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Long-term changes in the chemical properties of the Black Sea

Suleyman Tugrul (1), James W. Murray (2), Gernot E. Friederich (3), and Ilkay Salihoglu (4)

(1) Institute of Marine Science, Middle East Technical University, Erdemli-Mersin, Turkey (tugrul@ims.metu.edu.tr), (2) School of Oceanography, University of Washington, Seattle WA 98195 USA (jmurray@u.washington.edu), (3) MBARI, 7700 Sandholdt Road, Moss Landing CA 95039 USA (frgr@mbari.edu), (4) Near East University, Nicosia, Northern Cyprus (isalihoglu@neu.edu.tr)

The Black Sea possesses distinctly different biochemical properties due to the presence of an oxygenated upper layer, a sulfide-bearing deep waters and a transition zone (or suboxic zone SOZ) in between. Vertical distributions of oxygen, nutrients and redox-sensitive metals display distinct features in the transition zone, which has been modified drastically since the 1970's. New chemical data obtained during the Knorr 2001 cruise can be compared with historical data to assess spatial/temporal changes in the chemical properties of the Black Sea. Since the 1960s the first appearance of sulphide has remained almost unchanged but after 1970 the suboxic zone (SOZ) enlarged drastically, leading to a steep oxycline development in the central basin. The depths of the nitrate maximum, the phosphate minimum and the onset of Mn (II) and the maximum of particulate Mn shoaled by about 10 meters. These features are very sensitive to export of POM from the euphotic zone.

One important driver for these changes has been nutrient input from the Danube. Nitrate inputs increased due to anthropogenic fertilization while silicate inputs decreased due to dam construction. As a result the inventory of silicate in the upper layer has decreased by 40 to 50 μM whereas the nitrate inventory has increased (by 2-4 fold) compared to concentrations before 1970. Changes in the PO_4 inventory were not significant. The N/P ratio, which was very low (<2), has increased. The Si/N was initially very high, but has been increasing. Development of eutrophic conditions has modified the broad oxycline of the earlier period, leading to the development of a steeper oxycline in the central basin and a broad suboxic zone (SOZ). The enlarged SOZ and development of anoxic conditions in NW shelf has drastically limited the habitats of vertically migrating organisms.

The features of the SOZ vary spatially. In the central gyres nitrate reaches a maximum at the SOZ boundary (DO < 20 μM) and PO_4 has a distinct minimum at a depth which perfectly coincides with the onset of increasing Mn (II). The onset of ammonia is slightly deeper. In the SW coastal zone these distributions are modified due to lateral intrusions from the Bosporus Plume. In the SW region oxygen penetrates to greater depths and the first appearance of sulphide is deeper. These intrusions result in the co-existence of Mn(II), ammonia, nitrate and oxygen in the suboxic zone.

Temporal variations can be seen as well. Before the 1970s the SOZ was very thin. It has since enlarged gradually by about 30-50 m. Changes have also occurred in the distinct chemical features of the SOZ. Since the 1970s, the nitrate maximum formed at the upper SOZ boundary and the phosphate minimum have become more coherent and shifted to shallower density surfaces. The onsets of dissolved Mn and particulate Mn have also shifted upward.

In addition to these long-term trends the upper nitracline and oxycline have been observed to be degraded locally in the summer when export production of POM is larger. These processes have reduced the nutrient inventory of the halocline waters. Modeling studies of complex bio-mediated processes in the suboxic/anoxic transition zone are needed to fully understand what cyclic processes and flux rates of oxidizing agent(s) have primarily kept the anoxic boundary unchanged whereas the SOZ has drastically enlarged upward since the 70's.