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# Interannual variability of the Black Sea Proper oxygen and nutrients regime: The role of climatic and anthropogenic forcing

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ABSTRACT

The Black Sea is a unique, stratified, enclosed ocean basin of great importance. The water column provides a wealth of information concerning aerobic-anaerobic biogeochemistry, the responses of which can have links to anthropogenic and climatic forcing. Herein, we synthesize dissolved oxygen (DO) and nutrient data (phosphate, dissolved inorganic nitrogen (DIN), and silicate) for the period 1984–2010 received in the northeastern and western areas of the Sea. In the subsequent analysis we discuss the role of anthropogenic and climatic forcing in the context of the Black Sea oxic layer and oxic/anoxic interface characteristics.

The DO concentration in the surface layer and in the Cold Intermediate Layer (CIL) decreased in warm periods and increased in cold periods, correlating to North Atlantic Oscillation (NAO) index variation. The biogeochemical regime of the Black Sea oxygenated upper layer has notably changed since 1999. After 1999 DO concentration in the CIL decreased by 20% while the concentrations in the surface layer changed very little. This provides evidence that the CIL waters were not fully replenished during the winters of the last decade.

The nutrient concentrations (DIN and phosphate) in the surface layer decreased significantly in the 2000s compared with the 1980s–1990s. This decrease is regarded as improvement of the Black Sea ecosystem state. Oxygen and nutrient dynamics in the middle pycnocline have been decoupled since 1999. Presently physical (climatic) forcing is the dominant affecting factor controlling the Sea oxygen and nitrogen regime.



## 1. Introduction

The Black Sea is a unique water body that contains the largest hydrogen sulphide-rich anoxic zone in the World Ocean. This Sea is a deep stratified anoxic basin that is almost completely enclosed. It is bound to the northeast by the Sea of Azov and to the southwest by the Sea of Marmara. The only significant shallow area is the Northwestern (NW) Shelf, which is about 20% by area and only 1% by volume (Fig. 1). In this relatively small area the largest Black Sea rivers represent 80% of the total freshwater input (Kosarev and Kostianoy, 2008). This paper focuses in the Black Sea "Proper" rather than bound by the Rim current frontal zone localized processes of the NW Shelf.

Over time, the vertical structure of the Black Sea has evolved to form a strong permanent stratification of the water column primarily due to high salinity waters entering the Black Sea through the Bosporus strait and low salinity riverine inputs. Additionally, the upper and deeper water masses are separated by a permanent halocline. Winter mixing results in the formation of an oxygen-rich Cold Intermediate Layer (CIL) positioned above the permanent halocline at depths lying between 50 and 120 m. These surface-origin waters are characterized by a typical density of $\sigma_\theta = 14.3$–$14.7$ kg m$^{-3}$ and the rate at which CIL form varies in response to the intensity of winter cooling (Oguz et al., 2006; Oguz and Ediger, 2006; Kazmin et al., 2010).

The vertical diffusive flux of oxygen from the CIL is insufficient to meet the respirational consumption demands of degradation of sinking organic material. As a consequence, the strong vertical stratification results in a well oxygenated surface layer (from 0 to

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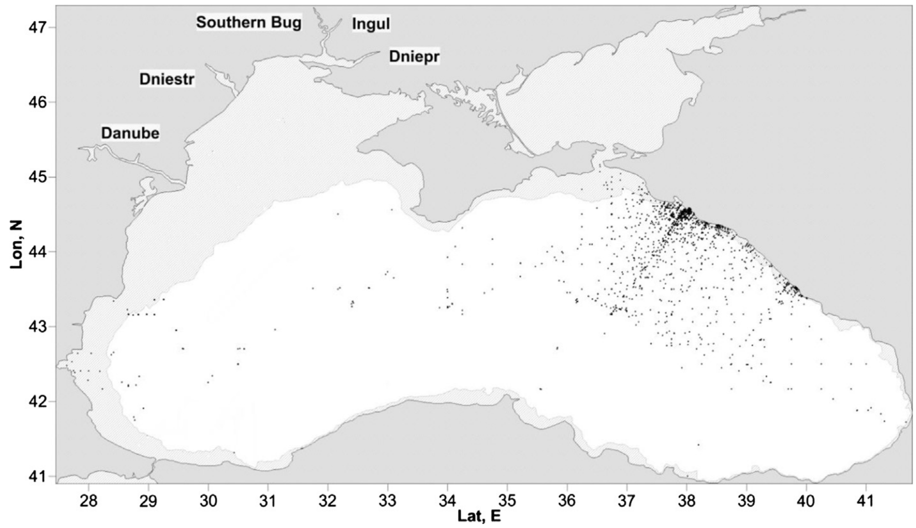


**Fig. 1.** Station locations in the Black Sea for period studied, 1984–2010 and principal river mouth positions. The areas shallower than 100 m are shaded.

