www.trjfas.org
ISSN 1303-2712
Turkish Journal of Fisheries and Aquatic Sciences 12: 485-491 (2012) DOI: 10.4194/1303-2712-v12_2_40

Comprehensive Assessment of Long-Term Changes of the Black Sea Surface Waters Quality in the Zmiinyi Island Area

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Received 15 March 2012
Accepted 20 July 2012

Abstract

On the basis of chlorophyll "a", dissolved oxygen, total nitrogen and total phosphorus concentrations measurements values of the Trophic index TRIX for 2004-2010 in the Zmiinyi Island area in the Black Sea were calculated. Inter-annual dynamics of the Trophic index TRIX is analysed. It has been shown that TRIX index in the Zmiinyi Island area varied in wide range between 3.1 and 6.9 that corresponded to the trophicity categories from low to very high. Results of TRIX seasonal dynamics analysis showed that minimal monthly average values were most often found during winter and summer period and maximal in spring and autumn and were connected with intensity of river discharge. Modelling of TRIX for 1988-2003 is presented. Comparison with the results of other Black Sea researchers has shown that sea water quality near the Zmiinyi Island is much higher than in the other coastal areas of the Black Sea. It has been proposed to use the marine research station "Zmiinyi Island" as a background one for estimation of quality of marine waters in the western part of the Black Sea.

Keywords: TRIX; Total N, total P, chlorophyll "a", dissolved oxygen.

Introduction

In the last decades one of the main problems in degradation of coastal ecosystems' health of European seas (EEA, 2001), including the Black Sea (BSC, 2008), was eutrophication caused by excessive content of nitrogen and phosphorus compounds in marine coastal waters. To decrease the nutrients flow and bring down eutrophication the European countries are spending significant efforts aimed at revealing the marine areas that are the most sensitive to nutrient pollution in accordance with the methodology proposed by the Water Framework Directive (WFD, 2000).

The general approach of the WFD to environmental state of sea waters assessment is characterized by quite complex integrated registration of biological communities' functioning and hydromorphological and physicochemical parameters. Recently simple method of coastal water quality integrated assessment using the TRIX trophic index proposed by (Vollenweider *et al.*, 1998) for some areas of Adriatic Sea is gaining ground more and more for other European seas including the Black Sea (Baytut, 2010; Dyatlov *et al.*, 2010; Medinets *et al.*, 2010; Moncheva *et al*., 2002; Zaika, 2003).

Results of recent studies of the coastal waters ecosystem adjacent to the Zmiinyi Island in the Black Sea (Medinets and Proschenko, 2008; Medinets *et al*., 2008b) have also shown that the main factor influencing the North-Western Black Sea (NWBS) water quality is eutrophication caused by nutrients input from coastal and land-based sources, reaching the Sea mainly through river inflow and atmospheric transport. The Marine Research Station "Zmiinyi Island" (MRS) of the Odessa National I.I. Mechnikov University, active since 2003, is carrying out a set of hydrological, hydrochemical, hydrobiological and other observations, that is enabling us to use the TRIX trophic index (Vollenweider *et al*., 1998), which integrally considers four parameters (Chlorophyll "a", Total Phosphorous and Nitrogen, Dissolved Oxygen) to determine sea water quality for living organisms.

The objective of our work is to study the dynamics of marine waters trophic state changes using TRIX index in the coastal waters of the Zmiinyi Island in the Black Sea, which according to the results of our investigations practically refer to open-sea water, though occasionally being influenced by the Danube, Dniester and Dnieper rivers discharge.

Materials and Methods

Material for analysis included authors' unpublished data for coastal waters of the NWBS (Figure 1) in the 1988 (28 samples), 1989 (22 samples), 1994 (25 samples) and 1995 (17 samples) and data for the Zmiinyi Island area in 2004-2010 (528 samples). Oxygen content, salinity, total nitrogen (TN), total phosphorus (TP), chlorophyll "a" and other hydrological and hydrochemical parameters every decade have been measured. Determination of chlorophyll "a" concentration was done using standard spectrometric method (Anonymous, 1980; Grasshoff *et al*., 1983). Salinity, nutrients (TN and TP) and oxygen were defined by routine methods (Grasshoff *et al*., 1983). Trophic index (TRIX) was calculated according to the equation below in order to determine the trophic level of coastal waters adjacent to the Zmiinyi Island (Vollenweider *et al*., 1998).

