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Biochemical quality elements for the assessment of eutrophication in Mersin & Iskenderun Bays (northeastern Mediterranean)

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Eutrophication-related physical and biochemical parameters were measured in shallow coastal waters of both bays located in northeastern Mediterranean during summer and winter for the period 2014-2018 to assess present trophic status of the coastal areas receiving substantial amount of nutrients and organic matter from the local perennial rivers and direct discharges of domestic wastewaters. For this goal, HELCOM Eutrophication Assessment Tool (HEAT 3.0) widely used in the enclosed Baltic Sea has been adapted to the Çukurova basin shelf waters. This tool is based on the determination of Eutrophication Ratios (ERs) of state (nutrients), direct (biomass; chlorophyll-*a*, phytoplankton composition; Diatom/Dinoflagellate ratio, Secchi Disk Depth) and indirect indicators (deep water dissolved oxygen saturation level) measured at selected sites of the two bays, relative to an average "Eutrophication Quality Target" for each indicator by using data sets obtained from the least contaminated offshore ones. The averages of ER values for each parameter were determined to obtain a final ER level from the state, direct and indirect indicators for each station (site) of the visited regions. The present results clearly show that 8 stations (out of 14 stations) in the inner bay waters of Iskenderun and Mersin have been affected from the eutrophication displaying ER values greater than 1.0 while offshore waters display oligotrophic properties (ER<1.0). This study is an initial attempt to use an integrated multi-metric assessment of trophic status in the NE Mediterranean including both direct and indirect indicators of eutrophication.

Keywords: Trophic status assessment, eutrophication, Mersin Bay, Iskenderun Bay, northeastern Mediterranean

Introduction

Offshore waters of the northeastern Mediterranean (Figure 1) are known as one of the highly oligotrophic basins with limited nutrient supply to its surface waters from internal and external sources (UNEP, 1989; Yılmaz & Tuğrul, 1998; Kress & Herut, 2001; Krom *et al.*, 2004). However, its coastal ecosystems composed mainly of shallower Mersin and Iskenderun inner bays (Figure 1) are highly influenced from nutrient and organic matter inputs of terrestrial origin carried by local perennial rivers. Moreover, pollutants of agricultural and industrial origin as well as municipal domestic waste water discharges add more to development of eutrophic conditions in the shallower inner bays (Dogan-Saglamtimur & Tugrul, 2004; Tugrul *et al.*, 2009; 2011; 2016; 2018; MoEU-DGEIAPI & TUBITAK-MRC, 2015; 2016; 2017). Eutrophication-related physical and biochemical parameters were measured in Mersin and Iskenderun bays in the summer and winter periods of 2014-2018 to assess present trophic status of the coastal waters fed by terrestrial inputs during the year. HELCOM Eutrophication Assessment Tool (HEAT 3.0) (Andersen *et al.*, 2015) developed for the highly eutrophic Baltic Sea has been adapted to the Çukurova shelf basin waters using state (nutrients), direct (biomass;

chlorophyll-*a*, phytoplankton composition; Diatom/Dinoflagellate ratio, Secchi Disk Depth) and indirect indicators (deep water dissolved oxygen saturation level) of eutrophication.

Material and Methods

Field surveys in the Mersin and Iskenderun Bay coastal and offshore regions (Figure 1) were conducted using R/V BILIM-2 of METU-IMS. At the selected stations, physical measurements (*in situ* temperature, salinity, density, fluorescence, turbidity) were carried out by a SEABIRD model CTD probe coupled to a 12-PVC Niskin Bottles Rosette System by which seawater samples were obtained from selected depths by remote-control. The Secchi Disk Depth (SDD), a rough estimation of water transparency, was measured at each station during day time (UNEP/MAP, 2005). Dissolved oxygen measurements were carried out by the automated Winkler titration method (Grasshoff *et al.*, 1983; UNEP/MAP, 2005). Dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate, silicate) were determined by the conventional automated colorimetric method using a Bran+Luebbe Model four-channel Autoanalyzer (Grasshoff *et al.*, 1983). Total phosphorus measurements were carried out by the colorimetric method at 880 nm wavelength (Strickland & Parsons, 1972; Grasshoff *et al.*, 1983) after persulfate digestion of samples in pre-cleaned glass bottles under high pressure and temperature (2 atm, 100 ˚C) (Menzel & Corwin, 1965). Chlorophyll-*a* (Chl-*a*) measurements were performed by the conventional spectrofluorometric method after digestion of filter samples by 90% acetone solution (vol/vol) (Strickland and Parsons, 1972; UNEP/MAP, 2005) using a HITACHI model F-2500 Fluorescence Spectrophotometer. Diatom/Dinoflagellate ratio was calculated following qualitative and quantitative inspection of glutaraldehyde fixed phytoplankton samples under a phase-contrast inverted microscope.

