Original paper

Trophic State of the Limensky Bay Water Area (Southern Coast of Crimea, Black Sea)

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Abstract
Increase in the water area trophic state is one of the unfavourable consequences of anthropogenic impact on the ecological state of the marine environment. The cause of water body eutrophication is often an excessive input of nutrients and easily oxidisable organics, the main source being river runoff and sewage. The main aim of the work is to determine seasonal changes in the trophic state of the Limensky Bay water area based on numerical modelling data. The data required to calculate the trophic state index were derived using a one-dimensional version of the water quality model and its eutrophication block. The annual course of chlorophyll a concentration, nitrate and nitrite nitrogen, ammonium, phosphate phosphorus and oxygen was obtained for the Limensky Bay water area. The trophic state index was calculated from these biogeochemical indicators. The sea water in the study area was of good quality and its state was mesotrophic. Only in the cold period on the 1^{st}–104^{th} and 356^{th}–365^{th} model days, the index was below 4, which corresponds to an oligotrophic state. The maximum index value (4.39) was on the 247^{th} model day and the minimum value (3.82) was on the 365^{th} model day. The best correlation of the trophic state index was observed for the concentration of chlorophyll a ($r = 0.84$), mineral nitrogen ($r = 0.80$) and total phosphorus ($r = 0.78$). The calculated relative contribution of the components, included in the calculated formula of the E-TRIX index, showed that the main factor determining the eutrophication level of Limensky Bay waters was the concentration of mineral forms of nitrogen. This study can be used for monitoring the areas where *in situ* sampling is difficult.

Keywords: trophic state, E-TRIX, Limensky Bay, biogeochemical modelling, chlorophyll a, total phosphorus, mineral nitrogen

Acknowledgements: The work was performed under state assignment FNNN-2024-0016 “Studies of spatial and temporal variability of oceanological processes in the coastal, near-shore and shelf zones of the Black Sea influenced by natural and anthropogenic factors on the basis of in situ measurements and numerical modelling”.

For citation: Slepchuk, K.A. and Khmara, T.V., 2024. Trophic State of the Limensky Bay Water Area (Southern Coast of Crimea, Black Sea). *Ecological Safety of Coastal and Shelf Zones of Sea*, (4), pp. 106–116.

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Уровень трофности акватории Лименского залива (Южный берег Крыма, Черное море)

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Аннотация
Повышение уровня трофности акватории является одним из неблагоприятных последствий антропогенного воздействия на экологическое состояние морской среды. Причиной эвтрофирования водоемов часто является избыточное поступление в них биогенных веществ и легкоокисляемой органики, главным источником которых являются речной сток и сточные воды. Основная цель работы – определить сезонные изменения трофического состояния вод в районе Лименского залива на основе данных, полученных с помощью численного моделирования. Необходимые для расчета индекса трофности данные вычислялись по одномерному варианту модели качества воды и ее блоку эвтрофикации. Получен годовой ход концентрации хлорофилла *a*, азота нитратов и нитритов, аммония, фосфора фосфатов, кислорода для акватории Лименского залива. На основе этих биогеохимических показателей рассчитан индекс трофности. Исследуемая акватория обладает хорошим качеством морских вод со средним уровнем трофности. Лишь в холодный период с 1-го по 104-й и с 356-го по 365-й расчетные дни индекс ниже 4, что соответствует низкому уровню трофности. Максимальное значение индекса (4.39) приходится на 247-й расчетный день, минимальное (3.82) – на 365-й. Наибольшая корреляция индекса трофности наблюдается с концентрацией хлорофилла *a* (r = 0.84), минерального азота (r = 0.80) и общего фосфора (r = 0.78). Расчет относительного вклада компонентов, входящих в расчетную формулу индекса *E-TRIX*, показал, что основным фактором, определяющим уровень эвтрофикации вод Лименского залива, является концентрация минеральных форм азота. Данное исследование может использоваться при мониторинге зон, в которых отбор проб на месте трудно осуществить.

