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Original article

Features of Water Chemical Composition in the River Mouths of the Bolshoi Sochi Region, North-Eastern Part of the Black Sea

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Abstract
Purpose. The study aims to identify the characteristic features of the content of dissolved macrocompounds and nutrients in estuarine areas of rivers in Bolshoi Sochi (Sochi, Matsesta, Khosta, Kudepsta and Mzymta).
Methods and Results. Surface water samples were collected from the estuaries of the Sochi, Matsesta, Khosta, Kudepsta and Mzymta rivers in early November during the autumn-winter flood season. Nutrient concentrations were determined using spectrophotometric methods, while macrocompound concentrations were measured via capillary electrophoresis. The distribution of hydrochemical characteristics follows the classical pattern typical of river-sea system. The chemical composition of river water is predominantly of the hydrocarbonate-calcium type, except for the Matsesta River, which exhibits a mixed composition. The highest concentrations of nitrogen compounds were observed in the Matsesta and Kudepsta rivers, while elevated phosphate levels were found in the Sochi River. The Kudepsta River water is characterized by exceptionally high total alkalinity. For domestic water use, measurements of nutrient concentrations showed no excess of maximum permissible levels.
Conclusions. The chemical composition of water in the river mouths under study is influenced by both natural and anthropogenic factors. In the Matsesta River, the primary natural factor is the discharge of mineral groundwater, while the main anthropogenic factor is wastewater discharge. The combination of these factors and the mouth overlap resulted in the development of eutrophication processes. In the Kudepsta River, the high background alkalinity is of natural origin, whereas elevated nutrient concentrations (nitrogen and phosphorus) are linked to intensive construction activities in the mouth area.

Keywords: mouth area, Black Sea, Bolshoi Sochi, anthropogenic impact, chemical composition of water, nutrients, hydrochemical composition, macrocomponents

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Introduction

River mouths are unique physiographic systems characterized by distinct geomorphology, geological structures and hydrological regimes, shaped by the complex interplay of physical, chemical and biological processes [1–3]. These zones exhibit high spatiotemporal variability in the intensity and direction of ongoing processes [4–6]. Consequently, investigating the transport and transformation of dissolved substances in the mixing zone of river and sea waters is a critical scientific task, as it represents a key stage in the migration of chemical elements within the global hydrological cycle [1, 2, 7–14]. River mouths also hold significant socio-economic importance for coastal regions [3]. This is particularly relevant for the Black Sea coast, including the Bolshoi Sochi region, which is a vital natural and recreational resource. The ecological state of the coastal areas of the Black Sea is increasingly critical due to growing tourism and the rapid development of infrastructure along shorelines and within the catchments of rivers flowing into the Black Sea.

Until recently (2006–2014), comprehensive studies of continental river discharge into the Black Sea were conducted annually across the entire Russian Black Sea coast [2, 10–12, 15, 16], including the discharge areas of the studied rivers. However, these studies primarily focused on marine areas and excluded river waters. Over the past decade, research in this region has significantly declined. Currently, only isolated studies address the chemical composition of the Mzymta and Sochi rivers [17, 18] and the mouth areas of small and medium-sized rivers along the northeastern Black Sea coast, relying on data from previous years [14]. Amid increasing anthropogenic pressures, accounting for ongoing climatic changes, evidenced by a rise in extreme weather events such as intense heat, droughts and heavy rainfall, has become particularly important. These factors directly influence river discharge and the transport of substances into the sea. In this connection, it seems necessary to investigate the chemical composition of river waters across different seasons.

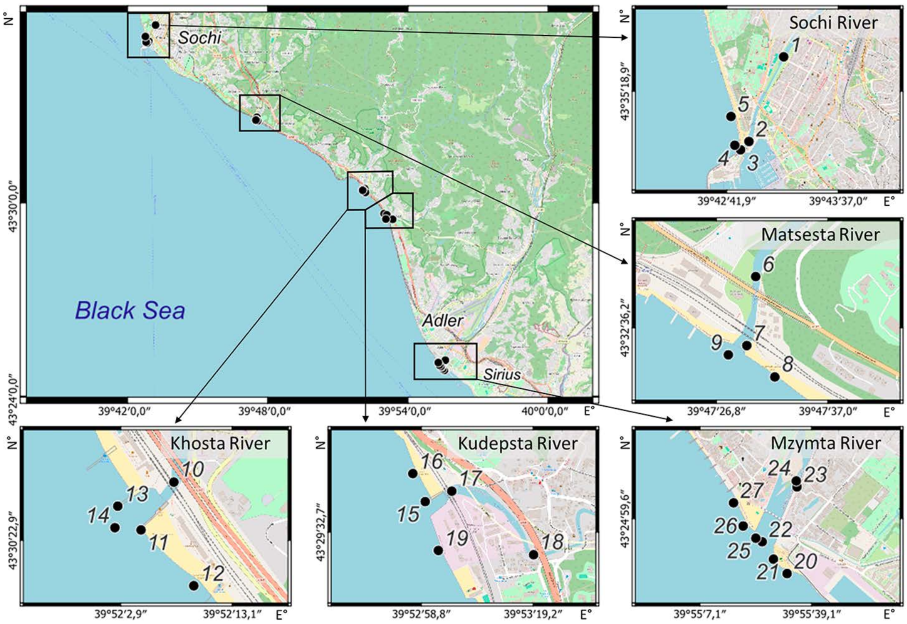
The Black Sea is a unique enclosed marine basin significantly influenced by freshwater continental discharge, with an annual volume of 350 km^3 [2, 10, 12]. This contributes to its relatively low salinity (18–20‰). Large rivers account for over 80% of the discharge into the Black Sea; however, along the Russian coast, small and medium-sized rivers predominantly contribute to the river discharge [2, 10, 12, 19]. Among these, the Shakhe River (1.2 km^3) and the Mzymta River (1.6 km^3) are the largest.