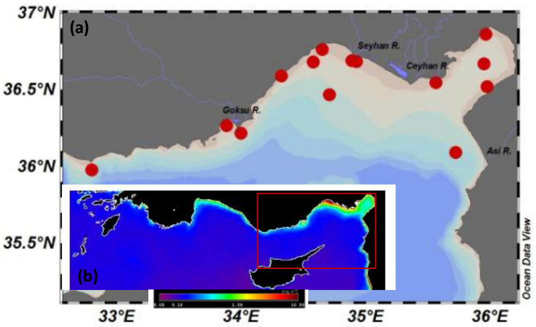

Figure 1. (a) Sampling locations and (b) average surface chlorophyll-*a* (mg/m^3) distribution obtained by Satellite MODIS Aqua in the Cilician basin of the NE Mediterranean in 2009.

Eutrophication status of Mersin and Iskenderun inner bays and offshore regions was determined by the third version of the HELCOM Eutrophication Assessment Tool (HEAT 3.0) (Andersen *et al.*, 2015) in which Eutrophication Ratios (ERs) were calculated using Eutrophication Quality Target (ET) values defined in the studied region of NE Mediterranean. The “good/moderate” boundaries (unaffected/affected by eutrophication) for eutrophication indicators defined for the NE Mediterranean were obtained from the results of Tugrul *et al.* (2018).

Results

Surface layer salinity in the Mersin and Iskenderun Bays varied regionally and seasonally between 37.3 and 39.8 with lower values in the river-fed coastal sites in wet winter periods. Surface salinity values were higher in the offshore during summer due to limited effect of freshwater inflows and increasing evaporation (Table 1). Similar spatio-temporal variations were observed in the SDD measurements, ranging <0.5 m in the nearshore zone to 39 m in the offshore waters in summer (Figure 2). Dissolved inorganic nutrient concentrations measured in surface waters of the visited sites displayed remarkable spatial and temporal variations (Table 1; Figure 2). Peak values were observed in the coastal waters fed by riverine and wastewater inputs. Summer nutrient concentrations were consistently lower than the wet winter values due to apparent decreases in river inflows and atmospheric wet deposition during dry summer period. NO_x (referred to NO_3+NO_2) concentrations varied regionally from 0.04-4.35 µM in summer to 0.07-24.50 µM in wet winter; higher NO_x values were observed in less saline coastal waters (S<39.0). Dissolved inorganic nitrogen ($DIN=NO_3+NO_2+NH_4$) concentrations ranged between 0.13 to 46.7 μM in surface waters of the two bays, with peak values in the polluted inner bay waters and river-fed less saline shallow zones. Surface PO_4 concentrations displayed similar spatial pattern in the NE Mediterranean shelf waters; lower values in the offshore waters (0.02-0.04 μM) increasing to 0.29 μM in the less saline coastal waters.

Table 1. The winter and summer results of eutrophication-related parameters measured in the Mersin and Iskenderun Bays during the 2014-2018 period.