Ключевые слова: трофность, *E-TRIX*, Лименский залив, биогеохимическое моделирование, хлорофилл а, общий фосфор, минеральный азот

Благодарности: работа выполнена в рамках государственного задания ФГБУН ФИЦ МГИ по теме FNNN-2024-0016 «Исследование пространственно-временной изменчивости океанологических процессов в береговой, прибрежной и шельфовой зонах Черного моря под воздействием природных и антропогенных факторов на основе контактных измерений и математического моделирования».

Для цитирования: *Слепчук К. А., Хмара Т. В.* Уровень трофности акватории Лименского залива (Южный берег Крыма, Черное море) // Экологическая безопасность прибрежной и шельфовой зон моря. 2024. № 4. С. 106–116. EDN OSAFQO.

Introduction

The Southern Coast of Crimea is a territory with a unique recreational potential. However, tourism activities influence the environmental situation in the region. In Crimea, especially on its southern coast, environmental risks once arose due to the haphazard planning of cities, which did not consider issues most important for the ecological state of the territories, including optimisation of the drainage system, primarily storm water drainage, transport infrastructure [1]. The main source of marine waters pollution of the Southern Coast of Crimea is wastewater discharge from sewage treatment facilities and recreational complexes such as health resorts and recreation centers [2]. At the height of tourist seasons, the risk of the coast overpopulation increases, which inevitably results in pollution of the beach zone and adjacent sea areas.

Recreational resources of the coastal sea zone rely mainly on the natural environment quality. Thus, the water area of the Crimean southern coast is monitored to determine the state of ecosystems and trends in their variability and to develop recommendations for the rational use of natural resources [2, 3].

One of the adverse consequences of anthropogenic impact on the ecological state of the marine environment may be an increase in the trophic state of the water area. Eutrophication of water bodies is often caused by excessive input of nutrients and easily oxidised organic matter, the main source of which is river runoff and wastewater, whose influence is local in nature. It is impossible to find a general method to assess the trophic state of different marine areas. Each study chooses an approach driven by the choice of indicators and their number when calculating various ecological indices, taking into account a limited set of measured parameters and indicators of the marine environment. The E-TRIX ecosystem trophic state index is based on the concentration of the main nutrients (nitrogen and phosphorus), the degree of water oxygenation and chlorophyll a concentration. The advantage of E-TRIX is the use of standard monitoring characteristics, which allows for a comparative analysis of trophic state in different marine areas, while not only qualifying but also quantifying the water body state.

In various studies (e. g. [4]), the E-TRIX index is calculated from monitoring data. However, a sufficient number of observations at different points in space is not always available. Mathematical modelling makes it possible to fill data gaps and assess the ecosystem state, while considering the variability of its components. In addition, mathematical modelling allows predicting the evolution of an ecosystem under the influence of natural, climatic and anthropogenic factors.

As study object, we have chosen Limensky Bay near the settlement of Katsiveli. This water area is under the least anthropogenic impact and distant from large-scale industrial sewage.

Limensky (Goluboy) Bay is located on the Southern Coast of Crimea between Cape Kikineiz and Mount Koshka. In the southwestern part of the bay, there is a stationary oceanographic platform (Fig. 1). The main pollution sources in the bay are wastewater from Katsiveli and the discharge pipe of used water from the fun water park Goluboy Zaliv.

The hydrological structure of the Limensky Bay waters mainly depends on coastal currents and their variability. An analysis of *in situ* data shows that

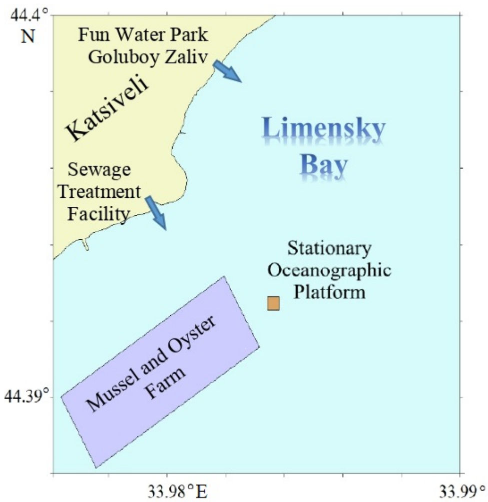


Fig. 1. Study area

a quasi-stationary west-south-west current is observed along the coast near Cape Kikineiz. The average annual modulus of the current velocity vector was maximum in the near-surface layer and varied within 5.8–9.4 cm/s during the monitoring period [5].

