

CHANGES IN THE VERTICAL CHEMISTRY OF THE BLACK SEA SINCE 1960

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ABSTRACT

The ecological impacts of large scale, man-made riverine diversions and anthropogenic inputs on the present biochemistry, and hence on the ecological state of the Black Sea has also been evaluated by utilizing the time-series data collected by RMRI around the Danube River mouth together with past and present chemical data. Recent field measurements of biochemical parameters, such as nutrients, dissolved oxygen, hydrogen sulfide, and physical parameters such as temperature, salinity, percent light transmission, current speeds and directions along the coastal-offshore transects were evaluated for describing the possible routes and mechanisms of transport of coastally trapped pollutants into the offshore, deep-basin waters through meandering rim current system.

The Black Sea, an inland sea having a surface area of $4.2 \times 10^5 \text{ km}^2$ and volume of $5.3 \times 10^5 \text{ km}^3$, possesses permanently anoxic basin below the depth of 70-80 m at the interiors and 100-200 m at the peripheries of the basin. Upper oxic layer, which comprises 10-15 % of the total volume of the Black Sea supports the biological production from primary planktonic level up to higher ecological levels, and receives wide spectrum of industrial, agricultural and domestic wastes of about 160 million population occupying a catchment area of nearly five times larger than its total surface area. Majority of the riverine freshwater discharges are located on the northern and northwestern shelf area which comprise 35% of the total drainage area of the basin. The Danube River alone represents 3/4 of the northwestern river run off and 2/3 of the total riverine input ($370 \text{ km}^3/\text{y}$) into the Black Sea basin and carries wastes amounting more than the total discharge to the North Sea.

The presence of a transition zone, so-called suboxic zone (SOZ), located between the oxygenated upper layer and the anoxic deep waters with low concentrations of both dissolved oxygen ($\text{DO} < 10 \text{ } \mu\text{M}$) and hydrogen sulfide ($< 1 \text{ } \mu\text{M}$) is a unique feature with its complicated biogeochemistry and related redox processes. Scientific evidences clearly indicate that profound changes have occurred in the Black Sea ecosystem during last two decades as a consequence of the increased nutrient and organic loads by rivers. Diversions of riverine discharges and intense agricultural and industrial activities has resulted in an increase in the annual loads of nitrate and phosphate but decreased that of silicate due to increased sedimentation in the dams. Overall effect of these modifications is the eutrophication of the coastal waters, shift from diatom based production to the dinoflagellate and nano-plankton type consumptive ecosystem. In coherent with the ecological changes, upper boundary of the suboxic zone has also shifted upward in the Black Sea.

The concentrations of inorganic nutrients in the productive surface waters ranged between $< 0.02\text{-}0.2 \text{ } \mu\text{M}$ for o-PO_4 and $< 0.1\text{-}0.5 \text{ } \mu\text{M}$ for the TNO_x species. Remarkably high values were recorded in the shelf waters, especially in the northwestern shelf area, due to the riverine inputs, accompanied with relatively high N:P ratios. In the open waters, the molar ratios of particulate nutrients in sestons were in range of 11-25 over the basin in 1995-1996, mostly comparable to the mean ratio ($\text{N:P}=16$) given for oceanic plankton. In the oxycline, the inorganic nutrient concentrations increase steadily with depth. The TNO_x profiles display distinct maxima between the specific density surfaces of $\sigma_\theta = 15.4$ and 15.6 within the oxic/suboxic interface. Interestingly, the TNO_x maxima were located at greater density surfaces by about 0.3-0.4 density units, but with markedly lower peak values during the 60's.

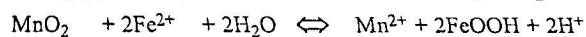
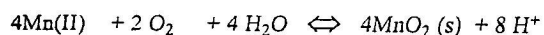
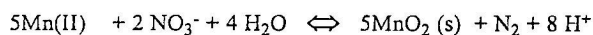
Even though the water layer just above the present suboxic zone is oxygenated down to $15.3\text{-}15.4$ density surfaces by vertical winter mixing and probably by horizontal advection processes, the gradient of dissolved oxygen became much steeper in 90's as compared to 60's. $50 \text{ } \mu\text{M}$ DO concentration measured at about $15.7\text{-}15.8 \text{ } \sigma_\theta$ surface in 60's has shifted upward by 0.3-0.4 density units to $15.4\text{-}15.5$ in 90's, clearly indicating pronounced biochemical and hence ecological changes had been occurred in the Black Sea ecosystem in recent decades. Vertical chemistry of the water masses located within dynamically different regions of the Black Sea; namely Cyclonic Gyres, Anticyclonic eddies and Rim Current Frontal Zones also shows distinct features. Onset of phosphocline always commences at greater density surfaces relative to that of nitracline; sub-surface PO_4 minimum is distinctly evident in the suboxic zone of the cyclonic gyres which weakens in anticyclonic eddies and almost disappears in the RCFZ.

In situ H_2S oxidation experiments implied that within SOZ of the western cyclonic gyre, H_2S removal rates are faster ($t_{1/2} = 2.5\text{-}3.4 \text{ hr}$) compared to those in anticyclonic eddies ($t_{1/2} = 2.3\text{-}15.4 \text{ hr}$). However, its removal rate is faster in the SOZ of the RCFZ ($t_{1/2} = 1.2\text{-}1.3 \text{ hr}$), probably due to the catalytic actions of particulate iron and manganese

species. These removal rates were shown to independent of dissolved oxygen concentration, i.e., DO does not seem to be directly oxidant the removal of H_2S diffusing from anoxic to the SOZ. Mass-balance calculations show that the oxidation of NH_4 and organic-nitrogen by MnO_2 may be the dominant process producing N_2 in Mn-rich continental margin sediments. Coincidence of Mn-Oxide maximum with that of NO_2^- , and positioning of particulate manganese layer between the layer of NO_3^- minimum, suboxic levels of DO, and particulate Fe oxides suggest that particulate manganese oxides couples the redox processes in the upper layer of the suboxic zone with those in the lower layer by carrying the oxidation potential of nitrate and oxygen to the lower section of SOZ where ammonia is oxidised to N_2 and/or to NO_2^- plus reduces NO_3^- to NO_2^- and/or N_2 while itself is oxidised.

Field studies and surveys have suggested that NH_4 is oxidised basically by the particulate MnO_2 , probably, to N_2 or NO_2^- . Observed decrease in the Mn(II) concentration within the oxygenated water layers is proposed to be due to the oxidation of Mn(II) back to $\text{MnO}_2(\text{s})$ by oxygen, which in turn oxidises NH_4^+ to N_2 or NO_2^- , and H_2S by coupling with iron cycle.

Possible sequence of redox reactions within the oxycline/suboxic/anoxic zones are suggested as follows;



In the given order, thus manganese cycle acts as a carrier and couples the electrons supplied by NH_4^+ and H_2S diffusing upward from the anoxic layer to O_2 and NO_3^- species diffusing downwad.