Winter	Salinity	TP (μM)	PO_4 (μM)	NO_x (μM)	DIN (μM)	Si (μM)	DWDO (% sat.)	Chl-*a* (μg/L)	SDD (m)	Diatom/Dinoflagellate
Mean	38.96	0.19	0.05	1.54	1.87	2.29	99.06	0.42	11.21	52.8
Std. Dev.	0.40	0.10	0.03	3.21	3.33	3.08	2.69	0.38	6.28	55.1
Min.	37.27	0.08	0.02	0.07	0.23	0.62	87.39	0.09	0.10	0.3
Max.	39.43	0.85	0.29	24.50	25.24	24.07	106.22	1.70	28.00	233.1
N	113	113	113	113	113	113	113	113	112	36
Summer	**Salinity**	**TP (μM)**	**PO_4 (μM)**	**NO_x (μM)**	**DIN (μM)**	**Si (μM)**	**DWDO (% sat.)**	**Chl-*a* (μg/L)**	**SDD (m)**	**Diatom/Dinoflagellate**
Mean	39.33	0.19	0.04	0.41	1.10	1.78	98.30	0.33	12.80	15.4
Std. Dev.	0.28	0.08	0.03	0.61	3.78	1.40	7.00	0.48	8.09	20.3
Min.	38.31	0.06	0.02	0.04	0.13	0.50	74.96	0.02	1.00	0.5
Max.	39.78	0.65	0.21	4.35	46.72	7.98	113.27	4.65	39.00	96.0
N	158	156	158	158	158	158	158	157	155	47

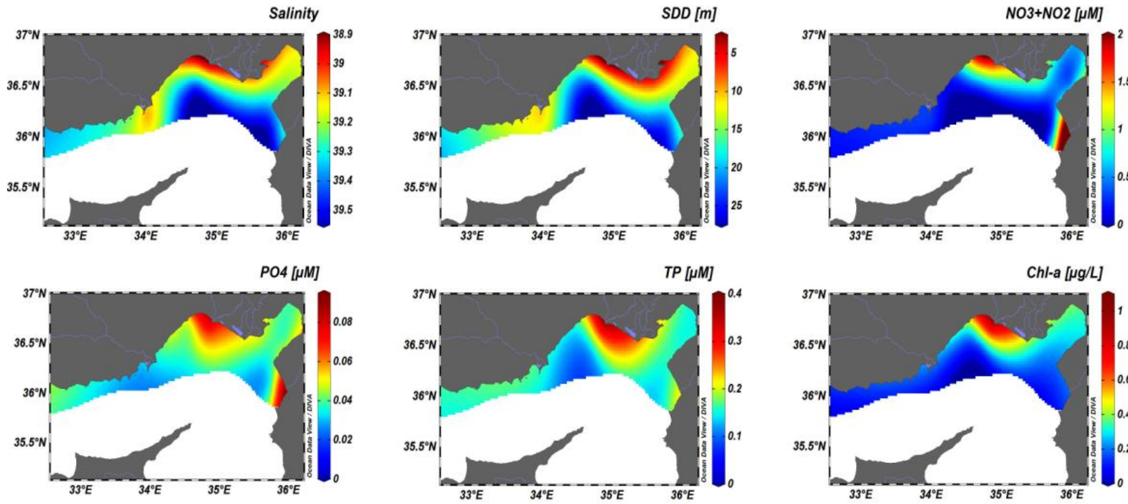

Figure 2. Surface layer (0-10 m average) distributions of summer-winter average values of eutrophication indicator parameters in the Cilician Shelf including two bays for the 2014-2018 period.

Surface Si concentrations were markedly low in the offshore (0.50-1.0 μM) reaching peak values (8-24 μM) in the river-fed delta waters. Expectedly, dissolved inorganic nutrients and TP values measured within the study period displayed similar spatio-temporal variations; increasing apparently in wet winter period (Table 1). Nutrient inputs from external sources enhanced algal biomass (in terms of Chl-*a*) in the coastal waters. Chl-*a* values varied from 1.0-4.65 μg/L in less saline coastal waters to 0.02-0.10 μg/L in the offshore waters of the two bays. No oxygen deficiency (suboxic condition) was observed in the bottom waters of Mersin and Iskenderun Bays (Table 1; Figure 2). Diatom/Dinoflagellate ratios based on individual cell counts varied between a summer minimum of 3.3 and a winter maximum of 116.6 in the region indicating direct role of changes in nutrient concentrations relative to each other as well as temperature regulating spatial and temporal heterogeneity in phytoplankton group assemblages in the area (Figure 3).