$$TRIX = \log([Chl\ a]*[DO_2(\%)]*[TN]*[TP]+1.5)/1.2$$

(TN, TP)

here: Chl *a* : Chlorophyll *a* concentration, (μg L^{-1})
DO_2(%): absolute deviation of measured dissolved oxygen content in % from 100% saturation;
TN: Concentration of total N, (μg L^{-1}).
TP: Concentration of total P (μg L^{-1}).

Trophic level was assessed from the TRIX values (Vollenweider *et al*., 1998), which characterized the trophicity of marine environment: low trophic level (<4), medium (4-5), high - (5-6) and very high (>6), which corresponds to the categories of water trophicity: oligotrophic, mesotrophic, eutrophic and hypertrophic.

Data on dynamics of the calculated TRIX index in the Zmiinyi Island area are presented for the years 2004-2010, changes of chlorophyll "a" concentrations and the modelled TRIX index in the NWBS area are analysed for the period 1988-2010.

Results and Discussion

Source data for the TRIX index assessment in the Zmiinyi Island coastal waters were the results of regular observations of salinity, content of DO_2(%), TN, TP and chlorophyll "a", the temporal distribution of which in the period 2004-2010 are presented on Figures 2-6 respectively.

Salinity level in the coastal waters adjacent to the Zmiinyi Island (Figure 2) in 2004-2010 varied from 9.18‰ (20.07.2005) to 19.19‰ (15.10.2005) with average value 15.21±0.11‰ and very typical seasonal distribution with minimal values in spring that were connected with the Danube River seasonal floods and maximal in winter, when processes of water exchanges with open part of the sea were very active. At that we should stress that significant negative correlation interrelationships have been only pointed out between salinity and TN content (r=-0.45; P=0.01), which means increase of TN concentration with decrease of salinity of coastal waters. So, we may conclude that salinity is an indicator of desalinated and enriched with nitrogen river waters inflow into the Zmiinyi Island area.

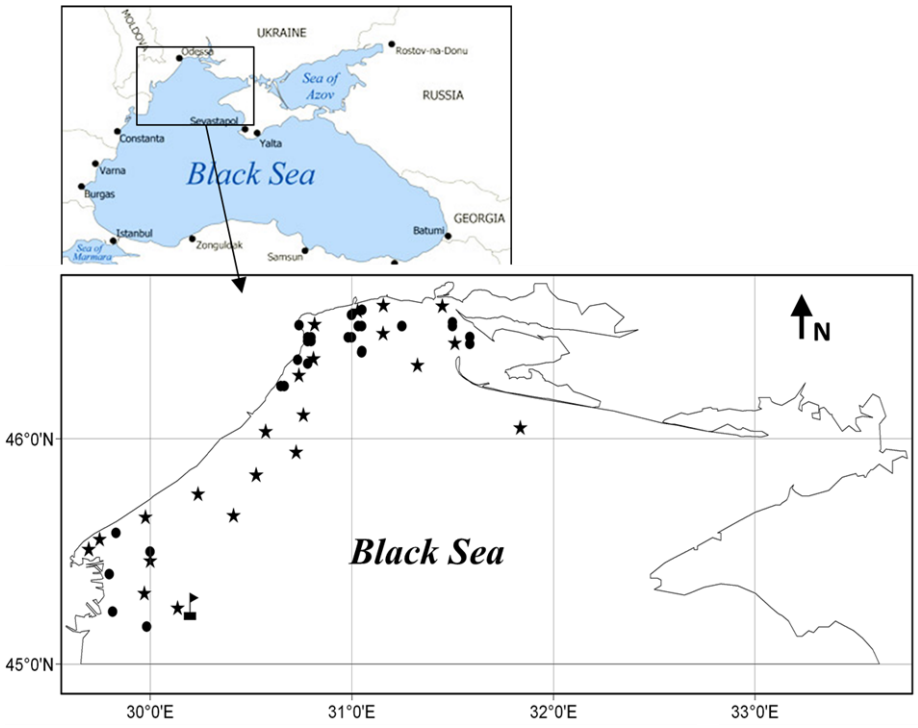

Figure 1. Map of authors observations in 1988-2010. ★- 1988-1989, ● ★- 1994-1995, ⚑- Zmiinyi Island (2004-2010)