The majority of river discharge (over 80%) from the northeastern Black Sea coast occurs during the winter-spring period, driven by rain-induced floods that dominate river recharge. However, for large rivers originating on the slopes of the Caucasus Mountains, such as the Mzymta River, spring-summer high-water periods are characteristic, accounting for 50–70% of the total annual discharge, accompanied by a stable winter low-water period [19]. In contrast, most rivers in the Bolshoi Sochi region (except the Mzymta River) exhibit peak discharge during autumn-winter period due to the predominance of rainfall-driven recharge and their significantly smaller catchment areas [10, 19]. Although the contribution of small and medium-sized rivers to the total fresh water influx into the Black Sea is minimal, their impact on the marine ecosystem can be substantial. These watercourses significantly alter the hydrochemical composition of coastal waters and influence the transport of substances in nearshore areas [9–14, 20]. Additionally, rivers along the eastern Black Sea coast exhibit variations in chemical composition due to distinct geomorphological characteristics (channel structure and composition of drained rocks), as well as the presence of additional water sources (groundwater and wastewater discharge).

The purpose of this study is to identify the characteristic features of the content of dissolved macrocompounds and nutrients in the estuarine areas of rivers in the Bolshoi Sochi region (Sochi, Matsesta, Khosta, Kudepsta and Mzymta).

Materials and methods

This study examined the chemical composition of waters in the mouth areas of the Mzymta, Khosta, Kudepsta, Matsesta and Sochi rivers, as well as adjacent coastal marine waters, based on samples collected from surface waters in early November during the autumn-winter flood period (Fig. 1).



F i g. 1. Map of sampling point locations in river mouths of the Bolshoi Sochi region

Water samples were collected in accordance with GOST 31861–2012 using 1.5-liter bottles for the analysis of nutrient compounds (Si, PO_4^{3-}, NO_2^-, NO_3^-, NH_4^+) and total alkalinity. All samples were filtered through a 0.45 μm membrane filter. The pH was measured using a HM Digital PH-200 portable pH meter and verified in a stationary laboratory with a Metrohm 913 pH meter, following the manufacturer's protocol with three buffer solutions (4.01, 7.00, 10.01). On-site measurements also included oxidation-reduction potential (Eh), total dissolved solids (TDS) and temperature (T) using portable waterproof HI991300 pH/EC/TDS and HM Digital ORP-200 meters. Dissolved oxygen concentrations were measured with a portable oxygen sensor with an accuracy of 0.01 mg/L.

Total alkalinity was determined in a stationary laboratory at 20°C under temperature control using a potentiometric direct titration method [1].

[1] Dickson, A.G., Sabine, C.L. and Christian, J.R., 2007. *Guide to Best Practices for Ocean CO_2 Measurements*. PICES Special Publication 3; IOOSS Report No. 8. Sidney, Canada: North Pacific Marine Science Organization, 191 p.

Nutrient compounds were analyzed using spectrophotometric methods within a few hours of sampling [2, 3]. Ammonium nitrogen was fixed directly during sampling and stored in a dark place according to the Sagey–Solórzano method, based on the formation of a phenol-hypochlorite complex [21] (detection limit (DL) 0.18 μg/L). Nitrate nitrogen was determined by reducing nitrates to nitrites using a cadmium-copper reductant, followed by photometric determination of the resulting nitrites (DL 0.62 μg/L). Nitrite concentrations were determined using a single-color reagent based on sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride (DL 0.14 μg/L). Phosphate concentrations were measured via the formation of a phosphomolybdic heteropoly acid complex (DL 0.95 μg/L) and dissolved silicon was determined using the Korolev method through the formation of a blue silicomolybdenum complex (DL 2.8 μg/L). The accuracy of the measurement methods ranged from 2.5 to 10%, depending on the element determined and its concentration. Nutrient concentrations are reported as $P–PO_4^{3-}$, $N–NO_2^-$, $N–NO_3^-$, $N–NH_4^+$, calculated from the respective compound concentrations.