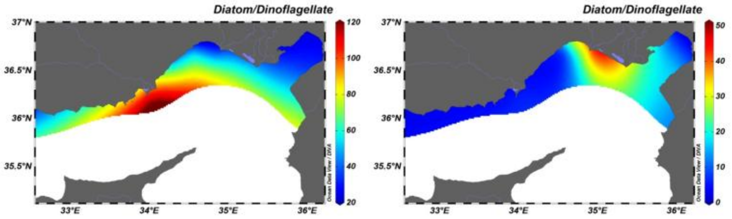

Figure 3. Winter (left) and summer (right) average values of Diatom/Dinoflagellate ratios at surface waters of both bays for the 2014-2018 period.

Discussion

Surface layer concentrations of eutrophication-related biochemical parameters displayed apparent decreases from inner bay/river delta to offshore waters (Figure 2). The present results are in agreement with the recent studies conducted in these bays and wide shelf waters of NE Mediterranean (Dogan-Saglamtimur & Tugrul, 2004; Tugrul *et al.*, 2009; 2011; 2016; 2018; MoEU-DGEIAPI & TUBITAK-MRC, 2015; 2016; 2017). Impacts of terrestrial inputs on nutrient and Chl-*a* concentrations were markedly high in the less saline coastal zone and inner bay waters of Mersin and Iskenderun Bays, leading to apparent decrease in SDD values.

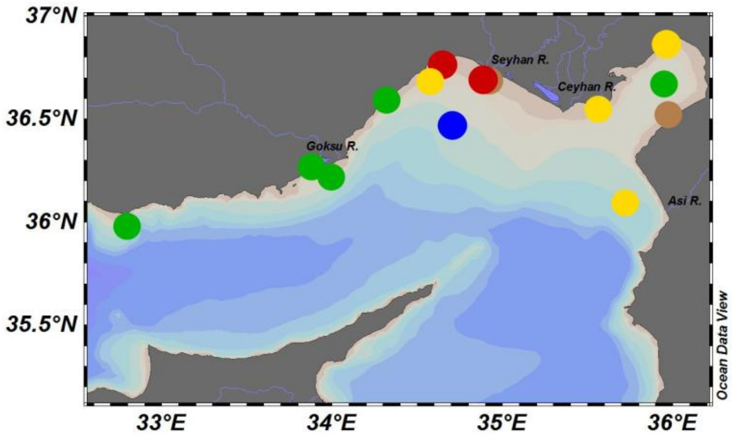

Figure 4. Present eutrophication status of the Cilician shelf including Mersin and Iskenderun Bays, NE Mediterranean, assessed by the HEAT 3.0 (color codes; Blue: High, Green: Good (unaffected by eutrophication), Yellow: Moderate, Brown: Poor, Red: Bad (affected by eutrophication).

These results show the development of eutrophication in the coastal and inner bay waters of the studied sites. For this goal, HELCOM Eutrophication Assessment Tool (HEAT 3.0) was used to assess the current trophic status of the studied regions. The averages of calculated ER values for each parameter are depicted in Figure 4, exhibiting the "bad" trophic conditions developed in the inner bay waters of Mersin Bay and coastal waters polluted by Asi River inflow enhancing markedly in winter period.

In conclusion, the present classification results clearly show that 8 stations (out of 14 stations) in the inner bay waters of Iskenderun and Mersin have been affected by eutrophication (both natural and human-induced nutrient inputs) having ER greater than 1.0 while offshore waters display oligotrophic properties (ER<1.0) (Figure 4). This study is an initial attempt to use an integrated multi-metric assessment of trophic status in the NE Mediterranean including both direct and indirect indicators of eutrophication.

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System-scale Environmental Research Approach to Varna Lake, Varna Bay and the Coastal Area of the Black Sea in front of Cape Galata

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One certain amount of water resources can support the social, economic, ecological, and environmental system in a certain region. Conservation and management of water resources generally balance the benefits of preservation and economic exploitation of resources. Governing an environmental medium, such as water may also conserve the recreational value of water bodies. The challenges related to natural system Varna Lake, Varna Bay, and coastal area in front of Cape Galata imply to be taken into consideration the interaction of humans and the natural environment toward the purpose of reducing the impacts of human activity, both on the natural environment and humans itself. A study on water environment in the 5-mile Black Sea area on the Bulgarian coast along Galata transect, in the Varna Bay and in the Varna Lake was performed in 2017, framing the challenge under a system-scale approach. Better environmental protection is necessary to achieve the most sustainable development of the natural system in the future. Improvements must be teamed with realising the unexplored potential that lies in better water management, along with changes in policy and production techniques.

