

Original article

## Variability of Nutrient Concentration in Waters of the Chernaya River Estuarine Zone (Sevastopol Region)

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### Abstract

Nutrient concentration in the water of sea mouths of rivers is a limiting factor in the life activity of hydrobionts. Therefore, studying this parameter is important for assessing the current state of mouth ecosystems and its forecasting. Until now, the variability of nutrients has been analysed by their average concentrations over heterogeneous or short-term periods, extremes or individual surveys, which do not reflect the regime of these elements in the modern climatic period. The paper aims to give a modern description of the nutrient concentration variability in the Chernaya River estuarine zone and to assess water quality based on these components of the ecosystem. For the analysis, we used data from hydrochemical surveys for 1991–2020. Water quality was assessed by the nutrient water pollution index, whereas self-purifying capacity of the estuarine zone was assessed using a transformation index of selected nutrients. The distributions of nutrient concentrations were found to be extremely asymmetrical. In this regard, we obtained for the first time the distributions of medians of nitrates, nitrites, ammonium nitrogen and phosphates in the water of the Chernaya River estuarine zone. In the study area, these median concentrations of nutrients did not exceed the maximum permissible values. Analysis of the temporal variability of average annual nutrient concentrations showed the absence of significant trends. The obtained results can be used for balance estimates and calculations of the assimilation capacity of the Chernaya River estuarine zone.

**Keywords:** Chernaya River, estuary, Sevastopol region, nutrient concentration variability, nutrients, water pollution index, water quality

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# Изменчивость концентрации биогенных веществ в воде устьевого взморья реки Черной (Севастопольский регион)

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## Аннотация

Концентрация биогенных веществ в воде морских устьев рек является лимитирующим фактором жизнедеятельности гидробионтов. Поэтому исследование этого параметра важно для оценки и прогнозирования современного состояния устьевых экосистем. До настоящего времени изменчивость концентрации биогенных веществ анализировали по средним значениям за неоднородные или короткие периоды, экстремумам или данным отдельных съемок, что не отражало режима этих элементов в современный климатический период. Цель работы – дать современную характеристику изменчивости содержания биогенных веществ в воде устьевого взморья р. Черной и оценить качество воды по этим компонентам экосистемы. Для анализа использовались материалы гидрохимических съемок за 1991–2020 гг. Качество воды оценивали по индексу загрязненности воды биогенными веществами, а самоочищающую способность устьевого взморья – по индексу трансформации отдельных биогенных веществ. Установлено, что распределения концентраций биогенных веществ крайне асимметричны. В связи с этим впервые использованы распределения медианных концентраций нитратов, нитритов, аммонийного азота и фосфатов в воде устьевого взморья р. Черной, которые в рассматриваемом районе не превышали предельно допустимых значений. Анализ временной изменчивости средней годовой концентрации биогенных веществ показал отсутствие значимых тенденций. Полученные результаты могут использоваться в балансовых оценках и расчетах ассимиляционной емкости устьевого взморья р. Черной.

**Ключевые слова:** Севастопольский регион, устье реки, река Черная, концентрация биогенных веществ, биогенные вещества, индекс загрязненности воды, качество воды

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## Introduction

The development of the natural and economic complex of the Sevastopol region depends on the condition of the sea mouth of the Chernaya River. In the modern climatic period of 1991–2020 adopted by the World Meteorological Organization (WMO)<sup>1)</sup>, a change in climate and abiotic components of the ecosystem is observed [1]. In addition, economic activity is actively carried out affecting negatively the ecological state of the estuary, which will reduce the quality of life of the local population.

The most important abiotic factor for hydrobionts is the content in water of nutrients that limit their life activity and affect water quality. Therefore, the study of variability in the concentration of nutrients that affect the trophicity of a water body and the identification of areas of environmental risks are relevant.

Content of nutrients both in certain parts of the estuary (in Sevastopol Bay, the lower reaches of the Chernaya River) [2–14] and in the estuary of the Chernaya River as a whole (see work<sup>2)</sup> and [15, 16]) has been actively studied by the Marine Hydrophysical Institute scientists.

The main sources of nutrients entering the receiving reservoir are the runoff of the Chernaya River, which integrates nutrients carried out from the entire river catchment area during precipitation, as well as wastewater discharges, washout from the shore and precipitation [15, 17]. In [15], it is shown that with river runoff the river estuarine zone receives on average: 3 t/year of phosphates, 10 t/year of ammonium nitrogen, 1 t/year of nitrites, 40 t/year of nitrates. Nitrates account for 80–90% of the structure of river nutrient removal [4].

Since previously (e.g., in [3, 4, 15]) mainly the variability of the concentration of nutrients at the top of the sea mouth of the Chernaya River and in its mouth area was studied, as well as the removal of nutrients with river runoff, the main attention in this article is on the analysis of the variability of nutrient concentration in the surface and bottom layers of the Chernaya River estuarine zone.