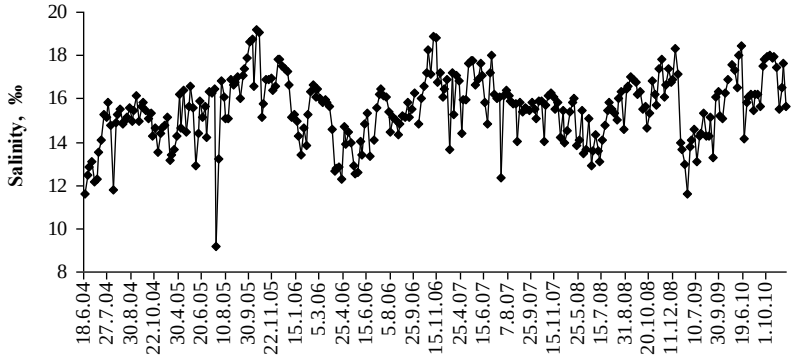

Figure 2. Temporal distribution of salinity (‰) in the coastal surface waters of the Zmiinyi Island.

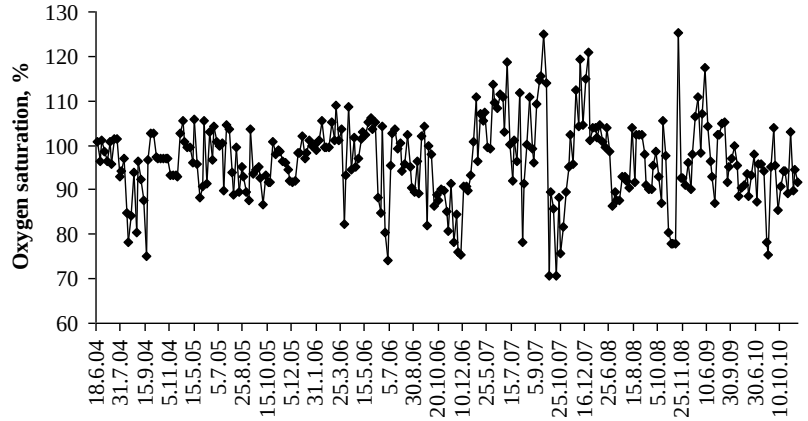

Figure 3. Temporal distribution of relative dissolved oxygen (%) in the coastal surface waters of the Zmiinyi Island.

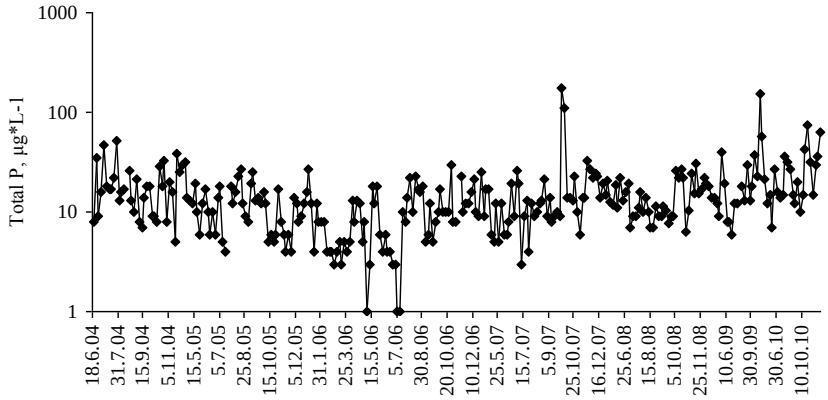

Figure 4. Temporal distribution of total phosphorus concentrations in the coastal surface waters of the Zmiinyi Island.

Relative oxygen content DO_2 (%) in the Zmiinyi Island coastal waters (Figure 3) in 2004-2010 varied from 70.8% (15.10.07) to 125.34% (15.11.08). Usually minimal values of DO_2(%) were observed in late summer – autumn, maximal – during winter – spring period of year.