Keywords: water environment, Black Sea, Cape Galata, Varna Bay, Varna Lake, Bulgaria

Introduction

Many sciences use a range of spatial, temporal, and thematic scales in their analysis (Perveen, 2012). Real risk on the ground is the end result of many factors in a dynamic complex system (Beck, 2015). Examples of the emergence of new spatial and temporal scales have been demonstrated in surface hydrology (Gentine *et al.*, 2012.). To improve water management and measure the achievement of internationally agreed goals on water, countries and organizations need access to relevant information and these data can be integrated.

Recent water characteristics variability in the Varna region of the Black Sea was reflected on some publications (Dineva, 2013a; Dineva, 2013b; Dineva, 2014; and Dineva, 2015a).

In the context of water-related global challenges and as an important aspect of ecology, a study on the water environment in the 5-mile Black Sea area on the Bulgarian coast along Galata transect, in the Varna Bay, and in the Varna Lake was performed in 2017, framing the challenge under a system-scale approach.

The purpose of this study will first be to raise awareness on the current state of the natural water system at national and transnational levels and a need for adequate diplomatic solutions to stimulate cooperation around the way the resource is managed to protect both the natural water environment and human health.

From an economic perspective, such water-related research may be understood as concerned with the present and future benefit by the natural water system.

Material and Methods

Study area maps (Figure 1) display a location of the stations where water environment research in the 5-mile Black Sea area on the Bulgarian coast along Galata transect, in the Varna Bay, and in the connected by two canals nearby area of Varna Lake was accomplished twice a year in 2017.

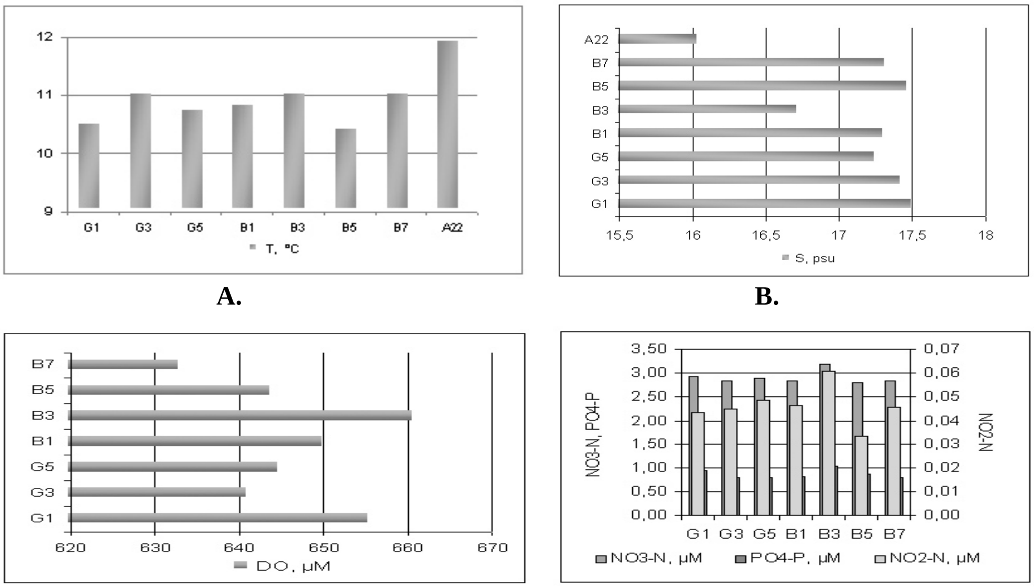
A. B.

Figure 1. Maps of sampling stations: (A) Varna Bay and the connected by two canals nearby area of the Varna Lake. (B) Galata transect of the Black Sea.