Upwelling occurs in this area under longshore winds with a westerly component (southwesterly, westerly and northwesterly). Such a rise of cold nutrient-rich deep waters to the surface has the greatest impact on the content of hydrochemical components in spring and summer periods. As a result, partial pollution of the coastal zone is possible.

The chemical composition of Limensky Bay waters is unique. The content of dissolved oxygen directly depends on the temperature indicators, and its concentration increases sharply (up to 115%) when surging phenomena occur [6]. Hydrochemical studies showed the presence of two unfavourable areas with reduced dissolved oxygen content (97%) [7].

Coastal waters are generally characterised by moderate concentrations of nutrients. The absence of phosphate deficiency (~ 0.1 μM) is typical of this area even during the phytoplankton growth and development [8], which, in turn, indicates active dynamic processes contributing to phosphate input from the underlying sea layers. The concentration of nitrogen forms was relatively low (0.2 μM) according to the data of the studies carried out in the recreational areas of the Southern Coast of Crimea.

From March 2010 to March 2012, comprehensive ecological studies were performed in Limensky Bay near the mussel and oyster farm located on the traverse of Kikineiz Bay (Fig. 1). An analysis of the obtained data showed [9–11] that during the study period, the hydrochemical regime around the farm was characterised by good aeration of the water column, relatively low nutrient content and insignificant anthropogenic pressure. Extremely high water temperature (over 26 °C) in July–August 2010 determined low quantitative indicators of phytoplankton (20 mg/L).

No water bloom, typical of coastal waters and caused by the development of certain phytoplankton species, was observed during the study period. High content of ammonium nitrogen (up to 30.3 μg/L) in the warm period of the year, as compared to other mineral forms of nitrogen, was due to organic matter degradation.

The main objective of this work is to determine seasonal changes in the trophic state of waters in the Limensky Bay area using the E-TRIX index based on numerical modelling data.

Materials and methods

The trophic state of Limensky Bay was assessed using the E-TRIX index. It is a function containing the following parameters: dissolved oxygen, mineral nitrogen, total phosphorus and chlorophyll a. According to [12], the trophic state index is determined by the formula

$$\text{E-TRIX} = (\lg[Ch \cdot D\%\text{O} \cdot N \cdot P] + 1.5) / 1.2,$$

where Ch – concentration of chlorophyll a, μg/L; D%O – absolute deviation of oxygen saturation from 100%; N – concentration of dissolved form of mineral nitrogen, μg/L; P – concentration of total phosphorus, μg/L.

E-TRIX index values can range from 0 to 10. Depending on these values, there are four trophic states: oligotrophic (< 4), mesotrophic (4–5), eutrophic (5–6) and hypereutrophic (6–10).

If the trophic state index exceeds 6, the investigated water area contains high concentrations of nutrients and has low transparency, which can lead to hypoxia in the bottom layers of its waters. If the index does not exceed 4, there are insignificant concentrations of nutrients, good air exchange throughout the entire water column and high transparency [13].

The data on the concentration of chlorophyll a, dissolved oxygen, mineral nitrogen, and total phosphorus, necessary to calculate the E-TRIX index, were derived using a one-dimensional version of the water quality model and its eutrophication module [14]. Before calculating, the model was calibrated using data for 2010–2012 on phytoplankton biomass concentration from [9, 10] and concentrations of nutrients and oxygen from the oceanographic database of the Marine Hydrophysical Institute.