The concentrations of macrocomponents (Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^-) were determined by capillary electrophoresis using a Kapel-205 analyzer, following methodological guidelines PND F 14.1:2:3:4.282-18 (M 01-58-2018) and PND F 14.1:2:4.167-2000. Total water mineralization was calculated as the sum of the concentrations of major ions.

Results

Hydrochemical parameters of waters

In November, water temperatures in the mouth areas of the studied rivers increased toward the sea. For the Sochi River, the temperature ranged from 11.5 to 18.7 °C; for the Matsesta and Khosta rivers, from 14.4 to 18.2 °C; and for the Kudepsta and Mzymta rivers, from 12.5 to 17.4 °C and 9.7 to 17.5 °C, respectively. This temperature distribution reflects the mixing of colder freshwater with warmer marine waters, with the highest temperature gradients observed in the Sochi and Mzymta rivers. The pH values in all studied mouth areas also increased toward the sea (Fig. 2, Table 1).

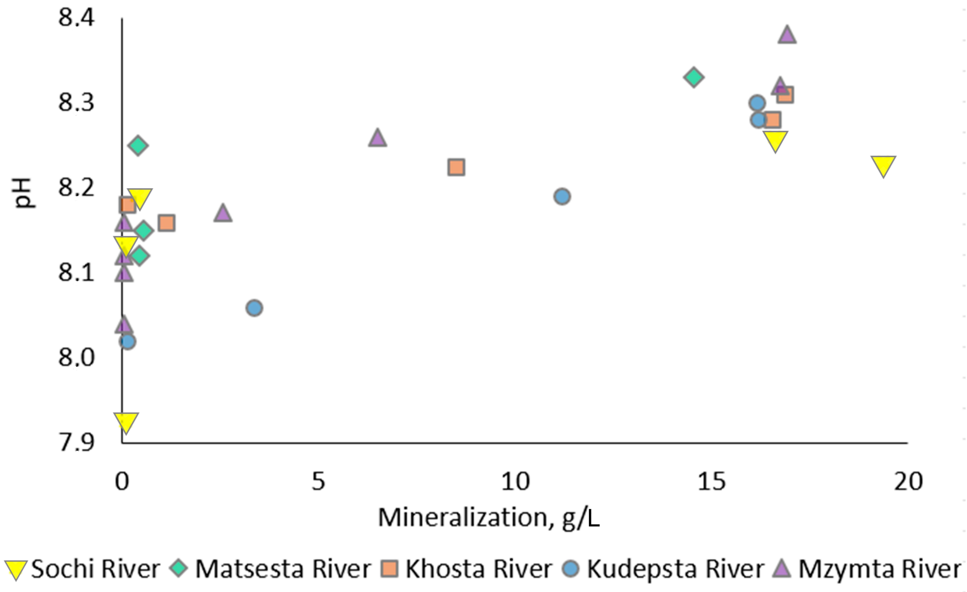
The Eh values exhibit a distribution pattern typical of river-sea mixing zones, consistent with the behavior of pH values. Relatively low Eh values were recorded in the Sochi River (30–71 mV) and the Matsesta River (38–87 mV), while higher ranges were observed in the Khosta, Kudepsta and Mzymta rivers (64–132 mV).

The distribution of total alkalinity in the Mzymta and Sochi rivers shows an increase from the riverine to marine waters. In the mouth areas of the Khosta and Matsesta rivers, alkalinity values remain within a narrow range (Table 1). In the Kudepsta River, alkalinity reaches 4.5 mg-eq/L and decreases upon mixing

[2] Sapozhnikov, V.V., ed., 2003. [*Guidelines for the Chemical Analysis of Marine and Freshwater in Environmental Monitoring of Fishery Waters and Prospective Fishing Areas of the World Ocean*]. Moscow: VNIRO, 202 p. (in Russian).

[3] Parsons, T.R., Maita, Y. and Lalli, C.M., 1984. *A Manual of Chemical and Biological Methods for Seawater Analysis*. Oxford; New York: Pergamon Press, 173 p.

with marine waters. Notably, the lowest total alkalinity values (Table 1) among the studied rivers were observed in the mouth area of the Mzymta River.