50–200 m), a suboxic zone where the concentration of oxygen is below the detection limit of traditional methods applied (Murray et al., 1995), and a permanently anoxic deeper layer (from 70-200 to >2000 m) containing high sulphide concentrations (Sorokin, 2002).

The various oxidation–reduction reactions in the Black Sea water column and in particular those reactions that are typical of the suboxic zone occur in narrow layers of water of similar water density. These relate to the hydrochemical features (e.g., maxima and minima, onset points) that are characterized by the typical stable density levels (Vinogradov and Nalbandov, 1990; Murray et al., 1995; Volkov et al., 1997; Konovalov and Murray, 2001; Konovalov et al., 2005). Such a relationship provides a unique opportunity for data comparison and statistical analysis of data that is spatially variable (acquired in different regions of the Black Sea and during different sampling campaigns) and temporally variable due to seasonality.

The pelagic ecosystem dynamics of the Black Sea water column are determined by the climate-induced fluctuations and anthropogenic forcing, mainly related to eutrophication. Cold winter conditions typically correspond to increased nutrient conditions and phytoplankton biomass whilst mild winters correspond to decreased nutrient concentrations, and phytoplankton biomass (Oguz et al., 2006). The excessive nutrient enrichment of the Black Sea during the peak eutrophication period in 1970s–1980s was originally a result of enhanced riverine nutrient (silicate, nitrogen and phosphorus) supply into the northwestern shelf of the Sea. This subsequently led to accelerated growth and over-production of algae and opportunistic species of higher trophic levels, a high rate of oxygen utilization, the development of hypoxia or anoxia beneath productive areas, and the consequent degradation of benthic communities.

The total flux of nitrogen from the River Danube catchment area increased from ~400 kilotonnes kt $y^{-1}$ in the 1950s to 900 kt $y^{-1}$ in 1985–1990 (daNUbs, 2005). This flux was then reduced to 760 kt $y^{-1}$ in 2000–2005. The flux of phosphorus was an order of magnitude smaller than nitrogen and increased from 40 kt $y^{-1}$ in 1950s to its peak value of 115 kt $y^{-1}$ during the first half of the 1990s. Subsequently this flux decreased to 70 kt $y^{-1}$ in 2000–2005. Both of these fluxes are thus approximately 1.5 times higher than the 1950s. The construction of the Iron Gate 1 dam and reservoir in 1975 has been estimated to impose a minor influence on the total-N load, but was more apparent in controlling the total-P load (daNUbs, 2005). Based on more recent measurements at the discharge point of the Sulina branch of the River Danube, this contribution was reduced to nearly 50% of the overall river-based dissolved inorganic nitrogen and phosphate loads (daNUbs, 2005; Oguz et al., 2008b) compared with 1970s –1980s.

The response of the Black Sea system to the above mentioned factors is being intensively studied to ensure proper nutrient management in the region and better knowledge on the possible impacts of climate changes (BSC, 2008; daNUbs, 2005); but there are still a lack of detailed estimates and descriptions of the Black Sea oxygen and nutrient regime dynamics. Responding to this deficiency, the present work focuses on the recent decadal changes of the oxygen, nutrient conditions and the position of the oxic/anoxic boundary of the Black Sea using the Northeastern (NE) and Western (W) Black Sea as reference areas to base these studies on. The choice of these regions was determined by oxygen and nutrient reliable data availability, which reflect the Black Sea Proper (the Black Sea without the northwestern shelf region) nature.

The data from the NE Black Sea has a larger geographical coverage (from the Russian coast of the Black Sea to the center of the Black Sea Eastern Gyre) than for the W Black Sea and are available for a longer period (from 1980s). Furthermore the observations from the NE region are more important for a long period revealing changes. The upper layer chemical dynamics in the NE Black Sea reflect "integrated" rather than local changes of the Black Sea chemical parameters because influence of the Bosphorus and NW Shelf rivers is less significant when compared to the western and southern parts of the Sea (Yakushev et al., 2005). The NE Black Sea is characterized by the absence of a significant shelf, and the chemical characteristics of the near-coast and open sea water column are similar. In contrast, the W Black Sea region has a wide shallow area comprising coastal waters with depths down to 22 m and the shelf waters (60–100 m depth) extending to about 50 km offshore. Compared to the NE region, the W Black Sea is more sensitive to the influence of the northwestern (NW) shelf waters and river discharge forcing changes there.

The objective of this study is to analyze recent decade changes of the Black Sea oxygen and nutrient regime aiming to reveal a comparative role of climatic and anthropogenic factors in these changes. The results of this study will contribute to the estimates received for the 1970s–1990s (Konovalov and Murray, 2001; Konovalov et al., 2005; Yakushev et al., 2007a, b; Mikaelyan et al., 2013).