TP content in the Zmiinyi Island surface waters (Figure 4) varied from 1.0 (05.05.06 and 15.07.06) to 176 (01.10.07) µg P $L^{-1}$with average value 16.0±4.0 µg P L^{-1}.At that, maximal values have been registered mainly in autumn (October 2007, 2009 and 2010) and minimal values were observed in summer.

TN content (Figure 5) usually varied from 7.2 (15.12.05) to anomaly high values 4300-4900 µg N L^{-1}, which were registered in spring 2006 during extreme flood of the Danube River (Michailov *et al*.,

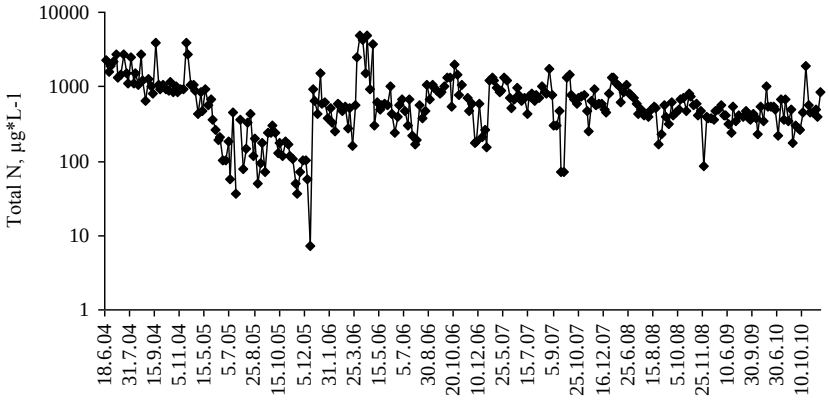

Figure 5. Temporal distribution of total nitrogen concentrations in the coastal surface waters of the Zmiinyi Island.

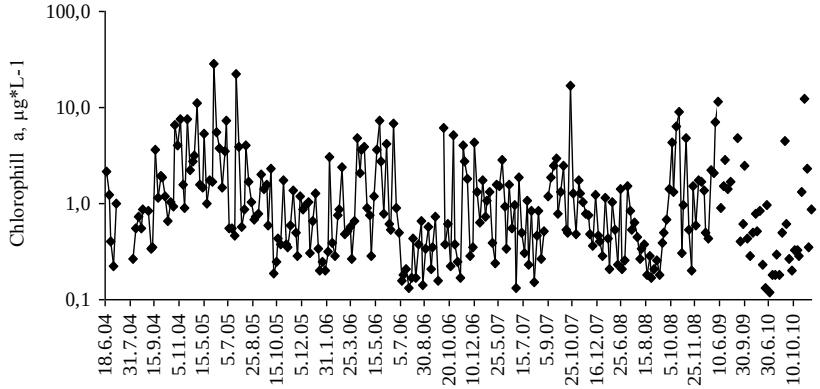

Figure 6. Temporal distribution of chlorophyll "a" concentrations in the coastal surface waters of the Zmiinyi Island.

2008). TN concentration average value was 739±31 µg N L^{-1}. Correlation coefficient between concentration of TN and salinity makes r=-0.45 (P=0.01), which indicates increase of TN concentration in the periods when salinity of coastal waters go down, i.e. when desalinated water from the Danube enter the island area.

Chlorophyll "a" content in 2004-2010 (Figure 6) varied from 0.12-0.13 µg L^{-1}(30.06.19 and 25.07.06) to 28.03 µg L^{-1} (05.06.05). Maximal values have been most often registered in spring and autumn, though in 2005 the maximum was registered at the beginning of summer period. Minimal concentrations of chlorophyll "a" have been characteristic of August and winter period when decline is observed in phytoplankton development.

