Original article

# Dynamics of Nutrients Concentration in the Chernaya River Waters (Crimean Peninsula) in 2015–2020

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### Abstract

*Purpose.* The study is purposed at assessing the intra- and inter-annual dynamics of nutrients concentration (compounds of inorganic nitrogen, phosphorus and silicon) in the Chernaya River waters. *Methods and Results.* The quarterly monitoring data on the water hydrochemical characteristics in the lower reaches of the Chernaya River and in the Chernorechenskoe reservoir obtained by Marine Hydrophysical Institute of RAS in 2015–2020 were used. The data obtained made it possible to study the distribution of inorganic nitrogen, phosphorus and silicon compound concentrations in the Chernaya River waters during the period under study, as well as its seasonal and interannual changes. As compared to 2010–2014, the ammonia nitrogen levels in 2015–2020 increased on average by 2.7 times. The mean long-term inorganic nitrogen outflow with the Chernaya River waters was 32.46 t/year in 2010–2014 and 27.8 t/year in 2015–2020, phosphorus and silicon – 0.23 and 57.93 t/year in 2010–2014 and 0.18 and 62.21 t/year in 2015–2020, respectively.

*Conclusions*. An increase in concentrations of all the nutrients under consideration was observed at the stations located near the villages in the Baydar Valley and hence, most susceptible to the anthropogenic impact, as well as in the area of water outlet of the *Sevagrosoyuz* agricultural firm, that can testify to the inflow of mineral fertilizers to the river waters. Recently the content of nutrients inorganic forms in the Chernaya River waters has increased as compared to the period before 2014, indicating the discussed over the past decade necessity in constructing a sewerage and wastewater treatment system both for the enterprises and the residential development of the Baydar Valley.

Keywords: Chernaya River, Crimean Peninsula, nutrients, inorganic nitrogen, phosphorus, silicon, anthropogenic pressure

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# Introduction

The Chernaya River is one of the main rivers of the Sevastopol region, the second deepest on the Crimean Peninsula that, unlike other rivers, almost never dries up. Its length is 41 km, the catchment area is 436 km and the average monthly discharge is  $1.82-1.94 \text{ m}^3/\text{s}$  [1]. The river originates from the Skelsky spring, near Rodnikovoe (Rodnikovskoe) village. The Chernaya River belongs to the river type with a flood regime. As many as 11 tributaries flow into it <sup>1</sup>. The Chernaya River is

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<sup>&</sup>lt;sup>1</sup> Government of Sevastopol. [Annual Report on the State and Protection of the Environment of the Federal City of Sevastopol for 2015]. [online] Available at: https://sev.gov.ru/files/iblock/a38/gosdoklad\_Sev\_2015.pdf [Accessed: 16 May 2024] (in Russian).

not only the main surface source of water supply of Sevastopol, but also the only permanent watercourse that discharges its waters into Sevastopol Bay [2, 3].

Intra-annual distribution of the Chernaya River runoff is determined by the nature of the river alimentation and climatic conditions. In Crimean rivers, floods occur mainly in the winter-spring period, from November – December to April, which is associated with the passage of Mediterranean cyclones. The minimum runoff is observed in August – September due to a decrease in the amount or a complete absence of precipitation and depletion of underground runoff [4].

It is known that an increase in the river runoff pollution level can lead to an increase in the concentration and accumulation of nutrients and pollutants in the river estuaries, as well as in the adjacent coastal zone of the sea [5]. In general, the distribution of average nutrient content along river beds reflects the impact of natural and anthropogenic factors on the formation of chemical composition of river waters [6]. The average level of inorganic nitrogen and phosphorus compounds in the rivers flowing near populated areas can be significantly higher than the content of these compounds in large and small rivers, whose runoff is formed under natural conditions. Quite high concentrations of nitrogen and phosphorus inorganic compounds are also observed in the rivers with heavily swamped catchment areas [6].

The work [2] identifies several main factors affecting the pollution level of the Chernaya River: pollution of the river catchment area and its tributaries, high water turbidity during floods, as well as water pollution of the Chernorechenskoe reservoir. The authors of this work suggest that the pollution sources are anthropogenic in nature due to the presence of ponds in the Chernaya River catchment area, which are used not only as water runoff regulators, but also as wastewater storage ponds<sup>2</sup>.