F i g. 2. Dependence of pH on water mineralization in river mouths of the Bolshoi Sochi region

T a b l e 1

Hydrochemical parameters of waters in river mouth areas of the Bolshoi Sochi region

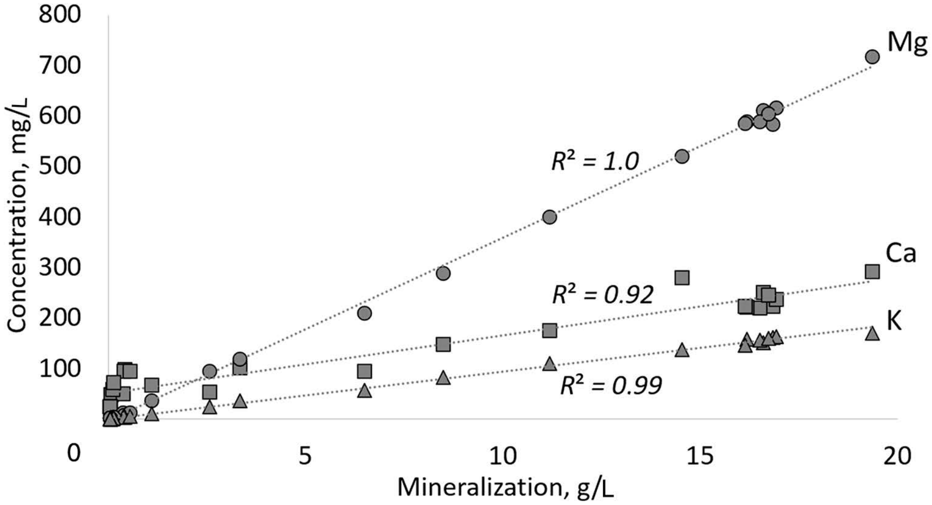
Name of the river	pH	*Alk*, mg-eq/L	O_2, %
Sochi	7.93–8.26 8.15	2.18–3.36 2.65	100.8–121.5 109.6
Matsesta	8.12–8.33 8.21	3.43–3.67 3.60	120.0–128.4 123.3
Khosta	8.16–8.31 8.23	3.11–3.37 3.26	119.6–125.4 122.4
Kudepsta	8.02–8.30 8.17	3.38–4.50 3.84	91.7–100.2 97.0
Mzymta	8.04–8.38 8.19	1.60–3.45 2.21	86.3–108.3 100.0

N o t e: The numerator indicates the range of minimum-maximum values, the denominator – the average.

During the study period, oxygen saturation in the river mouths varied between 86.3–128.4% (Table 1). Dissolved oxygen concentrations ranged from 8.41 to 11.39 mg/L. The highest dissolved oxygen concentrations were observed in the mouth areas of the Matsesta River (10.65–11.39 mg/L) and the Khosta River (10.61–10.97 mg/L).

General chemical composition

The distribution of major elements in waters during river-sea mixing is typically conservative [1, 13]. In this study, elements such as Ca^{2+}, Mg^{2+} and K^+ (Fig. 3) exhibit conservative behavior across all river mouth sections.



F i g. 3. Dependence of Ca, Mg and K concentrations on water mineralization in river mouths of the Bolshoi Sochi region

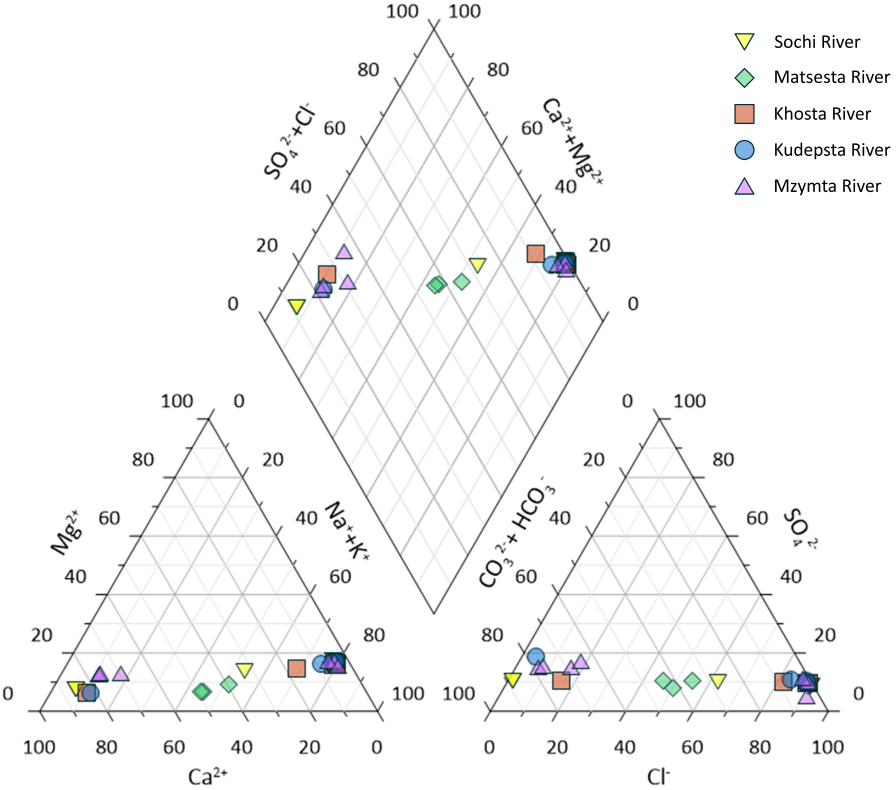
The waters of the Black Sea coastal zone are characterized by a chloride-sodium composition, whereas river waters are predominantly of the bicarbonate-calcium type. An exception is the water in the mouth area of the Matsesta River, which is classified as a bicarbonate-chloride sodium-calcium type (Fig. 4).