TRIX index values for the Zmiinyi Island coastal waters (Figure 7) varied in wide range between 3.0 and 6.9 that according to the classification of Vollenweider *et al*. (1998) included trophicity categories from low (oligotrophic waters) to very high (hypertrophic waters). The most parts of water samples correspond to the category of "mesotrophic waters" (43%) and of "eutrophic waters" (39%). 6% of water samples referred to the category of "oligotrophic waters" and 12% of hypertrophic waters. Results of TRIX seasonal dynamics analysis of monthly average data (Figure 8) has shown that minimal values (TRIX<4) were most often found during winter and summer period and maximal (TRIX=6-7) in spring and autumn when river discharge increased (Michailov *et al*., 2008; Medinets and Proschenko, 2008) and organic matter accumulated in the ecosystem (Kovalova *et al*., 2010). The similar peculiarity in seasonal variations of trophicity index with decrease of its values in summer period has been pointed out for the coastal waters of the Adriatic Sea (Vollenveider *et al*., 1998) and near Bulgarian coast (Moncheva *et al*., 2000). However, in Samsun Bay (southern Black Sea) minimal TRIX (TN, PO_4) values less as 6.0) were registered in April 2003 (Baytut *et al*., 2010).

Correlation analysis has shown that coefficients of linear correlation between TRIX index and TN, TP, DO_2(%) data made respectively 0.43; 0.43 and 0.11. The strongest correlation rate (Figure 9) has been observed between TRIX and Chlorophyll "a", (r=0.98; P=0.01), out of which it follows that with increase of chlorophyll "a" concentration trophic index grows practically proportionally to the natural

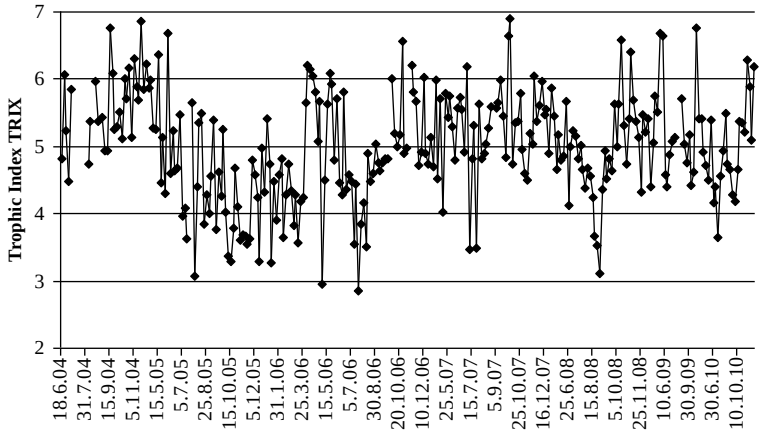

Figure 7. Dynamics of trophic index (TRIX) in the surface Black Sea waters at the coast of the Zmiinyi Island for 2004-2010.

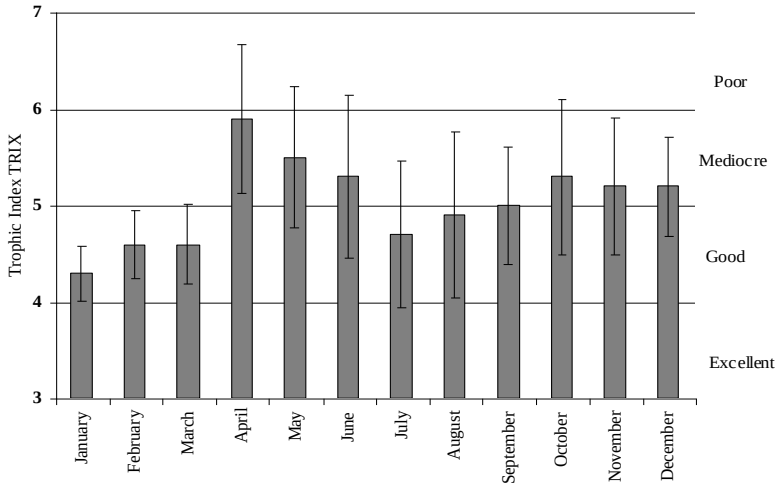

Figure 8. Seasonal dynamics of ındex TRIX in the surface Black Sea waters at the coast of the Zmiinyi Island in 2004-2010.