The relationship between the concentration of inorganic nitrogen and the amount of precipitation established in [17] indicates the significant role of atmospheric entry in the nutrient balance of coastal waters. An increase in precipitation leads to a decrease in the concentration of nitrogen in the atmosphere and an increase in its content in the catchment area, in the water of the Chernaya River and its estuary. Since the water surface area of the Chernaya River estuary is approximately 16 times smaller than the drainage (washoff) area, the main entry component of the nutrient balance of the river estuarine zone is its runoff.

An analysis of the spatial and temporal variability of nutrient concentration in the considered estuary for 1980–2004, 1978–2016, 2007–2016 and 1976–2012 was carried out previously in [3–6, 15, 16]. Moreover, the distribution schemes for these ingredients were constructed using the arithmetic average values of their concentrations. What is more, it is indicated that the nutrient concentrations did

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<sup>1)</sup> WMO, 2014. *Guide to Climatological Practices*. WMO no. 100. Geneva: WMO, 156 p.

<sup>2)</sup> Ivanov, V.A. and Minkovskaya, R.Ya., 2008. [*Sea Mouths of Ukrainian Rivers and Mouth Processes*]. Sevastopol: ECOSI-Gidrofizika. Part 1, 448 p. (in Russian).

not have any significant trends during the periods under consideration [5], were multidirectional [15] – positive [6] or negative [16]. The averaging periods in these works were different and did not cover the entire modern climatic period of 1991–2020 (WMO). Different levels of economic activity were not taken into account or analysis of individual hydrochemical surveys was carried out [7, 8]. This approach did not provide a reliable assessment of the current nutrient regime at the mouth of the Chernaya River, therefore, a number of studies substantiated the need to replace the average concentration value with the median and take into account natural and anthropogenic changes in the state of the water body (see work <sup>3)</sup> and [15]).

Biogeochemical zoning of the Sevastopol Bay water surface according to the maps of the distribution of nutrients and suspended matter for 1998–2004 is given in [7, 9, 11]. These works show that the waters of Yuzhnaya Bay and the central region of Sevastopol Bay are the areas most contaminated with nutrients.

The intra-annual variability of the E-TRIX trophicity index, which characterizes water quality based on the content of nutrients and other ecosystem components, is presented in [9]. However, this work does not give an idea of the average long-term content of nutrients in the water of the bay and confirms the conclusions stated in [7] about the most significant pollution of Yuzhnaya Bay with nutrients. At the same time, in contrast to the results presented in [7], it was established in [9] that the central part of Sevastopol Bay was least polluted with mineral forms of nitrogen in 1998–2012. The authors of [13] come to the same conclusion.

Fundamental work [2] analyzes the variability of nutrient concentrations in the Black Sea without detailing their content in the water of the estuarine zone where their concentration is usually higher than in the marine environment.

The ability of various parts of Sevastopol Bay to self-purify from nutrients and the factors influencing it are considered in [10–14]. The authors cited difficult water exchange and wastewater discharges as the reasons of the low self-purification of Yuzhnaya Bay concerning inorganic forms of nitrogen.

To assess water quality, the authors used the water pollution index (WPI) calculated based on the content of chemical ingredients of different groups (oxygen, nutrients, phenols, petroleum hydrocarbons) in work <sup>2)</sup> and [15]. Previously, no integral assessment of water pollution based on the content of nutrients has been carried out.

The sporadic nature of observations of the nutrient concentration with significant temporal variability of these ingredients makes estimates of the average annual concentration insufficiently substantiated, therefore, it was proposed to use the median as the center for grouping data instead of the arithmetic mean value in work <sup>2)</sup>. In the same work, based on an analysis of the distribution law of nutrient concentrations, the rationale for this method is given. In work <sup>3)</sup>, it is also recommended to use the median, since the arithmetic mean is a biased estimate of the sample center.

Thus, the analysis of previous works revealed a number of shortcomings of research methods: the use of arithmetic mean concentrations to analyze spatial variability;

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<sup>3)</sup> Gagarina, O.V., 2012. [Assessment and Standardization of Natural Water Quality: Criteria, Methods, Current Issues. Study Guide]. Izhevsk: Udmurtsky Universitet, 199 p. (in Russian).

the choice of short series of observations or unreasonably long ones that do not take into account climatic factors and the level of economic activity, in order to generalize the results of a study of temporal variability; incorrect use of statistical methods (lack of statistical assessments of the homogeneity and stationarity of series, the significance of trends and the reliability of the obtained dependencies). This makes reliable modern assessment of water quality difficult.

The purpose of this work is to give a modern description of the variability of the nutrient content in the water of the Chernaya River estuarine zone and to assess the quality of water in accordance with these ecosystem components. For this purpose, the database was systematized, statistical characteristics of nutrient concentrations were obtained, their variability in space and time was analyzed, and the quality and self-purifying ability of water was assessed.