In April and September, surface waters were investigated in the 5-mile zone (Station (St.) G1, Station G3, and Station G5) in front of Cape Galata (Figure 1 B), in the Varna Bay (Station B1, Station B3, Station B5, and Station B7), and in the Varna Lake (Station A22). Measurements of temperature, salinity, dissolved oxygen, and oxygen saturation were performed by Multi-meter (Oakton, 2010). Processing of water samples for nitrite nitrogen, nitrate nitrogen, phosphate phosphorus, and chemical oxygen demand (COD)-Mn was done by unified methods for marine waters. Nutrient concentrations were ascertained by HITACHI UV / Vis Spectrophotometer.

Results

The results here presented are original and have allowed an integrated water environment analysis of the investigated natural system.

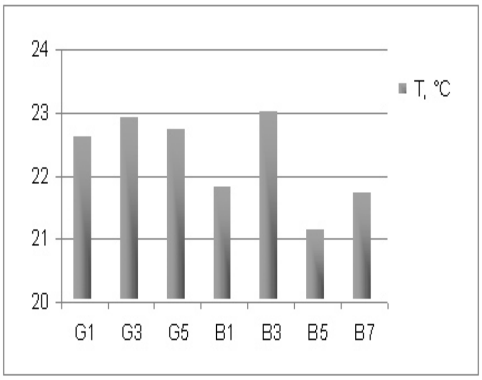


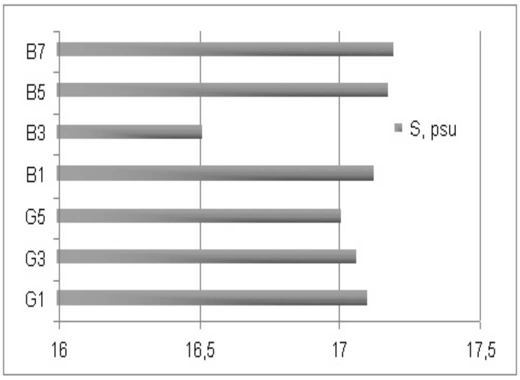
A. B.

C. D.

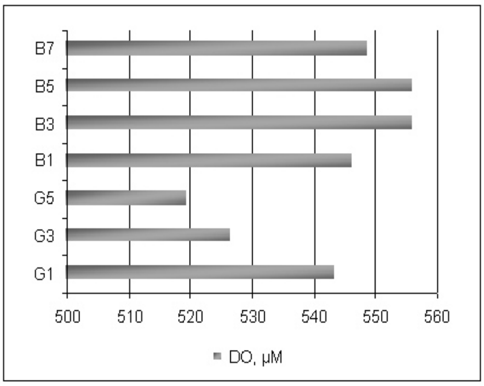
Figure 2. Temperature (A), salinity (B), dissolved oxygen (C), and nitrite nitrogen, nitrate nitrogen, phosphate phosphorus (D) on 1, 3, and 5 miles offshore of Cape Galata, in the Varna Bay, and in the nearby area of the Varna Lake in April 2017.

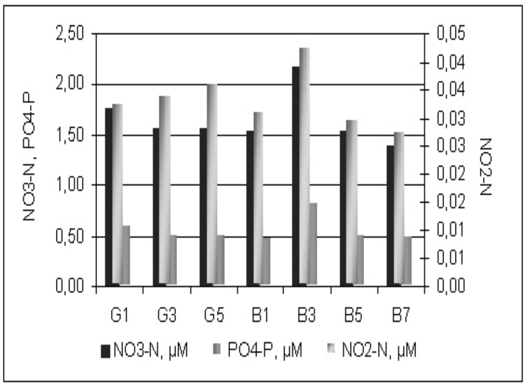
Temperature and salinity are important for the changes in the regional environmental characteristics, especially sea surface temperature (SST) and sea surface salinity (SSS) in terms of their relationship to climate change. Data distribution in Fig. 2 A. indicates SST range of 10.4°C (St. B5) - 11.9 °C (St. A22) in April 2017. SSS is also a factor in water mass formation and SSS variability can affect the intensity of the thermohaline circulation. SSS (Fig. 2 B.) has varied from 16.04 psu (St. A22) to 17.51 psu (St. G1) in the investigated water system. Overall, near-normal dissolved oxygen (Fig. 2 C.) and oxygen saturation (100.28 % - 104.23 %) were ascertained. Nutrient concentrations (Fig. 2 D.) have reached up to 0.06 µM nitrite nitrogen, 3.18µM nitrate nitrogen, and 1.05 µM phosphate phosphorus. Chemical oxygen demand (COD)-Mn was at an average of 1.36 mg.l^{-1}.