The greatest anthropogenic impact on the Chernaya River is exerted by the Sevastopol agglomeration with a population density of ~ 5,000 people per 1 km<sup>2</sup> (as of 2013). At the same time, since 2014, the population of the region has almost doubled, which has caused an increase in the share of untreated wastewater discharge in the total volume of wastewater by 8% in the last five years [7]. River pollution occurs as a result of the flow of drainage water from agricultural fields and household plots, discharges of domestic wastewater through the networks of *Sevgorvodokanal* utility company and unorganized discharges, as well as storm water runoff [8, 9]. In work [10], E.I. Ovsyany and co-authors noted that the Chernaya River water pollution in the middle reaches occurred as a result of the discharge of untreated wastewater from Orlinoe village into the Baydarka River and also due to the lack of sewerage in the nearest settlements. In the area of Sakharnaya Golovka village (the lower reaches of the river), conditionally pure wastewater was periodically discharged, which led to contamination of underground aquifers and entry of pollutants into the river with surface-slope runoff [10].

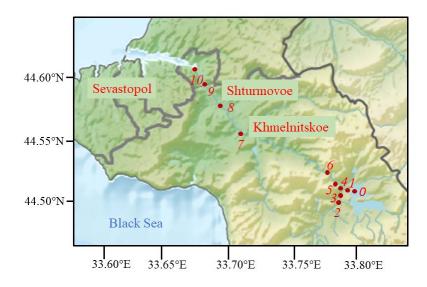
Based on the foregoing, the study of the nutrients content in the Chernaya River waters, its intra- and interannual variation is relevant from the point of view of assessing the ecological and recreational potential of both the river itself and

<sup>&</sup>lt;sup>2</sup> Lisovsky, A.A., ed., 2011. [Surface Water Bodies of Crimea. Management and Use of Water Resources: Reference Book]. Simferopol: KRP Publishing House "Krymuchpedgis", 242 p. (in Russian).

Sevastopol Bay. This work is purposed at studying the intra- and interannual dynamics of nutrients concentration in the Chernaya River waters.

# Methods and materials

Sampling area. During the monitoring of pollution state of the Chernaya River and Chernorechenskoe reservoir waters from 2010 to 2014, 551 samples were taken; from 2015 to 2020 – 787 samples of river water were taken to determine the content of inorganic nitrogen, inorganic phosphorus and silicon compounds in them. Expeditionary work was carried out quarterly and was part of the state assignment of Marine Hydrophysical Institute (MHI) of RAS (Fig. 1).



**F** i.g. 1. Location of long-term monitoring stations of the Chernaya River: station 0 – reservoir mirror above the water intake; station 1 – water intake under the reservoir; station 2 – the Baydarka River, former pond; station 3 – culvert under the road in Ozernoe village; station 4 – the Urkusta River (tributary from the pond in Peredovoye village); station 5 – automobile bridge between Ozernoye and Peredovoe village; station 6 – gauging station at Red Rock; station 7 – gauging station by Khmelnitskoe village; station 8 – automobile bridge by Shturmovoe village; station 9 – railway bridge near Inkerman; station 10 – automobile bridge near Inkerman

To assess changes in the degree of anthropogenic impact on the dynamics of the nutrients content in the Chernaya River waters we also considered 2010–2014 period, i.e., before active development of the Baydar Valley land.

*Methods of chemical analysis.* Concentration of the sum of nitrates and nitrites was determined by the spectrophotometric method (RD 52.10.243-92) on an automatic flow multichannel analyzer of nutrients *Scalar San*<sup>++</sup> (Netherlands). The method is based on the reduction of nitrates to nitrites through a copper-plated cadmium reducer. At the minimum detectable concentration of the sum of nitrates and nitrites of 0.36 µmol/l, the error is  $\pm 0.20$  µmol/l. The content of ammonium ions was determined by the modified spectrophotometric method of Saggi – Solorzano [11] based on the phenol-hypochlorite reaction with the formation of indophenol in

the concentration range of  $0.1-15.0 \ \mu mol/l$  with an error  $\sigma$  equal to  $\pm 12\%$ . The phosphorus concentration was determined by a spectrophotometric method based on the formation of a blue phosphomolybdenum complex with a concentration measurement range of  $0.05-100.0 \ \mu mol/l$ ; the maximum error of the method is  $\pm 15\%$ (RD 52.10.243-92). The silicon concentration was determined by the spectrophotometric method (RD 52.10.243-92) based on the formation of a blue silicomolybdenum complex with a range of determined concentrations of  $0.05-80.0 \ \mu mol/l$ . The error of the method ranges from 3 to 20%.