Meteorological data were used as model input parameters: wind speed and direction at 4 h intervals, air temperature at 3 h intervals, photosynthetic active radiation per day, humidity and cloud amount at 6 h intervals. We also used annual variations in transparency, values of seawater temperature, salinity and concentrations of phytoplankton, nutrients, oxygen, organic phosphorus and organic nitrogen. They were set starting from 1 January of the model year.

Results

During the model year, the E-TRIX index varied from 3.82 to 4.39 (average 4.09), which is a transitional trophic state of the study water area from the oligotrophic to mesotrophic one. It also indicates good water quality. The highest value on the 247th model day (5 September) coincided with the autumn peak of phytoplankton blooming, and the lowest value was recorded on the 365th day (31 December). From the 105th to 355th model day, the index exceeded 4, while on other days it was under that value. In terms of seasons, the average index was the highest in autumn (4.22) while in winter it was the lowest (3.96) (Table 1).

In paper [15], the trophic state index was calculated from *in situ* data in the Limensky Bay area using a modified formula. The authors used total nitrogen instead

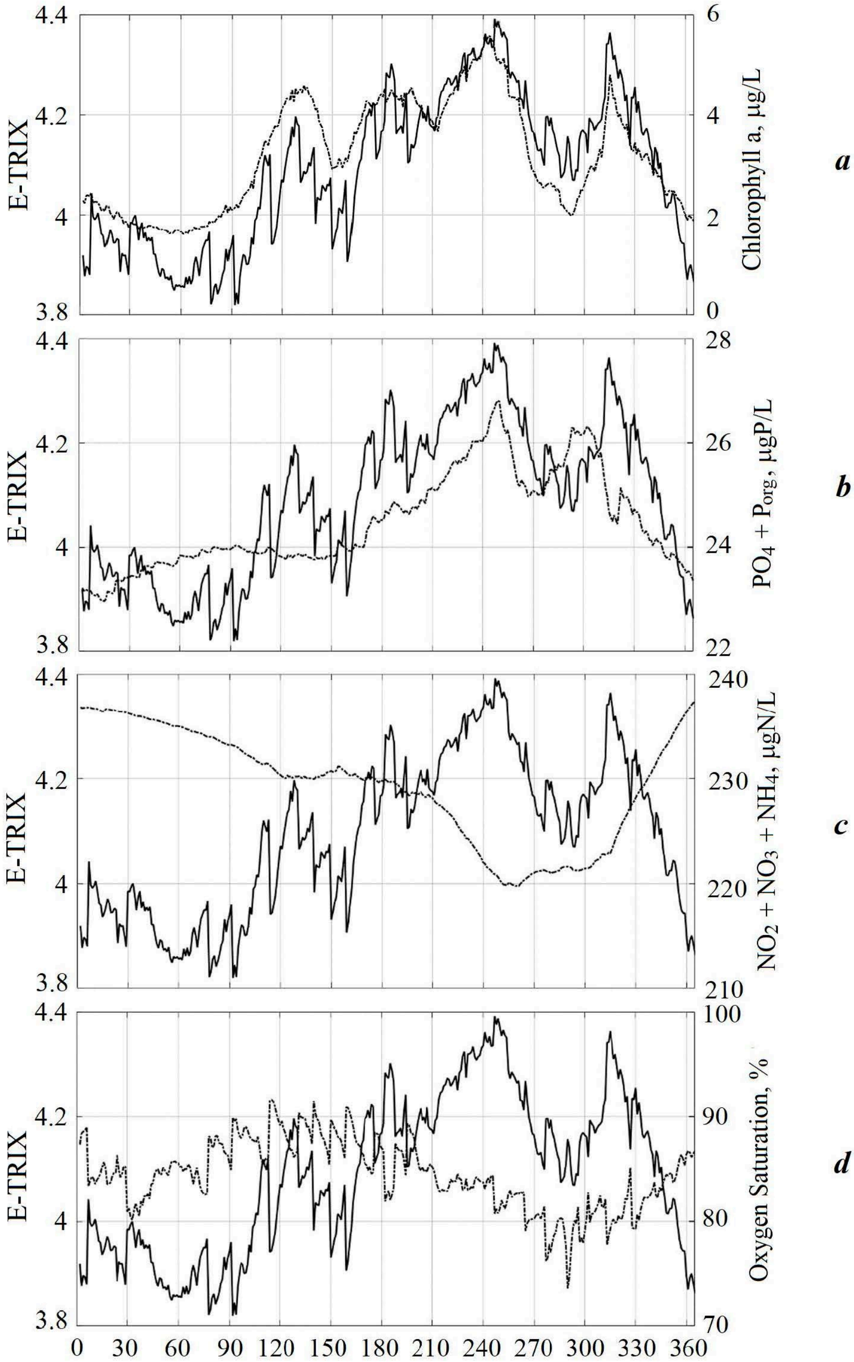
T a b l e 1 . Change in E-TRIX index depending on the season