Nutrient compounds

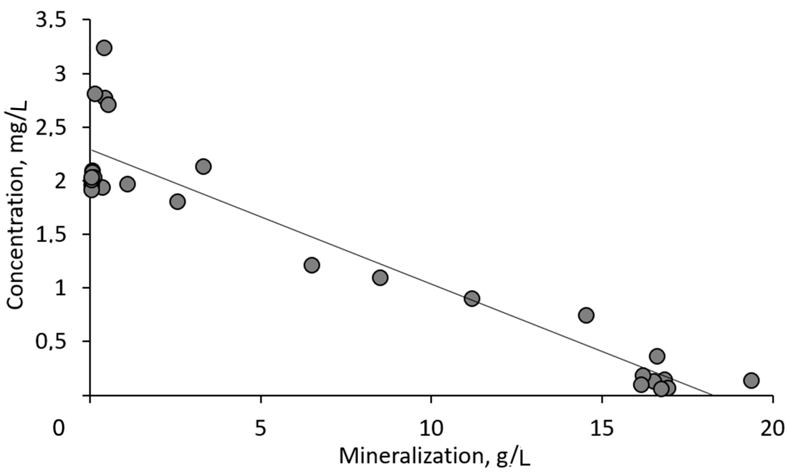
In the river-sea mixing zone, the distribution of nutrients is significantly influenced by chemical and biological processes within the river system, including sorption, desorption, coagulation and flocculation of colloids, resulting in their non-conservative behavior [1, 13]. Unlike other nutrients, changes in silicon concentration often indicate the dilution of marine waters by river waters. In this study, a linear relationship between the Si concentration and water mineralization was observed for all studied rivers (R^2 = 0.89, p < 0.05) (Fig. 5). The highest Si concentrations were recorded in the mouth area of the Matsesta River (Table 2).

Phosphate concentrations in surface waters for all studied mouth areas of the Bolshoi Sochi rivers, except for the Matsesta River, decreases from the river toward the sea. Within a mineralization range of 1 to 4 g/L, an increase in phosphate concentrations is observed, followed by a sharp decrease as mineralization increases further (Fig. 6). In the Matsesta River, phosphate concentrations in the marine zone (at a mineralization of 14.1 g/L) and in the mouth exceed those in the river. The highest phosphate concentrations were recorded in the Sochi and Kudepsta rivers, while the lowest were observed in the Khosta River (Table 2).

The distribution of ammonium nitrogen exhibits a pattern similar to that of phosphates across all mouth areas of the rivers under consideration (Fig. 6).



F i g. 4. Chemical composition of waters in river mouths of the Bolshoi Sochi region at the Piper diagram



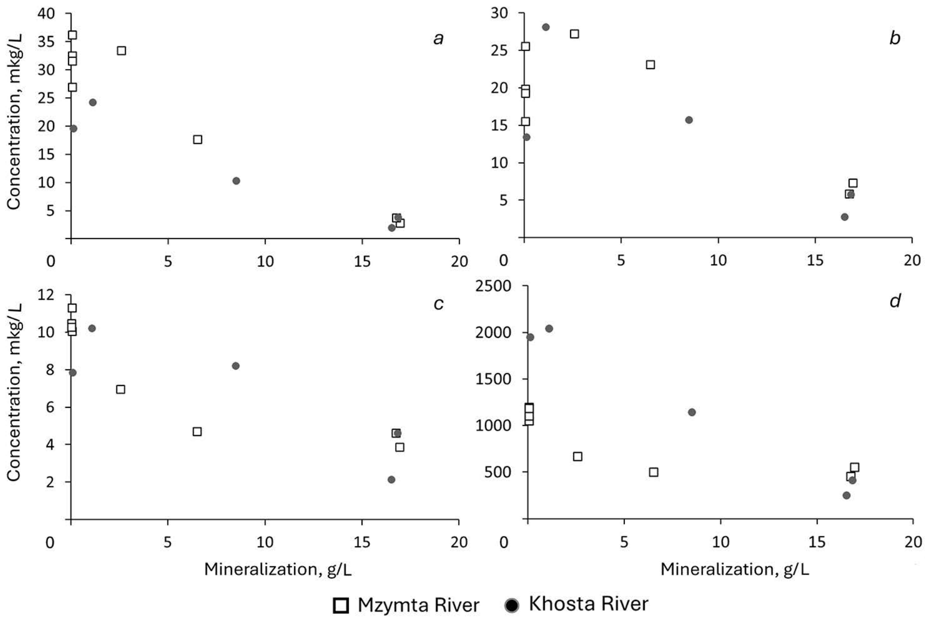
F i g. 5. Dependence of silicon content on water mineralization in river mouths of the Bolshoi Sochi region

