, vol. 40, no. 3, p. 295.
13. Nabivanets, B.I., Osadchii, V.I., Osadcha, N.M., and Nabivanets, Yu.B., *Analitichna khimiya poverkhnevikh vod* (Analytical Chemistry of Surface Waters), Kiev: Naukova Dumka, 2007.
14. Linnik, P.N., Ivanechko, Ya.S., Linnik, R.P., and Zhezherya, V.A., *Hydrobiol. J.*, 2013, vol. 49, no. 5, p. 90. https://doi.org/10.1615/HydrobJ.v.49.i5.100
15. Linnik, P.N., Ivanechko, Ya.S., Linnik, R.P., and Zhezherya, V.A., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 13, p. 2715. https://doi.org/10.1134/S1070363213130185
16. Altunin, V.S. and Belavtseva, T.M., *Kontrol' kachestva vody: Spravochnik* (Handbook: Water Quality Control), Moscow: Kolos, 1993.
17. Chernyavskaya, A.P., Denisova, A.I., Babich, I.I., Zimina, S.A., Gerashchenko, L.V., Serebryakova, T.M., Tsuranich, V.V., and Krut'ko, O.F., *Vod. Res*, 1993, vol. 20, no. 4, p. 440.
18. Berlinsky, N., Bogatova, Yu., and Garkavaya, G., *Estuary of the Danub*e, *The Handbook of Environmental Chemistry*, vol. 5, part H, p. 233. https://doi.org/10.1007/698_5_021.
19. Garkavaya, G.P, Bogatova, Yu.I, and Berlinskii, N.A., *Ekosistema vzmor'ya ukrainskoi del'ty Dunaya* (The Danube Ukrainian Delta Seaside Ecosystem), Odessa: Astroprint, 1998, p. 21.
20. Almazov, A.M., *Gidrokhimiya ustievykh oblastei rek* (Hydrochemistry of River Mouth Areas), Kiev: Akad. Nauk USSR, 1962.
21. *Five–year Report on Water Quality in the Danube River Basin Based on Trans–National Monitoring Network*, 1996–2000, Project Component 2.2: Development of Operational Tools for Monitoring, Laboratory and Information Management with Particular Attention to Nutrients and Toxic Substances, 2003.
22. Osadchii, V.I., Nabivanets, B.I., Osadcha, N.M., and Nabivanets, Yu.B., *Gidrokhimichnyi dovidnyk: poverkhnevi vody Ukrainy, gidrokhimichni rozrakhunky, metody analizu* (Hydrochemical Reference Book: Surface Waters of Ukraine, Hydrochemical Calculations, Analysis Methods), Kiev: Nika-Tsentr, 2008.

23. Lyashenko, A.V. and Zorina–Sakharova, Ye.Ye, *Hydrobiol. J.*, 2015, vol. 51, no. 2, p. 3. https://doi.org/10.1615/HydrobJ.v.51.i2.10
24. Romanenko, V.D., Zhukins'kii, V.M., Oksiyuk, O.P., Yatsyk, A.V.. Chernyavs'ka, A.P., Vasenko, O.G., and Vernychenko, G.A., *Metodyka ekologichnoi otsinky yakosti poverkhnevykh vod za vidpovidnymy kategoriyamy* (Methodology for Environmental Assessment of Surface Water Quality by Relevant Categories), Kyiv: Simvol–T, 1998.
25. Osadchyy, V., Nabyvanets, B., Linnik, P., Osadcha, N., and Nabyvanets, Yu., *Processes Determining Surface Water Chemistry*, Switzerland: Springer, 2016. https://doi.org/10.1007/978-3-319-42159-9
26. Linnik, P.N. and Ivanechko, Ya.S., *Hydrobiol. J.*, 2014, vol. 50, no. 6, p. 87. https://doi.org/10.1615/HydrobJ.v50.i6.100
27. Linnik, P.N. and Ivanechko, Ya.S., *Hydrobiol. J.*, 2015, vol. 51, no 2, p. 85. https://doi.org/10.1615/HydrobJ.v.51.i2.80
28. Zhuravleva, L.A. and Grubrina, N.A., *Hydrobiol. J.*, 1991, vol. 27, no. 6, p. 49.
29. Ryasintseva, N.I., Sarkisova, S.A., Savin, P.T., Sekundyak, L.Yu., and Dotsenko, S.A., *Ekosistema vzmor'ya ukrainskoi del'ty Dunaya* (The Danube Ukrainian Delta Seaside Ecosystem), Odessa: Astroprint, 1998, p. 63.
30. *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*, Findlay, S.E.G. and Sinsabaugh, R.L., Eds., San Diego: Academic Press, 2003.
31. *Rukovodstvo po khimicheskomu analizu poverkhnostnykh vod sushi* (Guidelines on Chemical Analysis of Land Surface Waters), Semenov, A.D. Ed., Leningrad: Gidrometeoizdat, 1977.
32. Rubini, P., Lakatos, A., Champmartin, D., and Kiss, T., *Coord. Chem. Rev.*, 2002, vol. 228, p. 137. https://doi.org/10.1016/S0010-8545(01)00467-2