A CHANGING COASTAL SEA: THE BLACK SEA

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Introduction

The Black Sea is a semi-enclosed marginal sea with a physical and chemical structure that is determined by its hydrological balance. Seawater flows in through the Bosporus. Freshwater inflow from several European rivers keeps the salinity low in the surface layer (S = 17). As a result, the water column has strong vertical density stratification. A consequence is that the surface layer (about 0 to 50 m) is well oxygenated whereas the deep layer (100 to 2000 m) has no oxygen and high sulfide concentration. At the boundary between the oxic surface and anoxic deep layers, there is a well developed suboxic zone (about 50 to 100 m deep) where O_2 and H_2S concentrations are extremely low and do not exhibit any perceptible vertical or horizontal gradients. This suboxic zone was first observed during the 1988 Knorr Black Sea Expedition (MURRAY *et al*., 1989).

The suboxic zone in the Black Sea (MURRAY *et al*., 1995) is an important biogeochemical transition zone between the oxic surface layer and sulfidic deep waters. Many interesting intermediate oxidation-reduction reactions involving species of N, Mn, Fe and other elements occur in this layer. The Black Sea is of interest to scientists studying the geochemistry of tidal flat sediments. The redox reactions that occur in tidal flat sediments are in many ways easier to study in the Black Sea because they are spread out over depths of meters, rather than centimeters as observed in sediments.

The suboxic zone appears to be a permanent structure (at least since the early 1960s). The average thickness varies several-fold on a time scale of decades (KONOVALOV & MURRAY, 2001). The balance between oxygen injected due to climate determined ventilation of the thermocline (including the Cold Intermediate Layer or CIL) and oxygen consumption by oxidation of eutrophication-enhanced organic matter governs the depth of the upper boundary of the suboxic zone (KONOVALOV & MURRAY, 2001). The injection of oxygen into the upper part of the sulfide zone by the Bosporus plume is also an important control for the depth of the onset of sulfide (KONOVALOV & MURRAY, 2001). Redox processes involving nitrate-manganese-sulfur are important in the lower part of the suboxic zone (OGUZ *et al.*, 2001).

Recent cruises

Two recent US research cruises were conducted on R/V Knorr. Knorr 2001 (J.Murray, chief scientist) consisted of two legs from May 23 to June 10, 2001. Leg 1 was primarily in the SW region near the Bosporus outflow, Leg 2 in the central and NW regions. The new data are available on the web at: oceanweb.ocean.washington.edu/cruises/Knorr2001. Knorr 2003 (G. Luther, chief scientist) consisted of three legs from April 15 to May 15, 2003. On Legs 1 and 3 a detailed study of the Bosporus outflow region was conducted whereas Leg 2 went to the western, central and eastern gyre regions.

Reference data for the suboxic zone

The suboxic zone was first observed in 1988 using samples from a pump profile system developed by G. Friederich (now at Monterey Bay Aquarium Research Institute) (MURRAY *et al.*, 1989). The data in Figs. 1 and 2 are plotted versus density rather than depth. Observed features occur at different depths because of the physical circulation of the Black Sea. The surface circulation is dominated by a Rim Current which defines a cyclonic central gyre characterized by upwelling. As a result, specific biochemical features are observed at shallower depths in the central gyre than near the margins.