The object of the study is the estuarine zone which is influenced by the river runoff and wastewaters and makes up most of the Chernaya River sea mouth (Fig. 1).

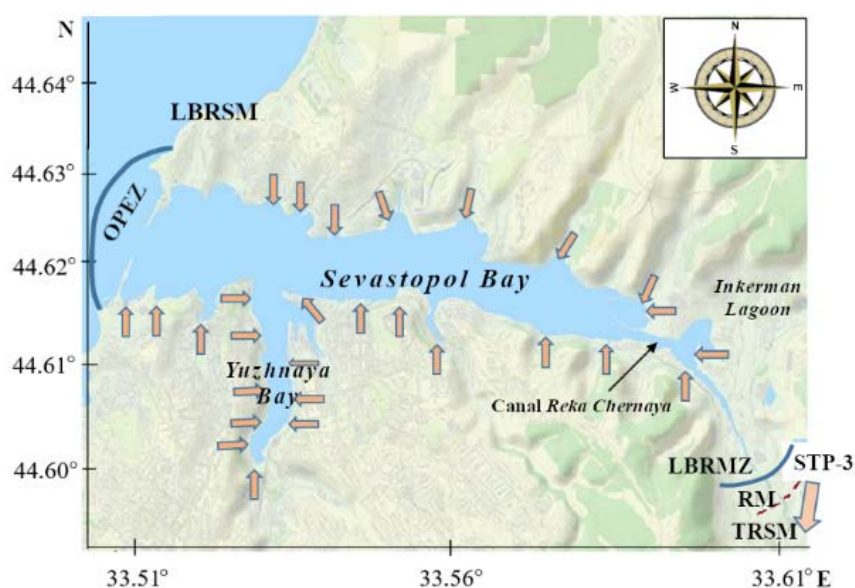


Fig. 1. Sea mouth of the Chernaya River (arrows show constant sources of water pollution taken from paper [4]). LBRSM – lower boundary of the river's sea mouth; OPEZ – open part of the estuarine zone of the Chernaya River; LBRMZ – lower boundary of the river mouth zone; RM – river mouth; TRSM – the top of the river's sea mouth; STP-3 – sewage treatment plant in the village of Sakharnaya Golovka. The blue line shows the boundaries of the Chernaya River estuarine zone

The Chernaya River sea mouth (Fig. 1) includes:

- river mouth (RM);
- complex estuarine zone consisting of Sevastopol Bay with a complex of smaller bays, the Inkerman Lagoon created artificially in the mid-1950s and open part of the estuarine zone (OPEZ) [15].

Due to the lack of data on the Chernaya River OPEZ, the object of our study is limited to the Inkerman Lagoon, Sevastopol and Yuzhnaya bays. The subject of the study is the variability of the content of inorganic forms of nitrogen (nitrates, nitrites, ammonium nitrogen) and phosphorus (phosphates) in the water of the Chernaya River estuarine zone in 1991–2020.

The results obtained can be used in further work for balance calculations, modeling the evolution of the ecosystem and assessing the future state of the abiotic and biotic components of the Chernaya River estuary.

### Materials and methods

Monitoring of the Sevastopol Bay and the adjacent part of the sea has been carried out by scientific and regulatory authorities since 1951, while since the 1960s – on a regular basis [15]. The observation network has been optimized several times. Fig. 2 shows its present state on the Chernaya River estuarine zone.

The results of 1991–2020 *in situ* observations provided by N.N. Zubov State Oceanographic Institute (SB SOI) and Marine Hydrophysical Institute of RAS (MHI RAS) were used as initial information. Observations were carried out within the boundaries of the Chernaya River sea mouth (Fig. 1), including its estuarine zone (Fig. 2).

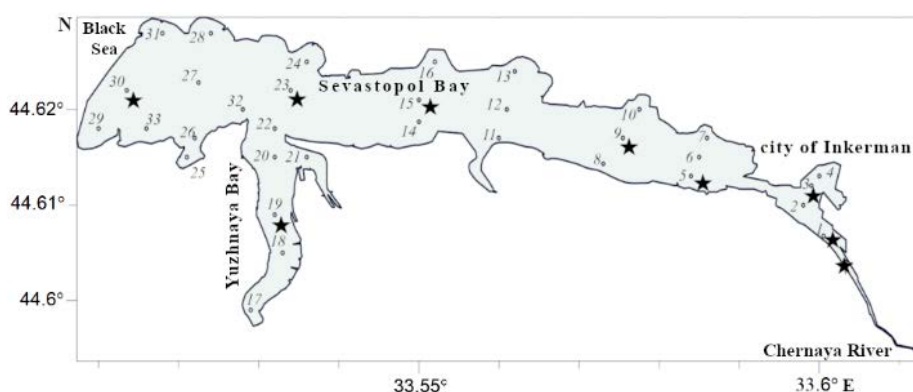


Fig. 2. Map of hydrochemical observational stations of MHI RAS and SB SOI in the Chernaya River estuarine zone in 1991–2020. The dots are for hydrological and hydrochemical surveys carried out by MHI RAS from 1998; the stars are for those carried out by the SB SOI from 1961

The availability of primary hydrochemical data is sufficient to assess the variability of the nutrient concentration in space and time. The generalization period was selected in accordance with the recommendations<sup>1)</sup> taking into account changes in the regional economy occurred in the 1990s. The correctness of this choice is confirmed by the previously performed analysis of climatic and anthropogenic changes in the region under consideration [1].