Season	Value range	Average
Winter	3.82…4.17	3.96
Spring	3.82…4.20	3.98
Summer	3.91…4.36	4.19
Autumn	4.07…4.39	4.22

of mineral nitrogen and added silicon concentration as a multiplier under the common logarithm sign. Total nitrogen was taken as recommended in paper [16]. Silicon concentration was included in the general formula by the authors of study [15] for a more accurate assessment of water quality, since silicon is an important nutrient. Therefore, the average E-TRIX value in the above work is slightly higher (4.42) than in our results. Due to the absence of silicon in the chemical-biological module of the water quality model we used, it is not possible to numerically verify the result obtained in paper [15] for Limensky Bay.

Fig. 2 shows the annual variability of the eutrophication indicator with chlorophyll a, total phosphorus, mineral nitrogen and absolute deviation of oxygen saturation from 100%. Of note, phosphates, organic phosphorus and ammonium did not have a pronounced seasonal variability. Nitrates had maximum concentrations in the cold period from December to March and minimum concentrations in the warm period of the year, which is shown in Fig. 2, *c*. A similar result was described by the authors of paper [9]. The winter nitrate input is caused by convective mixing of waters, while the summer one is due to upwelling. Nitrites have maximum values during the increased dynamic activity of waters from December to March. In the water area of Limensky Bay, the river runoff has no direct influence on the hydrochemical structure, which was noted in [10].

The relative contribution of the components included in the E-TRIX calculation formula was calculated. The highest relative percentage contribution to the calculation formula was made by mineral nitrogen (44.48...51.88%, average 48.17%), followed by the chlorophyll a module (−38.71...−24.02%, average −31.19%), total phosphorus (26.59...30.12%, average 28.32%). The smallest contribution was made by absolute deviation of oxygen saturation from 100% (19.44...28.49%, average 24.09%).



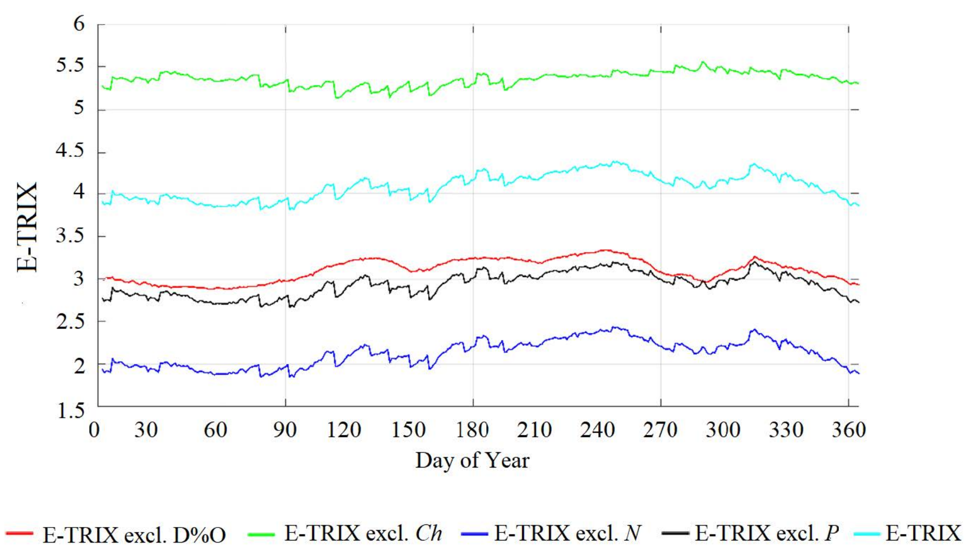
F i g . 2 . Annual variations of E-TRIX index (solid curve) and concentrations (dashed-dotted curve) of chlorophyll a (*a*), total phosphorus (*b*), mineral nitrogen (*c*), oxygen saturation (*d*) in the Limensky Bay waters