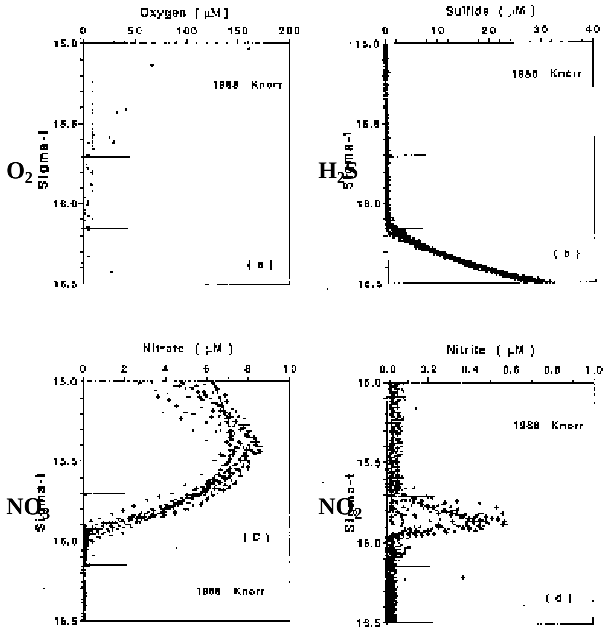

Fig. 1. Data from the 1988 R/V Knorr cruise (w/Pump Profiling System) used to illustrate the suboxic zone in the Black Sea. The horizontal lines refer to the upper boundary defined by the decrease of O_2 to less than 10 µM and the lower boundary defined by the increase of sulfide to greater than 1 µM (LUTHER *et al*., 1991).

However they always occur on the same density surfaces (except in the SW region near the Bosporus outflow). The data in Figs. 1 and 2 were obtained throughout the Black Sea and you can observe how tightly constrained they are when plotted versus density (Table 1).

Table 1. Key density surfaces

Feature	σ_t (kg/m^3)
PO_4^{3-} shallow maximum	15.50
O_2 <10 µM	15.65
NO_3^- maximum	15.40
Mn_d <200 nM	15.85
Particulate Mn maximum	15.85
PO_4^{3-} minimum	15.85
NO_2^- maximum	15.85
NO_3^- <0.2 µM	15.95
NH_4^+ >0.2 µM	15.95
Fe_d <10 nM	16.00
H_2S >1 µM	16.15
PO_4^{3-} deep maximum	16.20

NOTE; The density values of these features, determined from the pump profile data, have a range of about 0.05 density units.

Region of the Bosporus outflow

In the southwest region of the Black Sea, downstream from the high salinity, high temperature Bosporus outflow, the tight density control breaks down. Evidence of the Bosporus outflow can be seen by the positive temperature anomalies that occur in the water column (Fig. 3). The Bosporus outflow ventilates the Black Sea with relatively warm and salty water. As it flows across the continental shelf it entrains water from the overlying cold intermediate water (CIL) with an average ratio of 1:4. The CIL is a layer with a temperature minimum at about 40 m depth which forms at the surface of the Black Sea in the winter. All of the deep water in the Black Sea is composed of a linear mixture of Bosporus outflow and the CIL. The rates of this physical ventilation process were obtained by modeling the distributions of CFC tracers (LEE *et al*., 2002). The rate of ventilation decreases with depth.

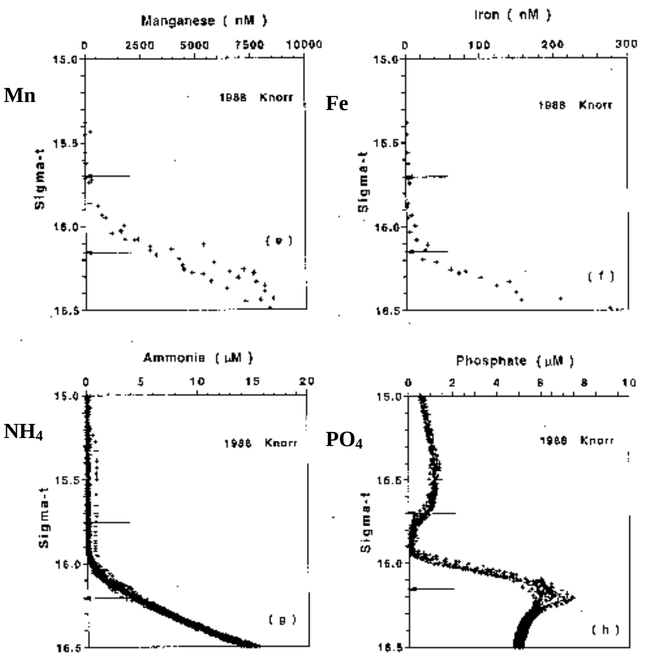

Fig. 2. The distributions of total manganese, iron, ammonium and phosphate in the suboxic zone.