#### Results

The main nitrogen forms during the study period were ammonium (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) nitrogen. Their contribution to the total content of inorganic nitrogen compounds in the Chernaya River waters was 9.97 and 87.51%, respectively. Nitrites, as an intermediate element in the ammonium oxidation to nitrates, were found in much lower concentrations, so the work considers the concentration of the sum of nitrates and nitrites (oxidized nitrogen, NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>). Some statistical characteristics of the determined elements concentrations are presented in Table 1 and 2.

The ammonia nitrogen content in the Chernaya River waters in the 2015–2020 period varied from 0.00 to 161.58  $\mu$ mol/l. The maximum concentration was recorded in April 2018 by a railway bridge in Inkerman (station 9).

The concentrations of the sum of nitrates and nitrites varied in the range of  $5.41-499.76 \mu mol/l$ , the maximum content of oxidized nitrogen was determined in April 2018 also at station 9.

Table 1

Characteristic	$\mathrm{NH_4^+}$	NO <sub>2</sub> <sup>-</sup> +NO <sub>3</sub> <sup>-</sup>	SiO <sub>3</sub> <sup>2-</sup>	PO4 <sup>3-</sup>
$C_{\min}$	0.00	5.41	1.61	0.00
$C_{\max}$	161.58	499.76	256.85	13.12
Median	3.14	31.32	38.75	0.10
Standard deviation	11.92	47.36	42.75	1.49

Concentration of nutrients, µmol/l, in the Chernaya River waters in 2015–2020

The variation range of the concentration of phosphorus ( $PO_4^{3-}$ ) in the river waters was 0.00–13.12 µmol/l. Their maximum content was recorded in August 2020 at station 9. Moreover, in September 2015, the concentration of phosphorus at this station was also high and amounted to 11.34 µmol/l.

Maximum silicon (SiO<sub>3</sub><sup>2-</sup>) content in 2015–2020 was noted in September 2016 in a tributary of the Urkusta River (station 4) and in November 2017 in the area of the gauging station at Red Rock (station 6), the concentrations reached 256.85 and 201.90  $\mu$ mol/l, respectively. The overall range of concentration changes during this study period was 1.61–256.85  $\mu$ mol/l.

In 2010–2014, the median content of ammonia nitrogen and silicon was lower than in 2015–2020 (Table 2). The variation range in the ammonia nitrogen concentration was  $0.00-30.46 \mu mol/l$ , silicon –  $0.99-308.15 \mu mol/l$ .

Table 2

Characteristic	$\mathrm{NH_4^+}$	NO <sub>2</sub> <sup>-</sup> +NO <sub>3</sub> <sup>-</sup>	SiO <sub>3</sub> <sup>2-</sup>	PO4 <sup>3-</sup>
$C_{\min}$	0.00	11.17	0.99	0.00
$C_{\max}$	30.46	302.19	308.15	6.22
Median	1.01	39.16	35.85	0.13
Standard deviation	6.20	50.34	48.63	0.95

Concentration of nutrients, µmol/l, in the Chernaya River waters in 2010–2014

The median concentrations of the sum of nitrates and nitrites are the same as the ones of phosphorus, in 2010–2014 they slightly exceeded the corresponding concentrations in 2015–2020. The oxidized nitrogen content varied from 11.17 to  $302.19 \mu mol/l$ , phosphorus – from 0.00 to 6.22  $\mu mol/l$ .

## Seasonal variability of nutrients concentrations

When considering seasonal distribution of ammonia nitrogen in 2015–2020 (Fig. 2, a), it can be noted that the concentrations at stations in the area of the Chernorechenskoe reservoir and along the entire course of the Chernaya River were distributed almost evenly. The exception was increased values in summer at stations 3, 4, located near Ozernoye and Peredovoye villages, as well as at station 9 throughout the year.