Water sampling for the nutrient content was carried out at 33 stations of the estuarine zone (Fig. 2) and 1 station at the RM lower boundary (Fig. 1). The concentration of nitrates ( $\text{NO}_3$ ), nitrites ( $\text{NO}_2$ ), ammonium nitrogen ( $\text{NH}_4$ ) and phosphates ( $\text{PO}_4$ ) in the surface and bottom layers of water was studied.

The choice of the studied elements is due to the lack of information on the content of pollutants in the water of the estuarine coastal zone. A reliable statistical assessment of *in situ* data can so far be made only within the largest part (90%) of the Chernaya River estuarine zone, including Sevastopol Bay and the Inkerman Lagoon. Therefore, the characteristics of nutrient variability are given for this part of the estuarine zone (Fig. 2).

Analysis of samples for the content of nutrients was carried out in accordance with standardized methods<sup>4)</sup> in certified hydrochemical laboratories of SB SOI and MHI RAS.

On average, 360 water samples were taken and analyzed for nutrient content at each station in 1991–2020 (Fig. 3). 90 analyzes of each ingredient were performed, i.e., 45 samples from the surface and bottom layers of water. This is sufficient for an objective statistical assessment [18].

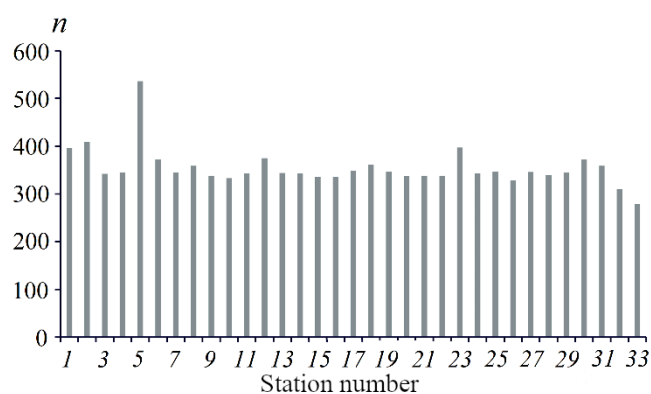


Fig. 3. Number of samples for nutrient content ( $n$ ) in the water of the Chernaya River estuarine zone in 1991–2020 (data from SB SOI and MHI RAS)

<sup>4)</sup> Oradovsky, S.G., ed., 1993. *Guide on the Chemical Analysis of Sea Waters*. RD 52.10.243-92. Saint Petersburg: Gidrometeoizdat, 264 p. (in Russian).

Nutrient concentrations in water samples were determined by SB SOI and MHI RAS on a unified methodological basis. Therefore, after checking the hydrochemical survey data for homogeneity using the Student's t test [19] for a significance level of 0.95, the series of nutrient concentration values were combined.

Unlike previous works, the distribution diagrams of nutrient concentrations in the surface and bottom layers of water were constructed using medians, since it was established that the distribution of these water quality characteristics was extremely asymmetrical at all stations. Fig. 4 shows the example of a histogram of phosphate distribution at station 30. Therefore, the arithmetic mean is not a sufficiently representative parameter of the sample center in this case and it is advisable to use the median according to works<sup>2), 3)</sup> and [15, 18]. During the period under review, median concentrations at all stations of the Chernaya River estuarine zone were 15–95% less than their arithmetic average values due to right-sided asymmetry (Fig. 4).

To calculate statistical characteristics, standard statistical generalization methods were used [19], and distribution diagrams of nutrient concentrations were constructed with the standard Surfer 13 software package.

The use of integral and complex indices for assessing water quality (pollution coefficient, water quality index, water pollution index, combinatorial water pollution index, specific combinatorial water pollution index, etc.) discussed in work<sup>3)</sup> is difficult due to the lack of data on many indicators. Therefore, a simplified version of assessing water quality using the nutrient water pollution index (WPI<sub>N</sub>) was used as follows:

$$WPI_N = \left( \sum_{i=1}^4 \frac{C_i}{MPC_i} \right) / 4, \quad (1)$$

where  $C_i$  is average long-term nutrient concentration;  $MPC_i$  is its maximum permissible concentration.