Table 2

Concentrations of nutrients in river mouth areas of the Bolshoi Sochi region

Name of the river	Si, mg/L	P-PO_4^{3-}	N–NO_2^-	N–NO_3^-	N–NH_4^+
		μg/L			
Sochi	0.13–2.09 1.32	9.1–24.2 17.5	0.7–4.9 3.0	65.7–465.1 297.8	3.9–38.6 25.5
Matsesta	0.74–3.24 2.37	6.1–10.9 8.5	4.1–8.2 7.0	170.5–821.4 604.4	22.2–101.3 78.0
Khosta	0.13–2.03 1.07	0.6–7.9 3.9	0.6–3.1 2.0	56.5–460.5 261.4	2.1–21.8 10.2
Kudepsta	0.10–2.81 1.22	0.3–22.4 10.5	1.0–10.9 5.1	53.6–863.9 414.1	3.1–128.3 64.6
Mzymta	0.06–2.03 1.38	0.9–11.8 7.5	1.2–3.5 2.4	102.2–270.3 189.8	4.6–21.2 14.0

N o t e: The numerator indicates the range of minimum-maximum values, the denominator – the average.



F i g. 6. Distribution of the phosphate (*a*), ammonium nitrogen (*b*), nitrite (*c*) and nitrate (*d*) concentrations depending on water mineralization in the Mzymta and Khosta rivers' estuaries and coastal waters

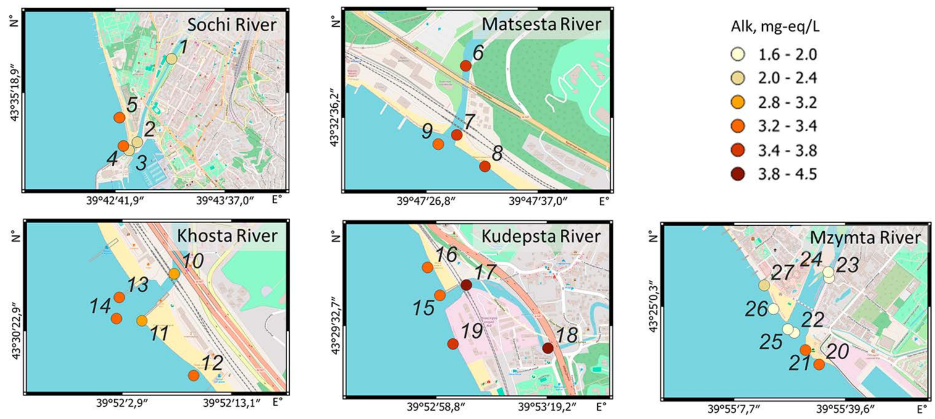
The distribution of nitrites and nitrates exhibits distinct patterns. In the estuarine areas of the Sochi and Kudepsta rivers, a gradual decrease in their concentrations is observed toward the sea. In contrast, the Mzymta River shows a sharp decrease in concentrations at the initial stage of river-sea mixing, followed by stabilization at mineralization levels of 8 g/L and above (Fig. 6). The highest concentrations of all dissolved nitrogen forms (NH_4^+, NO_2^-, NO_3^-) were recorded in the Matsesta River (Table 2).

Discussion

The waters in the lower reaches of the Bolshoi Sochi rivers are predominantly bicarbonate-calcium composition of the is characteristic of this natural and climatic zone [17, 18]. In terms of mineralization, almost all the rivers are classified as ultra-fresh (0.05–0.15 g/L). An exception is the Matsesta River, which exhibits a mixed chemical composition with higher mineralization (0.44–0.55 g/L). This is attributed to the contribution of sulfide-rich mineral groundwater [4] to its recharge, which also increases water mineralization and elevates sulfate concentrations.

Total alkalinity distribution in the river-sea mixing zone within the study area follows a typical pattern of increasing values from the river to the sea. The Kudepsta River exhibited the highest total alkalinity values among the studied rivers (Fig. 7), consistent with published studies [8, 10–12]. These elevated alkalinity levels are attributed to the geological features of the river's catchment, which is predominantly composed of carbonate rocks and includes karst caves in the upper reaches, contributing alkaline water during rain-induced floods. Similar geological conditions characterisize the Khosta River, but its total alkalinity values are lower, likely due to higher flow velocity, which reduces water-rock interaction time [5].