A. **B.**





C. **D.**

Figure 3. Temperature (A), salinity (B), DO (C), and nitrite nitrogen, nitrate nitrogen, phosphate phosphorus (D) on 1, 3, and 5 miles offshore of Cape Galata, in the Varna Bay, and in the nearby area of the Varna Lake in September 2017.

SST has varied from 21.1°C (St. B5) to 23.0 °C (St. B3) in September (Fig. 3 A.). SSS (Fig. 3 B.) was lowest at St. B3 - 16.52 psu, while it was above 17 psu and similar in the other areas. Oxygen super-saturation of surface water has occurred throughout in the investigated water system – up to 109.30 %. Nutrients (Fig. 3 D.) were at a highest level at St. B3: 0.04 µM nitrite nitrogen, 2.18 µM nitrate nitrogen, and 0.80 µM phosphate phosphorus. Organic matter (OM) exceeded the concentrations in April, with COD-Mn above 1.7 mg.l^{-1}.

Discussion

The observations in the 5-mile Black Sea area on the Bulgarian coast along Galata transect, in the Varna Bay, and in the Varna Lake in 2017 were accomplished by analyzing also other related previous data sources (Dineva, 2007; Dineva, 2014; Dineva, 2017).

Water temperature varies seasonally with air temperature. SST analysis reveals a decrease in 2017 compared to 2014-2016 (Dineva, 2014; Dineva, 2017) but 2017 SST was generally above the 1990s (Dineva, 2007) in the investigated natural water system.

The low salinity of the surface waters is maintained by fresh water inputs into the Black Sea. The Black Sea has a positive water balance, in which the inputs from freshwater sources exceed losses by evaporation (Bolshakov, 1970; Adrianova & Ovchinnikov, 1991; Rjabinin *et al.*, 1991).

The level of salinity in aquatic systems is important to aquatic plants and animals as species can survive only within certain salinity ranges. Although some species are well-adapted to surviving in saline environments, growth and reproduction of many species can be hindered by increases in salinity.

SSS in the water system in 2017 was above both 1990s (Dineva, 2007) and 2014-2016 (Dineva, 2014; Dineva, 2017). Values of SSS in 2017 along with SSS data for 1990s and 2014-2016 periods indicated that when SST increases, SSS decreases and vice versa. Water mass forming of the Varna Lake was mainly by seawater.

In the upper layer, the oxygen dynamics is mainly governed by photosynthesis and respiration processes as well as by air–sea exchanges. ≈71% of the oxygen produced by phytoplankton (photosynthesis + nitrate reduction) is lost through respiration, ≈21% by outgasing to the atmosphere, ≈5% through nitrification and only ≈2% in the oxidation of reduced components (e.g. Mn^{2+}, Fe^{2+}, H_2S) (Grégoire & Soetaert, 2010). If the supply of organic matter is increased to a point where the consumption of O_2 is greater than the supply then de-oxygenation begins (Topping, 1976).

Localized depression of oxygen was not detected in the investigated areas in 2017.

Varna Lake, as an anthropogenic factor (Rozhdestvensky, 1986; Dineva, 2015b), has strongly affected the south area of the Varna Bay about nutrients which led to highest level of nitrite nitrogen, nitrate nitrogen, and phosphate phosphorus at St. B3 compared to the other areas in 2017.

COD is a common measure of water quality that reflects the degree of organic matter pollution of a water body. COD is a measure of the oxygen equivalent of the organic matter in a water sample that is susceptible to oxidation by a strong chemical oxidant (Chapman, 1996).

COD-Mn in the Varna Bay was slightly higher than in front of Cape Galata in 2017. Organic matter in the Varna Lake has exceeded the level in the other areas.

Better environmental protection is necessary to achieve the most sustainable development of the natural system in the future. Improvements must be teamed with realising the unexplored potential that lies in better water management, along with changes in policy and production techniques.

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