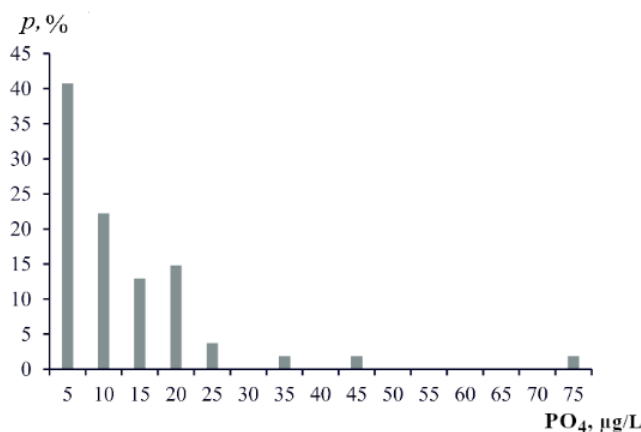


Fig. 4. Repeatability of phosphate concentration at the western Sevastopol Bay



$WPI_N$  characterizes the total impact of nutrients on the aquatic environment without taking into account the influence of other water quality indicators.

For an approximate assessment of the average long-term transformation of nutrients in the water of the Chernaya River estuarine zone under the influence of hydrophysical, hydrochemical and hydrobiological factors, the transformation index of nutrients ( $TI_N$ , %/km) was used showing by what percentage on average the concentration of an individual nutrient changed for each kilometer of the longitudinal axial section of the estuarine zone. Work [4, p. 291] proposes the following formula to calculate  $TI_N$

$$TI_N = \left( \frac{\Delta C}{C_{\text{нач}} \cdot L} \right) \cdot 100\% , \quad (2)$$

where  $\Delta C$  is difference between the average long-term nutrient concentration at the final and initial sections of the area under study;  $L$  is distance between sections.

The significance of trends in the concentration of the studied ingredients was assessed using the F-criterion (Fisher test) for the probability of inequality of the slope to zero at the level of 95% [20].

### Discussion of results

*Temporal variability.* For 1991–2020, the average annual nutrient concentration calculated from 3–4 hydrochemical surveys per year did not exceed the MPC at all stations. Although some surveys showed the extreme concentrations of elements 2–500 times higher than the MPC: 595  $\mu\text{g/L}$  of phosphates (MPC 150  $\mu\text{g/L}$ ) (27.04.2016), 10,471  $\mu\text{g/L}$  of nitrites (MPC 20  $\mu\text{g/L}$ ) (05.09.2016), 17,755  $\mu\text{g/L}$  of nitrates (MPC 9000  $\mu\text{g/L}$ ) (04.02.2014). Such anomalies can be caused by emergency wastewater discharges and rainfall.

Analysis of the variability of the nutrient concentration in the bottom and surface layers of water in the Chernaya River estuarine zone revealed no significant trends. Fig. 5 shows typical distribution of nutrient concentrations in the surface layer of water in the central part of the river estuarine zone (Sevastopol Bay), where the most intense interaction of heterogeneous waters (river, sea, bay and wastewaters) occurs.

Earlier works (e.g., in [16]) in 1989–2008 revealed a decrease in the concentration of ammonium nitrogen (by 10  $\mu\text{g/L/year}$ ) and nitrites (by 2  $\mu\text{g/L/year}$ ) entering the water of the estuarine zone with the Chernaya River runoff, and work [6] identified trends towards an increase in the content of phosphates and nitrates in the water of Sevastopol Bay in 2007–2016 since 2012.

The absence of significant trends in nutrient concentration changes in 1991–2020 confirms the conclusions made in [5, 15]. During the same period, no significant trends in other abiotic components of the ecosystem, such as river runoff, precipitation and water level, were observed [1]. During this period, multidirectional trends in the nutrient concentrations were identified in wastewaters [4]. Obviously, the integral influence of all these factors (economic activity and warming) and sources of nutrient entry (river runoff and wastewaters) during the period under review did not significantly affect the nutrient temporal variability.