The lowest total alkalinity values were observed in the Mzymta River (Fig. 7), consistent with published studies [8, 10–12, 14]. This is attributed to the glacial recharge of the river and the geological characteristics of its basin, which is primarily composed of igneous and metamorphic rocks. The Mzymta's discharge, characterized by low total alkalinity, contributes to reduced carbonate concentrations in the coastal zone of the Black Sea. Furthermore, this parameter can serve as an integrative indicator for tracking the spread of the Mzymta River plume over long distances in the marine environment.



F i g. 7. Distribution of total alkalinity values in river mouths of the Bolshoi Sochi region

Elevated dissolved oxygen concentrations were observed in the river-sea mixing zones (mineralization range: 1.1–8.5 g/L) compared to river waters in the mouths of the studied rivers. The greatest increase in oxygen saturation, 16.65%, was recorded in the mouth of the Sochi River, whereas for the Khosta, Kudepsta and Mzymta rivers,

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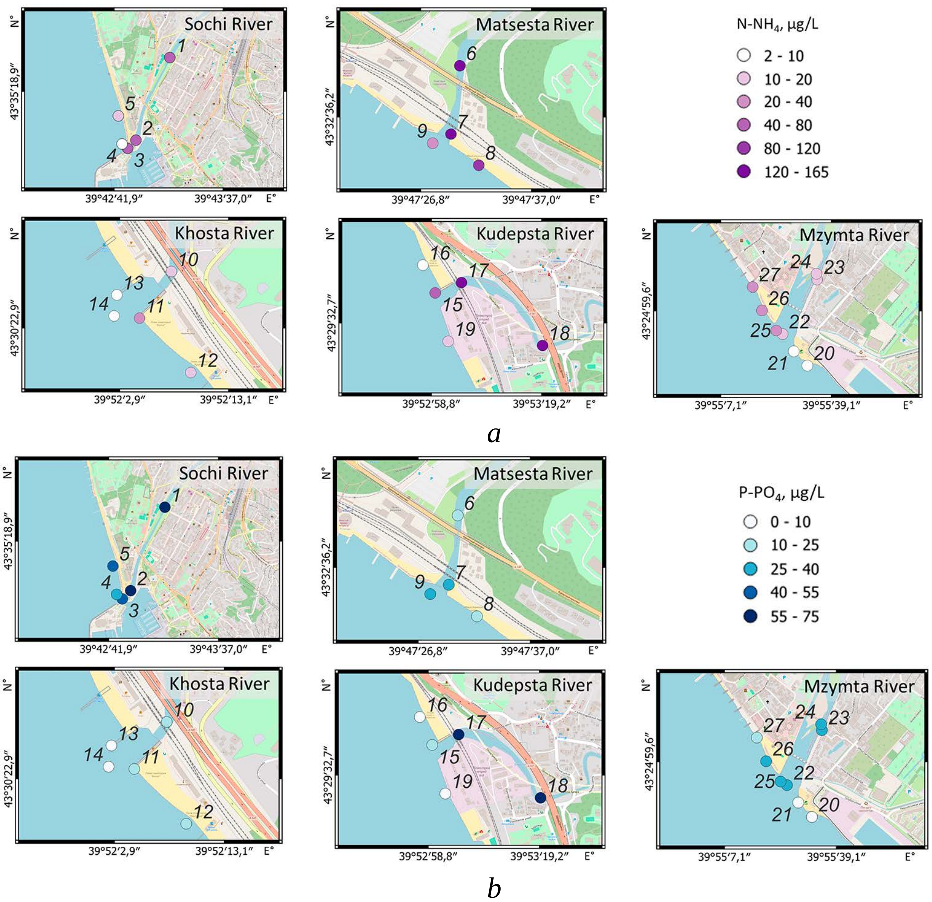
[4] Bityukov, N.A., 2016. *Prospects of Mineral Water Use in Sochi Resort*. Saarbrücken, Germany: Lambert Academic Publishing, 92 p. (in Russian).

[5] Shvartsev, S.L., 2012. *General Hydrogeology*. Moscow: Alliance, 600 p. (in Russian).

the increase did not exceed 5%. This relative increase in dissolved oxygen concentrations in the mixing zones is likely due to the formation of areas with high biological productivity, driven by nutrient inputs from river waters [2, 10, 12]. The relatively low oxygen saturation (below 100%) in the Kudepsta River is likely associated with the predominance of organic matter oxidation over production processes.