The minimum concentrations of the sum of nitrates and nitrites (Fig. 2, b) occurred in the summer period, the maximum ones were typical for the springwinter period. An increased content of oxidized nitrogen was determined in winter in the the Baydarka River area (station 2) and a culvert under the road in Ozernoe village (station 3), as well as during all seasons by the railway bridge in Inkerman (station 9).

Throughout the entire study period, the maximum phosphorus content was observed at station 9 (Fig. 2, c). Its increased concentrations were determined during all seasons in the area of stations 2, 3. A decrease in phosphorus content throughout the river occurred in the summer and autumn periods.

Increased silicon concentrations (Fig. 2, d) were observed at stations 2, 3, 4, as well as at station 9. The maximum values were observed in the autumn period in the Urkusta River tributary (station 4), into which the wastewater from Peredovoe village inflows.

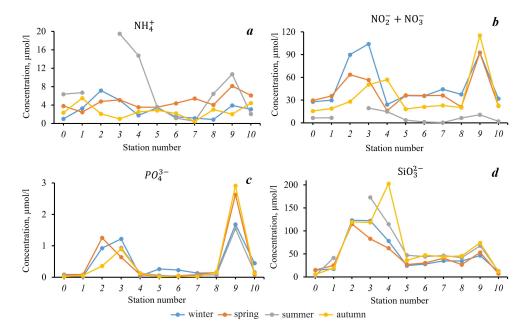
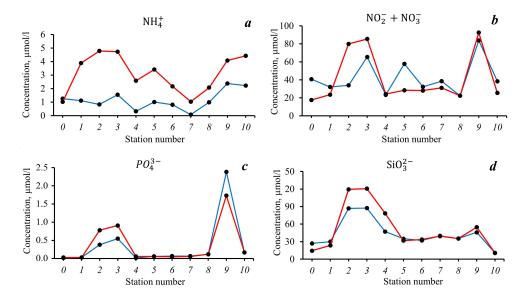


Fig. 2. Seasonal distribution of nutrients in the Chernaya River waters in 2015–2020

Interannual variation of nutrient content.

Compared to the period from 2010 to 2014, in 2015–2020 the ammonia nitrogen supply increased on average 2.7 times throughout the entire course of the river (Fig. 3, a). This increase is especially obvious at stations 1, 2 and 3.



**F i g. 3.** Mean long-term nutrients content in the Chernaya River waters (blue line denotes 2010–2014, red line – 2015–2020)

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An analysis of changes in the oxidized nitrogen concentration (Fig. 3, b) also revealed its increase in 2015–2020 in the area of stations 2 and 3 and a twofold decrease at station 5, located between Shirokoe and Ozernoye villages.

Variation of phosphorus concentration along the river course in 2015-2020 and 2010-2014 has a similar character (Fig. 3, *c*), in the same way as for inorganic nitrogen compounds, an increase in concentrations at stations 2 and 3 takes place.

Variation of silicon concentration in both periods under consideration is similar (Fig. 3, d). At the same time, there is an increase in its content compared to the earlier period at stations 2, 3 and 4.

# Quantitative estimates of nutrients supply with river waters

According to [12], the mean long-term runoff of the Chernaya River is  $\sim 57.7$  million m<sup>3</sup>/year. In this case, two periods are distinguished – high-water (December – April) with the runoff amount of 51.2% from the annual one and low-water (May – November). Based on these values, as well as data on the median concentration of nutrients in the river waters, we calculated the nutrients outflow into Sevastopol Bay for two periods under consideration: 2015–2020 and 2010–2014 (Table 3).

Table 3

Outflow	$\mathrm{NH_4^+}$	NO <sub>2</sub> <sup>-</sup> +NO <sub>3</sub> <sup>-</sup>	SiO <sub>3</sub> <sup>2-</sup>	PO4 <sup>3-</sup>
Mean long-term, t/year	0.82 / 2.50	31.64 / 25.30	57.93 / 62.21	0.23 / 0.18
High water period, t/season	0.36 / 1.33	17.85 / 16.01	35.86 / 29.55	0.11 / 0.12
Low water period, t/season	0.78 / 1.14	11.41 / 9.02	13.60 / 32.18	0.12 / 0.08

Nutrients outflow with the Chernaya River waters in 2010–2014 and 2015–2020

# **Discussion of the results**

Regular variations were observed in the nutrient content along the Chernaya River course. They were caused, as was shown earlier in [13], by the activity of the consumption processes of these elements by plants and organic matter mineralization, as well as their entry with surface runoff from the catchment area and with wastewater.