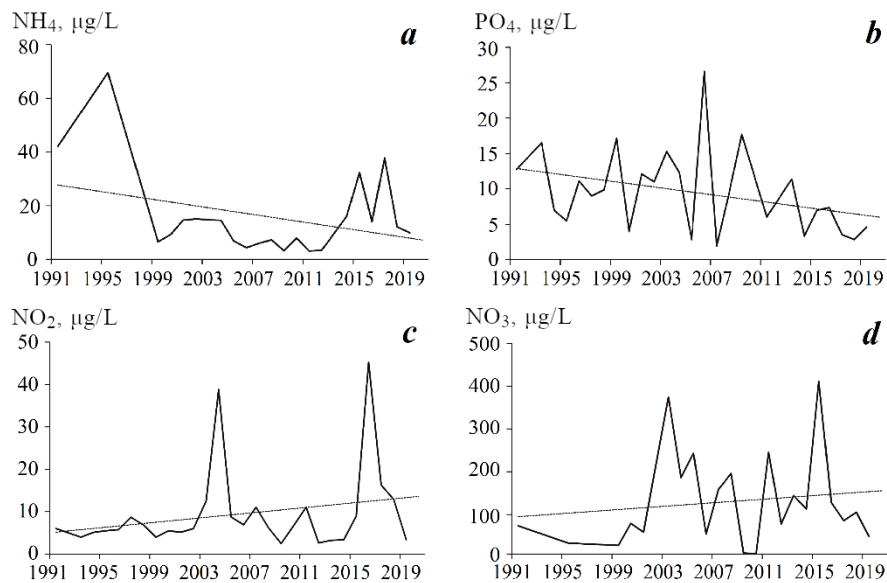


Fig. 5. Nutrient concentrations, µg/L, in the water of the Chernaya River estuarine zone: *a* – ammonium nitrogen, *b* – phosphates, *c* – nitrites, *d* – nitrates

*Spatial variability.* General character of the distribution of nutrient median concentrations (Fig. 6) indicates that the eastern part of the estuarine zone is influenced by the river runoff, which carries nutrients out of the river basin when washed off during precipitation, and wastewaters.

The content of all nutrients in the bottom layer of water is lower than in the surface one, excluding the concentration of ammonium nitrogen, especially in the area of station 8 (see Fig. 2). Ammonification increases under anaerobic conditions in the deep-sea part of the bay. Therefore, an increased concentration of ammonium nitrogen is observed in the bottom layer of water.

Compared to previous works [5, 15], the distribution of nutrient concentration over depth is less homogeneous (Fig. 6). Obviously, this is due to the use of medians for analysis, and not because of less accurate arithmetic average values of the nutrient concentrations which are significantly influenced by the extreme values of the ingredients.

The highest concentration of all nutrients was observed in the water of Yuzhnaya Bay exposed to the impact of storm water runoff, emergency sewage discharges, under-channel runoff, etc. Pollution of this part of the estuarine zone by nutrients is facilitated by difficult water exchange with Sevastopol Bay due to its geomorphological features (see Fig. 2). The decontaminating effect of sea water with a lower nutrient concentration extends to the western part of the estuarine zone, but at the same time denser sea water and prevailing wind direction (along the axis of the estuarine zone) complicate water exchange between Yuzhnaya and Sevastopol Bays. This promotes the accumulation of pollutants at the top of the stagnant Yuzhnaya Bay.

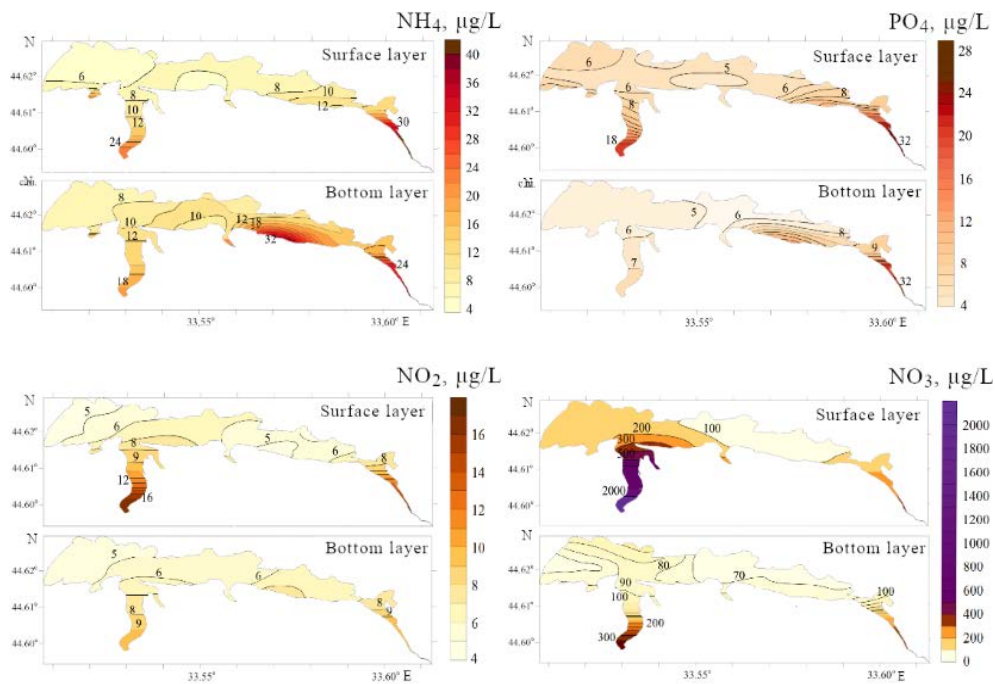


Fig. 6. Distribution of median concentrations of ammonium nitrogen ( $\text{NH}_4$ ), phosphates ( $\text{PO}_4$ ), nitrites ( $\text{NO}_2$ ) and nitrates ( $\text{NO}_3$ ) in the surface and bottom layers of water in the Chernaya River estuarine zone

The median values of nutrient concentrations at all stations did not exceed the MPC (Fig. 6). Their highest values were revealed at station 17 (see Fig. 2) in Yuzhnaya Bay:  $18 \mu\text{g/L}$  – for phosphates and nitrites,  $2346 \mu\text{g/L}$  – for nitrates,  $25 \mu\text{g/L}$  – for ammonium nitrogen.