The dissolved silicon concentration serves as a key indicator of river discharge influence on seawater chemistry, as confirmed by the results from the mouths of the Bolshoi Sochi rivers. The highest dissolved silicon concentrations (2.8–3.2 mg/L) were recorded in the mouth of the Matsesta River, likely due to subsurface recharge by thermal waters combined with wastewater discharge. Unlike other studied rivers, such as the Sochi and Mzymta, the Matsesta River has relatively few tributaries, which limits dilution processes and influences its chemical composition. Thermal waters, characterized by elevated temperature and mineralization, promote the intense dissolution of silicon and other elements (calcium, magnesium, iodine, bromine, etc.) from rocks [6] [22].



F i g. 8. Content of dissolved ammonium nitrogen (*a*) and phosphorus (*b*) in river mouths of the Bolshoi Sochi region

[6] Krainov, S.R. and Shvets, V.M., 1992. *Hydrogeochemistry*. Moscow: Nedra, 463 p. (in Russian).

The elevated concentrations of phosphate and ammonium nitrogen in the mixing zone (1–4 g/L), compared to river and marine waters, are likely due to the remineralization of organic matter in bottom sediments. These sediments are resuspended in the mixing zone, contributing additional nutrients to the water column. The intensity of this process is influenced by flow velocity and the quantity of settling suspended matter. Notably higher phosphate concentrations in the Sochi and Kudepsta rivers (Fig. 8, *b*) and ammonium nitrogen levels in the Matsesta and Kudepsta rivers – 3–5 times higher than in other rivers (Fig. 8, *a*) – along with correspondingly elevated nitrite and nitrate concentrations (1.5–2 times higher), suggest localized pollution in these rivers. Documented cases of wastewater discharge into the rivers, combined with low flow velocity in the mouth areas in some instances, confirm these observations. For example, a separating coastal bar frequently forms between the mouth of the Matsesta River and marine waters, creating conditions conducive to eutrophication. In the lower reaches of the Kudepsta River, intensive construction activities, including the concreting of foundations for new interchange structures, have likely disturbed the soil layer. This disturbance, when introduced into the river, may contribute to elevated concentrations of dissolved nitrogen and phosphorus compounds.

Although phosphate concentrations in the Sochi and Kudepsta rivers are significantly higher than in other rivers, they remain below the maximum permissible concentrations (MPC) for domestic water use as specified by SanPiN 2.1.4.1074-01. No exceedances of MPC for other nutrient compounds were detected.

The complex distribution pattern of nutrient compounds can be attributed to their involvement in biological processes and their transformation into suspended forms [1]. A similar mechanism of transport and transformation of dissolved nitrogen and phosphorus compounds is observed in the estuarine areas of the Khosta and Kudepsta rivers, as evidenced by strong linear correlations ($R^2 = 0.98$ and 0.97, respectively, $p = 0.05$). For other rivers, this relationship is weak or absent ($p > 0.05$). For all rivers except the Mzymta, a linear dependence was established between the concentrations of dissolved silicon and various nitrogen compounds ($R^2 = 0.89…0.99$, $p = 0.05$). A correlation between silicon and phosphorus concentrations is observed for the Khosta, Kudepsta, and Mzymta rivers ($R^2 = 0.95$, $p = 0.05$). The weak correlation between dissolved phosphorus and silicon concentrations in the Sochi and Matsesta rivers suggests that phosphorus enters and is transported not only with river discharge into the sea but also as a result of resuspension of bottom sediments in the mouth and coastal areas.

Conclusion

Hydrochemical studies of the distribution patterns of dissolved macrocomponents and nutrients in the mouth areas of the Bolshoi Sochi rivers revealed conservative behavior of major water ions. While the bicarbonate-calcium type is characteristic of river waters in this natural and climatic zone, the Matsesta River exhibits a bicarbonate-chloride sodium-calcium type, attributed to the contribution of mineral groundwater to its recharge.

The hydrochemical characteristics of the waters (pH, Eh, *Alk*) exhibit a typical distribution pattern in the river-sea mixing zone. An exception is the elevated total alkalinity values in the Kudepsta River, which are attributed to the distinct geological structure of its catchment.

The distribution of silicon is conservative across all mouth areas. The highest concentrations of nitrogen compounds were recorded in the Matsesta and Kudepsta rivers and the highest phosphate concentrations were observed in the Sochi River. However, concentrations of all nutrient compounds remained below the MPC for domestic water use.

This study demonstrates that the chemical composition of waters in the mouth areas of the studied rivers is influenced by both natural and anthropogenic factors, often acting simultaneously. For example, the chemical composition of the Matsesta River is shaped by sulfide-rich groundwater, while eutrophication processes in its mouth are driven by wastewater discharge and mouth blockage. In the Kudepsta River, which naturally exhibits high total alkalinity, elevated concentrations of nitrogen and phosphorus compounds compared to other rivers are attributed to construction activities near its mouth area.

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