LONG-TERM CHANGES IN THE HYDRO-CHEMICAL PROPERTIES OF BLACK SEA UPPER LAYER

Suleyman Tugrul [1]*, Gernot E. Friederich [2], James W Murray [3] and Ilkay Salihoglu [4]
[1] METU-IMS - tugrul@ims.metu.edu.tr
[2] School of Oceanography, University of Washington
[3] MBARI
[4] Near East University

Abstract
Long-term hydro-chemical data, including pump-cast measurements obtained during the Knorr 2001 cruise, have been evaluated to assess spatial/temporal changes in distinct hydro-chemical features, lateral intrusions of Bosphorus plume and NW shelf waters to western basin of the Black Sea. The suboxic zone, having distict chemical features, remained enlarged since 80's. The upper layer silicate stock has decreased drastically as the phosphate and nitrate displayed opposite trends since late 60's.
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The Black Sea, a land-locked deep basin occupied with brackish waters, possesses distinctly different biochemical properties due to the presence of oxygenated in the upper layer and sulfide-bearing waters below a depth of 100-150 m and a transition zone in between [1-5]. The occurrence of hypoxia and anoxia in the Black Sea causes nutrients and other redox-sensitive elements to exhibit distinct vertical features in the Black Sea water column that are different from those profiles in the oxygenated basins of the world's oceans [1-5]. Though principal hydrochemical properties of the Black Sea system are known, spatial and temporal changes in the Black Sea and processes responsible for these variations are still poorly understood due to the lack of high-quality and high-resolution historical data and complicated biogeochemical reactions in the oxic/anoxic transition zone. Lateral and vertical oxygen influxes together with the catalytic reactions of manganese in the interface keep the sulfide-bearing waters in the deep basin at similar density surface over the basin for years [2-5]. Comparison of the new and historical data sets indicates long-term changes in Black Sea upper layer chemistry. Increasing inputs of nutrients by the polluted rivers with modified N/Si/P molar ratios have severely altered bio-chemical properties of the whole Black Sea [1-4]. Increasing load of DIN by the Danube and concurrent depletion of phosphate in the NW shelf euphotic zone and cold intermediate layer (CIL) in 80's, has led to markedly high N/P ratios in shelf waters down to CIL depths. In this period, the nitrate stock of the upper layer has increased by 2-3 times as silicate stock displayed an opposite trend in the upper layer down to onoxic intreface since the 60's [2-4]. Thus, nitrate/silicate ratio decreased drastically in the upper layer throughout the basin [4]. However, there has been a slow increasing trend in the surface silicate values in the last decade, suggesting progressive changes in the Black Sea ecosystem. It has been documented that oxygen and sulfide do not co-exist in the interface due to high rate of sulfide oxidation by oxygen [3-5].

Until the Knorr 1988 cruise, no integrated studies have been carried out in the Black Sea to provide real-time and near real-time chemical measurements and oxidation-reduction rates of redox-sensitive elements in the oxic/anoxic transition zone in the western basin. During the 2001 Knorr cruise, we have obtained high-resolution data of nutrients, dissolved manganese (and reduced iron at two stations) by both pump-profiling system and bottle-casts. The Knorr 2001 results demonstrate regional variability in vertical structures of nutrients and dissolved manganese in the western Black Sea Black Sea upper layer, depending on circulation patterns, particle influx from the surface layer and lateral intrusion of oxygen via Bosphorus plume. Lateral intrusions of partly oxygenated and nitrate-rich Bosphorus plume by mixing with cold intermediate layer (CIL) appear to ventilate and thus modify characteristic chemical structures in the oxic/anoxic transition layer of the rim current in the SW basin. Specifically, secondary broad nitrate peaks appears in the oxygen depleted transition zone, as well as to the co-existence of nitrate, ammonia, dissolved manganese and nitrite in the suboxic/anoxic interface. Silicate profiles also displayed undulating patterns with depth. Thus, the onset of sulfide-bearing water shifts to greater density surfaces by about 0.2 density units in the SW region. Moreover, small undulating patterns of nitrate profiles in the suboxic zone of the northern slope and central gyre imply weak intrusions of CIL waters from western shelf with different chemical properties. Climatic warming in recent years seems to have decreased the nitrate content of CIL waters evolved in NW shelf, which flows towards SW coastal region via rim current system.

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