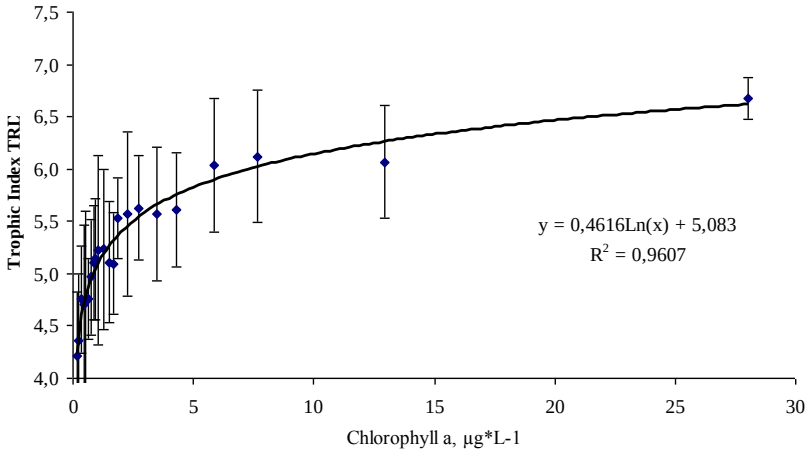

Figure 9. Dependence of trophic index (TRIX) changes on concentrations of Chlorophyll "a" in the coastal surface waters of the Zmiinyi Island.

logarithm of chlorophyll "a" content. Thus, we may conclude that the main influence on the quality of marine waters in the Zmiinyi Island area is produced by natural processes of photosynthesis whose indicator is chlorophyll "a", as well as by pollution with nitrogen compounds entering with the Danube inflow.

This dependence between chlorophyll "a"

content and the TRIX value (Figure 9) enables us to use it for estimation of the TRIX values directly from chlorophyll "a" concentrations only - in case there are no data on oxygen, TN and TP content. Figure 8 shows the many years' dynamics of chlorophyll "a" in the coastal waters of the NWBS and the mathematically modelled values of the trophic index TRIX for 1988-2010. Comparison of modelled TRIX values (Figure 10) with the actual data for the period 2004-2010 (Figure 7) has shown high linear correlation (r=0.65; P=0.01).

Analysis of the Black Sea coastal waters existing trophicity data during 1988-2010 (Table 1) shows that the average value of TRIX in 1988-1989 (6.1) corresponded to the category of hypertrophic sea waters. In 1994-1995 the average trophic index dropped down to 5.9 and corresponded to the category of eutrophic sea waters. In the 2004-2010 average TRIX values were gradually going down and reached the minimums in 2005, 2006 and 2008, which corresponded to the category of mesotrophic sea waters.

Comparison of the data collected by the authors (Table 1) with the results of other Black Sea researchers shows that in Varna Bay the average value of TRIX index for 1994-2000 was 5.3±1.16 (Moncheva *et al*., 2002); in the coastal area near the Danube River (Dyatlov *et al*., 2010) the TRIX average value in spring 2008 was 5.8±1.0 and in autumn it reached 6.9±1.1; in the Samsun Bay (Baytut *et al*., 2010) the TRIX index values varied during a year from 6.9 to 7.7. At that, average TRIX value for 2004-2010 near the Zmiinyi Island was 5.0±0.22, varying from 4.6±0.9 in 2005 to 5.3±0.7 in 2007. In total the TRIX value in western part of the Black Sea is between eutrophic and hypertrophic level.

Thus, the current sea water trophicity of the Zmiinyi Island area is minimal among the studied Black Sea areas, and the Zmiinyi Island area could be used as a reference for the open waters of the western part of the Black Sea.