Oxidation of the upward flux of sulfide

The ventilation of the Black Sea with Bosporus outflow also injects oxygen. This O_2 could consume H_2S directly but that reaction is thought to be unfavorable. A plausible alternative is that O_2 oxidizes reduced Mn(II) to Mn(III, IV) species and this oxidized Mn then reacts directly to oxidize sulfide:

$$O_2 + Mn^{2+} \rightarrow MnO_2$$

$$MnO_2 + HS^- \rightarrow Mn^{2+} + SO_4^{2-}.$$

In this way Mn species act as a catalyst and are cycled between oxidized and reduced forms, resulting in the net reduction of O_2 and oxidation of H_2S. KONOVALOV & MURRAY (2002) calculated that ventilation of the upper sulfide layer by Bosporus outflow could account for consumption of more than 50% of the upward flux of sulfide. A detailed data set from the SW region near the Bosporus outflow using the pump profiling system and *in situ* electrochemical analyses shows thin layers (~1 to 5 m) of water with positive temperature anomalies and positive O_2 anomalies (Fig. 3) (KONOVALOV *et al*., in press). It has been hypothesized that much of the O_2 consumption occurs in the SW region with the results spread laterally on isopycnal surfaces throughout the rest of the Black Sea (KONOVALOV & MURRAY, 2001).

Anaerobic ammonium oxidation

Nitrate and ammonium decrease to zero at the same density level (σ_t = 15.95), which is in the middle of the suboxic zone. These distributions suggest that they are reacting with each other in some way. This is the Anammox reaction written as:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2\,H_2O.$$

Recent advances by Kuenen, Jetten and colleagues in the Netherlands has changed that (e. g. KUENEN & JETTEN, 2001). They used laboratory bioreactors with waste water to discover Anammox bacteria from the order Planytomycetales. KUYPERS *et al*. (2003) used 16S RNS gene sequences, RNA probes, ^{15}N tracer experiments and "ladderane" membrane lipids to verify that Anammox bacteria exist in the suboxic zone and play an important role for nitrogen cycling in the Black Sea.

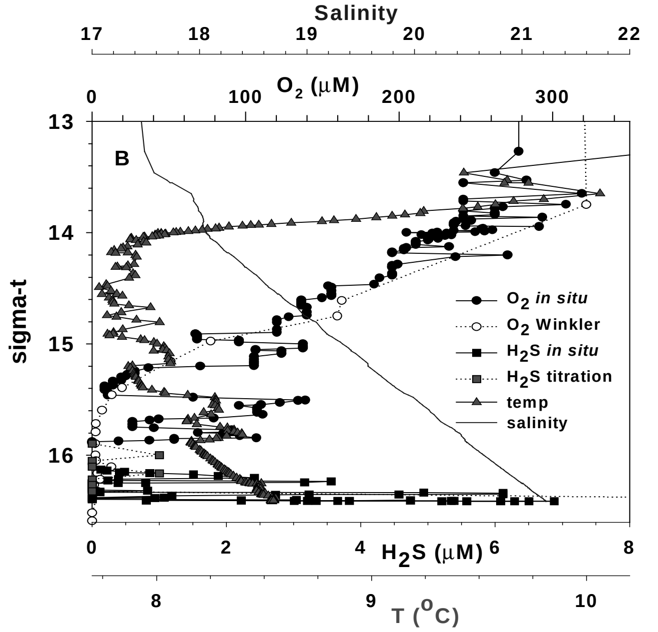

Fig. 3. Detailed vertical profile of T, S, O_2 and H_2S near the Bosporus outflow (from KONOVALOV *et al.*, in press).

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