Nitrates make the greatest contribution to the supply of nutrients to water. They come with river runoff in an amount that is an order of magnitude greater than the amount of other incoming nutrients [4, 15], as well as with precipitation [17], wastewaters [4] and during intra-reservoir hydrochemical and hydrobiological processes [2].

Analysis of the distribution of median nutrient concentrations in the water of the Chernaya River estuarine zone (Fig. 7) showed that under the influence of various self-purification factors (mixing with cleaner sea water, sedimentation, biogeochemical transformation of nutrients and other hydrophysical, hydrochemical and hydrobiological processes), the nutrient concentrations decreased mainly along the axis of the estuarine coastal zone, with the exception of nitrates. The content of nitrates decreased from the top to the middle of the river estuarine zone and then increased (Fig. 7) which is due to their entry into the southern and western parts of the estuarine zone with wastewaters.

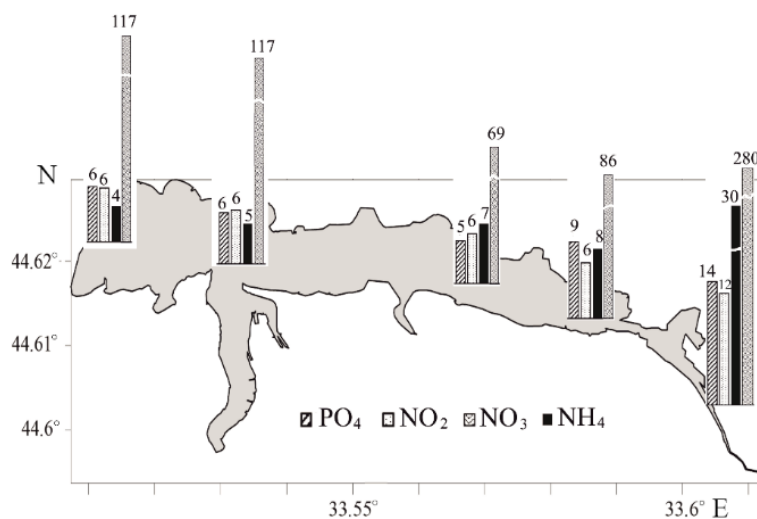


Fig. 7. Variability of the median concentration of the nutrients in the surface water layer in the Chernaya River estuarine zone,  $\mu\text{g/L}$

Fig. 7 shows that the concentration of all nutrients decreased most intensively in the Inkerman Lagoon and the adjacent part of the bay, in the zone of the frontal section of heterogeneous waters, where self-purification processes are most active. The concentration of nitrates decreased by 2.4, ammonium nitrogen by 7.5, nitrites by 2.0, and phosphates by 2.3 times along the axis of the Chernaya River estuarine zone. At the same time, the concentration of phosphates and nitrites changed insignificantly along the axis of Sevastopol Bay (the main part of the estuarine zone).

The resulting schemes can be used for zoning the Chernaya River estuarine zone according to hydrochemical indicators, identifying the most vulnerable ecological areas, assessing water quality comprehensively, as well as calculating the nutrient balance and the accumulative capacity of this receiving reservoir.

*Assessment of water quality and self-purification.* The assessment of the water quality of the Chernaya River estuarine zone in terms of nutrient content was carried out according to formula (1) using average (Fig. 8, a) and median (Fig. 8, b) concentration values. Fig. 8 shows that  $\text{WPI}_N$  calculated from arithmetic mean concentrations is 2–6 times greater than  $\text{WPI}_N$  calculated from median concentrations. The highest value of  $\text{WPI}_N$  calculated from median concentrations (Fig. 8, b) is observed in the surface layer of water of the Inkerman Lagoon, since the main source of nutrients is the Chernaya River runoff.

The average long-term  $\text{WPI}_N$  in the bottom layer was 2.5 times less than in the surface layer of water in the Chernaya River estuarine zone in 1991–2020. This is due to the fact that nitrates make the greatest contribution to the structure of water pollution: denitrification processes reducing the concentration of nitrates occur more actively in the bottom layer of water under anaerobic conditions, and nitrates enter the surface layer from various sources with the increase of their concentration