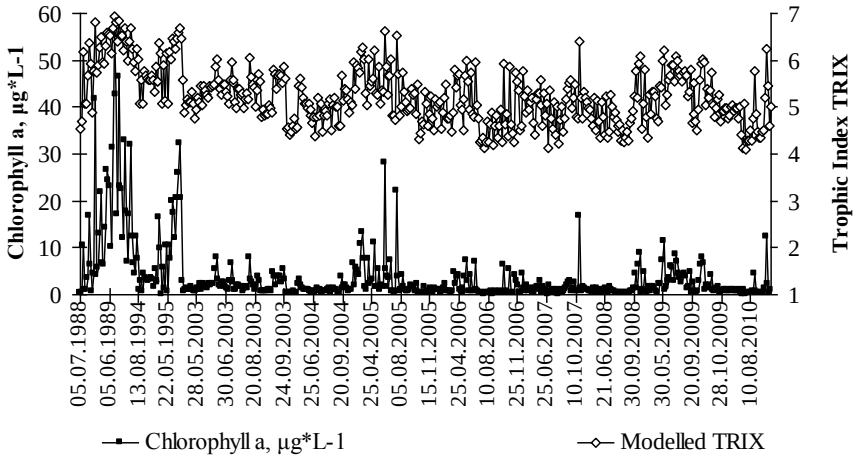

Figure 10. Temporal distribution of measured chlorophyll "a" concentrations and modelled trophic index TRIX in the NWBS coastal surface waters.

Table 1. TRIX Index data in the coastal waters of the Black Sea and estimation of average trophic category

Year	Source (TRIX method)	The Black Sea Area	N	Average	Std	Min	Max	Trophic category
1988-1989	Authors TN, TP)	NWBS (Figure 1)	32	6.1	0.66	4.5	6.9	Hypertrophic
1994-1995	Authors (TN, TP)	NWBS (Figure 1)	42	5.9	0.47	5.1	6.7	Eutrophic
1994-2000	Moncheva, 2002 (min N, min P)	Varna Bay	N/A	5.3	1.16	2.85	7.86	Eutrophic
2002-2003	Baytut, 2010 (TN, PO_4)	Samsun Bay	60	6.9-7.7	>6	<6	7.7	Hypertrophic
2003	Authors (TN, TP)	Zmiinyi island	77	5.2	0.38	4.4	5.04	Eutrophic
2004	Authors (TN, TP)	Zmiinyi island	88	5.2	0.45	4.4	6.3	Eutrophic
2005	Authors (TN, TP)	Zmiinyi island	104	4.6	0.9	3.1	6.7	Mesotrophic
2006	Authors (TN, TP)	Zmiinyi island	136	4.8	0.8	3.0	6.6	Mesotrophic
2007	Authors (TN, TP)	Zmiinyi island	96	5.3	0.7	3.5	6.9	Eutrophic
2008	Authors (TN, TP)	Zmiinyi island	88	4.9	0.7	3.1	6.6	Mesotrophic
2008	Dyatlov, 2010 (TN, TP)	Near Danube Delta	N/A	6.43	-	4.4	8.12	Hypertrophic
2009	Authors (TN, TP)	Zmiinyi island	44	5.2	0.7	4.4	6.8	Eutrophic
2010	Authors (TN, TP)	Zmiinyi island	36	5.0	0.7	3.7	6.3	Mesotrophic - eutrophic

Conclusions

Comparison of the results of our TRIX estimation for the Zmiinyi Island coastal waters (average value 5.0±0.22 for 2004-2010) with results of other scientists for other areas of the Black Sea coastal waters convincingly shows that quality of coastal waters adjacent to the Zmiinyi Island is higher than in other investigated regions of the Black Sea and can be used as background level for the western part of the Black Sea. In this connection the MRS "Zmiinyi Island" can be proposed as a background marine station for the western part of the Black Sea.

Method of coastal waters quality estimation using TRIX index and respective observations of chlorophyll 'a', dissolved oxygen, nitrogen and phosphorus compounds are strongly recommended for including into national and international Monitoring programs.

The level of TRIX index in coastal water of the Zmiinyi Island area depends mainly on the processes of organic matter natural photosynthesis and partly on influence of pollution with nutrients from the Danube River discharge.

Acknowledgements

The studies had been carried out in framework of research activities funded by the Ministry of Education and Science of Ukraine (2003-2010) and as contribution to the European FP7 project (2009-2010) No. 226740 EnviroGrids (Building Capacity for a Black Sea Catchment Observation and Assessment System supporting Sustainable Development). We also would like to thank the staff of the Regional Centre for Integrated Environmental Monitoring and Ecological Studies of the Odessa National I.I. Mechnikov University for field sampling and observations at the MRS "Zmiinyi Island", as well as the chemists Irina Gruzova and Anatoliy Sorokoumov for the chemical analyses of N and P compounds.

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