### Seasonal variations in 2015–2020

Minimum concentrations of the sum of nitrates and nitrites (Fig. 2, b) in summer can be explained by their active consumption by autotrophic bacteria. Maximum concentrations of these nutrients during spring-winter floods are typical for the period of maximum surface washout, as well as for the low-water period due to the oxidation of autochthonous organic substances and a relative increase in the share of wastewater with a decrease in natural runoff [2].

Increased concentrations of phosphorus at stations 2 and 3 can be explained by their entry into the Chernaya River waters as a result of the washout of water containing fertilizers from the fields. The decrease in phosphorus content in summer and autumn periods is probably due to their transition to organic form as a result of their consumption by aquatic organisms in the process of life. Silicon content level in river waters, compared to the content of nitrogen and phosphorus compounds, is determined to a lesser extent by the action of anthropogenic factors [6]. The highest silicon concentrations were noted during the flood period, which is consistent with [3].

Wastewater discharges from sewage treatment plants (STP 5) located near Ozernoe village can have an effect on the increase of the nutrients content in the area of stations 2 and 3 [14]. These treatment facilities have a biological type of water purification, the essence of which is in the breakdown of nitrogen-containing organic compounds by microorganisms, and as a result ammonia is released in large quantities <sup>3</sup>. Under natural conditions, ammonia oxidation (nitrification) occurs with the formation of nitrous acid salts (nitrates). According to [14], the volume of wastewater discharged from STP 5 is about 18 thousand tons/year. An average concentration of ammonia nitrogen in wastewater is 21.42  $\mu$ mol/l, the sum of nitrates and nitrites – 2157  $\mu$ mol/l, phosphorus – 93.55  $\mu$ mol/l.

The constantly increased concentrations of all the considered nutrients in the river waters at station 9, recorded every year in all seasons, are noteworthy. In the area of the specified sampling station there is a permanent water outlet, presumably from the *Sevagrosoyuz* agricultural firm. The main activity of this company, according to the information on the website <sup>4</sup>, is growing vegetables. In April and August 2023, we took water samples from this outlet and analyzed them for nutrients content. It was found that the concentration of ammonium ions exceeded the maximum allowable concentration (MAC) for water bodies of fishery importance <sup>5</sup> by 5.5 times, nitrites by 9.1 times, nitrates by 4.5 times, phosphorus by 8.7 times, silicon – by 22 times.

It can be assumed that such high nutrients concentrations are the result of the washout of mineral fertilizers (nitrogen, phosphorus, etc.) from the fields of an agricultural company and their entry with groundwater or wastewater. Apparently, the runoff of water containing such significant amounts of inorganic forms of nutrients from this outlet can contribute to an increase in their concentrations in the Chernaya River waters at station 9.

In addition, in [14] it is noted that in the area of this station there is a point of wastewater discharge from sewage treatment plants located in Sakharnaya Golovka village with a volume of discharge into the river of 420 thousand tons/year. An average concentration of ammonia nitrogen in these waters is 21.42  $\mu$ mol/l, the sum of nitrates and nitrites is 2435  $\mu$ mol/l and phosphorus – 196.75  $\mu$ mol/l. In addition, slightly upstream of the river there are water treatment facilities with a discharge volume of 1680 thousand tons/year, where the average concentration of ammonia nitrogen is 3.57  $\mu$ mol/l, the sum of nitrates and nitrites is 1143  $\mu$ mol/l and

<sup>&</sup>lt;sup>3</sup> Golubovskaya, E.K., 1978. [*Biological Principles of Water Purification*]. Moscow: Vysshaia Shkola, 271 p. (in Russian).

<sup>&</sup>lt;sup>4</sup> Sevagrosoyuz. *Details*. [online]. Available at: https://spark-interfax.ru/sevastopol-balaklavski/ooosevagrosoyuz-inn-9202002342-ogrn-1149204043526-aea1ce5322814e16b93d772bdf926635 [Accessed: 10 May 2024] (in Russian).