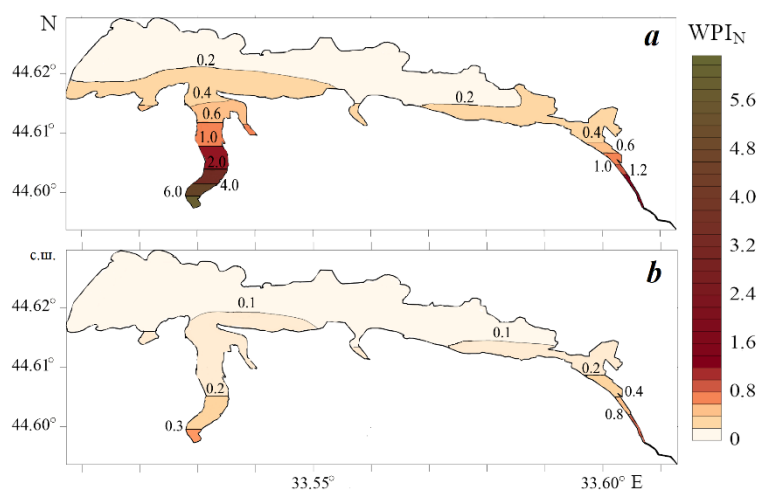


Fig. 8. Distribution of the index of water pollution with nutrients ( $IWP_N$ ) in the Chernaya River estuarine zone calculated using average (*a*) and median (*b*) concentration values for 1991–2020

due to nitrification processes. The nutrient content in the water of the western and central parts of the estuarine zone was the lowest one (Fig. 8), since the western part of the estuarine zone received sea water depleted of nutrients, and in its central part fewer sewage and storm water collectors are located. (see Fig. 1).

The resulting assessment of water quality based on  $WPI_N$  coincides with the conclusions in [7, 15] where  $WPI$  was calculated using the generally accepted method [18] taking into account not only nutrients, but also pollutants. The  $WPI_N$  distribution (Fig. 8) corresponds to the presence of sources of pollutants at the Chernaya River mouth indicated in Fig. 1 and discussed in [15]. Consequently, the surface layer of water of the Inkerman Lagoon and Yuzhnaya Bay, which are parts of the Chernaya River estuarine zone with the lowest self-purifying ability of the aquatic environment, can be under greatest risk of eutrophication.

To quantify the nutrient transformation along the longitudinal axis of the river estuarine zone, a simplified method was used to calculate the average long-term  $TI_N$  using formula (2). This indicator characterizes the ability of water to self-purify from nutrients taking into account the complex influence of abiotic and biotic factors on the concentration of separate nutrients.

The water of the Chernaya River estuarine zone most purified itself from ammonium nitrogen: its concentration decreased by an average of 11.4%/km. The concentration of nitrates decreased by 7.7%/km, phosphates – by 7.3%/km and nitrites – by 6.8%/km.

The self-purification of water from phosphates improved (by 3.5%/km), and from nitrates it worsened (by 2.6%/km) in the modern period in comparison with previously obtained results [15].

$TI_N$  can be applied for approximate estimates of changes in concentration at any point of the estuarine zone depending on the concentration at the source of nutrient entry.

### **Conclusion**

In numerous previous studies, the analysis of the variability of the nutrient content in the water of the Chernaya River estuarine zone for the entire modern period (1991–2020) was carried out on the basis of an arithmetic mean value, which represents an insufficiently correct statistical assessment of primary information.

For the first time, hydrochemical observational data accumulated in the databases of MHI RAS and SB SOI for 1991–2020 were systematized, checked for homogeneity and stationarity and combined into one series, which made it possible to obtain a modern characteristic of the nutrient variability.

It was established that water quality in terms of the content of phosphates, nitrates, nitrites and ammonium nitrogen in 1991–2020 generally corresponded to the standard. No significant trends in the average long-term values nutrient concentrations were detected.

Since the distributions of urgent values of nutrient concentrations are extremely asymmetrical at all stations, the obtained patterns of distribution of their median concentrations in the surface and bottom layers of water in the Chernaya River estuarine zone are more reliable compared to previous works in which less accurate arithmetic average values were used.

It is proposed to use the water pollution index ( $WPI_N$ ) to assess the integral pollution of the aquatic environment by the complex of nutrients. Differences between  $WPI_N$  calculated from medians and arithmetic mean concentrations are shown for the first time. It was established that when median concentrations are used to calculate  $WPI_N$ , the highest nutrient content is determined for the water of the eastern part of the estuarine zone. In the future, it will be possible to establish water quality classes based on  $WPI_N$  and zone the estuarine zone according to them.

The  $TI_N$  (nutrient transformation index) calculation revealed that the concentration decreases naturally from the river to the sea along the axis of the Chernaya River estuarine zone. The nutrient content in the most enriched surface layer of water decreases by an average of 8%/km. The  $TI_N$  can be applied for an approximate assessment of changes in the content of various nutrients with a lack of *in situ* data.

The results obtained are applicable for improving the monitoring system, balance and forecast estimates, modeling the evolution of the estuary ecosystem, developing a scientific justification for economic activities in the region, as well as measures to preserve and protect the natural environment of the Chernaya River sea mouth.

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