T a b l e 2 . Relative contribution (%) of the components to the E-TRIX calculation formula

E-TRIX	*D*%O	*Ch*	*N*	*P*
Max	24.27	−24.66	44.63	27.18
Min	23.86	−38.36	51.88	29.86

Table 2 shows the relative contribution in percent of the components resulting from the formula at the minimum and maximum values of the eutrophication index. At the maximum value of the index, the relative contributions of mineral nitrogen and chlorophyll a modulus are minimal, and at the minimum value of E-TRIX, the contributions of these components are maximal. A similar fact was described in paper [17] for Sevastopol and Yuzhnaya Bays.

If a hydrochemical parameter in the original formula is replaced by 1 (i. e. excluded from the formula), the trophic state index can either increase (if chlorophyll a concentration is excluded) or decrease (if total phosphorus concentration, mineral nitrogen concentration, absolute deviation of oxygen saturation from 100% are excluded) (Fig. 3). The figure shows that the E-TRIX value decreases most of all (almost twice) when mineral nitrogen is excluded, which once again shows that its contribution to the calculation formula in this region is maximum.



F i g . 3 . Contribution of individual hydrochemical characteristics to E-TRIX quantity

We calculated correlation coefficients between E-TRIX index and absolute deviation of oxygen saturation from 100%, concentration of total phosphorus, mineral nitrogen and chlorophyll a. The highest values of the correlation coefficient were obtained with the concentration of chlorophyll a (r = 0.84), mineral nitrogen (r = 0.80) and total phosphorus (r = 0.78). The correlation with absolute deviation of oxygen saturation from 100% is weak (r = 0.47).

Conclusion

Modelling of biogeochemical indicators of Limensky Bay and further calculation of the trophic state index showed that the seawater quality of the water area is good with a transitional (from oligotrophic to mesotrophic) trophic state. During the cold period from the 1^{st} to 104^{th} and from 356^{th} to 365^{th} model days, E-TRIX was below 4, which corresponds to an oligotrophic trophic state, while on other model days it was higher. The maximum value of the index was on the 247^{th} model day (4.39), and the minimum value was on the 365^{th} day (3.82).

The highest correlation of the trophic state index is observed with the concentration of chlorophyll a (r = 0.84), mineral nitrogen (r = 0.80) and total phosphorus (r = 0.78). Calculation of the relative contribution of the components included in the E-TRIX calculation formula showed that the main factor determining the level of eutrophication of Limensky Bay waters is the concentration of mineral forms of nitrogen. Thus, ecosystem modelling and further calculation of E-TRIX may help to assess the ecological status of other water bodies, where *in situ* sampling is difficult.

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Submitted 12.06.2024; accepted after review 30.07.2024;
revised 18.09.2024; published 20.12.2024

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Kira A. Slepchuk – problem statement, numerical experiments, processing and interpretation of modelling results, preparation of text and graphic materials of the article

Tatiyana V. Khmara – analysis and description of the study results, preparation of the text

All the authors have read and approved the final manuscript.