<sup>&</sup>lt;sup>5</sup> Russian Ministry of Health, 1998. *Maximum Allowable Concentrations (Macs) of Chemicals in the Water of Water Objects Used for Drinking and Domestic-Recreation Purposes: GN 2.1.5.689–98.* Moscow: Ministry of Health, 77 p. (in Russian).

phosphorus  $-16.13 \mu mol/l$ . Perhaps this source may also be the cause for high content of nutrients in the river waters at this station.

Note that sampling stations 9 and 10 are located in the mixing zone of river and sea waters, i.e., they belong to the marginal filter. Therefore, increased nutrient concentrations in the river waters at these stations have a significant impact on Sevastopol Bay ecosystem.

### Interannual variation of nutrient content

The increase in ammonia nitrogen concentration is especially obvious in 2015-2020 compared to the earlier period, it manifests itself at stations *1*, *2* and *3*, located near Shirokoe and Ozernoye villages. Livestock farming and agricultural activities are quite developed in these villages, but there are no sewage systems or wastewater treatment.

The identified increase in concentrations of the sum of nitrates and nitrites, as well as phosphorus in the area of stations 2 and 3, that took place in 2015–2020, may be associated with the inflow of nitrogen-phosphorus fertilizers into groundwater from farmland. At the same time, the fact that nutrients concentration at station 5 has doubled (between Shirokoe and Ozernoe villages) can be explained by mixing of relatively pure waters from station 1 (water intake under the reservoir) and polluted water from stations 3 and 4 (Ozernoye village and the inflow from the pond in Peredovoe village).

Increase in silicon concentrations in 2015–2020 at stations 2 and 3 may be the result of anthropogenic impact, namely agricultural work and the growth of residential development in nearby villages. In addition, near station 3 we noted active construction of a group of cottages on the hill, not indicated on the online maps. This activity leads to a release of silicates into groundwater and then into the river. Station 4 is less anthropogenically loaded, so the increase in silicon concentration here can probably be explained by leaching of rocks.

## Conclusion

The work considers nutrients content (average and seasonal) in the Chernaya River waters, as well as its variation in the river waters in two separate periods: from 2010 to 2014 (before the active development of the Baydar Valley lands) and from 2015 to 2020.

During the periods under consideration, regardless of the season, increased concentrations of all nutrients were observed at stations in the Baydar Valley area and at the railway bridge in Inkerman. The main sources of inorganic nitrogen and phosphorus compounds entering the river in the station 9 area may be a water outlet (presumably from the *Sevagrosoyuz* agricultural firm) and wastewater from STPs located in Sakharnaya Golovka village. The maximum concentrations of silicon were observed in the Urkusta River tributary and in the gauging station area at Red Rock, which may be the result of leaching of rocks and earthworks.

During the analysis of interannual variations in nutrients concentration, it was found that in 2015–2020 their content, compared to the period before 2014, increased at stations in the Baydar Valley area, while the ammonia nitrogen content increased along the entire course of the Chernaya River.

The flow of phosphorus with river waters into Sevastopol Bay in both periods under consideration was almost unchanged. The average long-term outflow of ammonia nitrogen with river waters in 2015–2020 was three times higher than this index for 2010–2014 period. The silicon flow with the Chernaya River waters in May – November in 2015–2020 exceeded the one in 2010–2014 almost 2.5 times, which can be explained by the intensification of construction work during the warm period of the year.

The data obtained during the work indicate the need for the construction of sewerage and wastewater treatment systems for enterprises and residential buildings in the Baydar Valley, which has been discussed over the past decade.

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#### *Contribution of the co-authors:*

**Maria A. Myslina** – formulation of goals and objectives of the study, qualitative and quantitative analysis of the results and their interpretation, discussion of work results, preparation of graphic materials

**Alla V. Varenik** – general scientific supervision of the study, formulation of conclusions, qualitative and quantitative analysis of results and their interpretation

**Diana V. Tarasevich** – review of the literature on the research problem, qualitative and quantitative analysis of the results and their interpretation

The authors have read and approved the final manuscript. The authors declare that they have no conflict of interest.