2001 R/V Knorr Cruise: New Observations and Variations in the Structure of the Suboxic Zone (040)

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Abstract- The new data from the Knorr 2001 cruise has been combined with historical data and additional new data from SBSIO in the NE Black Sea to study temporal and spatial variability in the thickness of the suboxic zone. There are spatial variations in the characteristics of the suboxic zone as classically defined ($O_2 < 10\mu M$; $HS^- < 10$ nM). It is absent in the SW region due to injection of O_2 associated with the Bosporus Plume but it exists in the rest of the Black Sea. There are significant regional differences in the thickness of the suboxic zone and most of the variability is due to variations in the density of the upper boundary. The variability of this boundary is due to variability in ventilation of the Cold Intermediate Layer (CIL) and variability in the export flux of organic matter. There are also variations in the intensity of manganese cycling. The most intense biogeochemical cycling as reflected by the magnitude of the particulate Mn maximum occurs in the SW region. Mn (III, IV) oxides produced by oxidation of Mn (II) by injected O_2 is in turn probably the main oxidant of sulfide. The central gyre has a smaller particulate Mn maximum that is disconnected from the onset of sulfide. There are three maxima of particulate Mn in the NW region. Mn cycling is more intense here than in the central gyre but still much less important than downstream from the Bosporus Plume in the SW Black Sea. Variations in ventilation have occurred are climate related. During the Knorr 2001 cruise we observed some of the warmest conditions in the CIL seen in the past decades. The export flux of carbon increased from the early 1970s to the early 1980s as the surface Black Sea became more eutrophic.

Keywords-Black Sea, Suboxic Zone, Ventilation, Temperature, Salinity, Oxygen, Sulfide

Introduction

The Black Sea is a semi-enclosed marginal sea with a physical and chemical structure that is determined by its hydrological balance (Caspers, 1957; Sorokin, 1983). Seawater flows in through the Bosporus to the deep layer of the basin. Freshwater inflow from several European rivers keeps the salinity low in the surface layer. As a result, the water column is strongly stratified with respect to density. A consequence is that the surface layer (about 0 to 50m) is well oxygenated while the deep layer (100m to 2000m) has no oxygen and high sulfide concentration. At the boundary between the oxic surface and anoxic deep layers, there is a suboxic zone (at approximately 100m depth) where O_2 and HS^- are extremely low and do not exhibit any perceptible vertical or horizontal gradients (Murray *et al.*, 1989).

The suboxic zone in the Black Sea (Murray, et al., 1989; Murray, et al., 1995) is an important biogeochemical transition zone between the oxic surface layer and sulfidic deep waters. This suboxic zone was first recognized during the 1988 Knorr Black Sea Expedition (Murray and Izdar, 1989; Murray, 1991). However, the boundaries of this zone were arbitrarily chosen from the vertical distribution of oxygen and sulfide observed in the central gyre. Since its discovery, the processes controlling its origin have been extensively discussed. Spatial variability in its structure has not been discussed because of the absence of regional data.

The suboxic zone has been demonstrated to be a permanent structure (at least since the early 1960s) of the Black Sea (Buesseler, et al., 1994; Murray, et al., 1995) rather than a new feature resulting from anthropogenic change as suggested by Murray et al., (1989). The average thickness of this zone varies several-fold on a time scale of decades (Konovalov and Murray, 2001). The balance between oxygen injected due to ventilation of the thermocline (including the Cold Intermediate Layer or CIL) and oxygen consumed by oxidation of organic matter governs the depth of the upper boundary of the suboxic zone (Konovalov and 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 and Murray, 2001; Konovalov, et al., these proceedings). Redox processes involving nitrate-manganese-sulfur are important in the lower part of the suboxic zone (Oguz et al, 2001).

New data

New hydrographic (T, S and density) and oxygen/sulfide data were collected during the 2001 R/V Knorr research cruise to the Black Sea (23 May to 10 June 2001). The cruise was divided into two legs which allowed participation by 48 scientists from US, Turkey, Ukraine, Russia and Romania. One goal of this cruise was to analyze spatial and temporal variability in the suboxic zone in the western part of the Black Sea in order to determine what role may be played by boundary processes, especially the Bosporus Plume. At about the same time new data was also collected at the NE coast of the Black Sea near Gelendzhik, Russia by researchers from the Southern Branch of the P.P. Shirshov Institute of Oceanology (SBSIO). The station locations for the Knorr legs 1 and 2 and the SBSIO station are shown in Fig. 1.

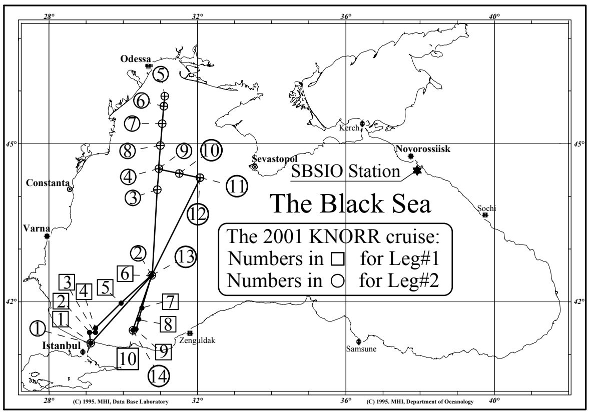

Fig. 1 Station Locations for the R/V Knorr 2001 and SBSIO cruises.

The station locations were well situated to study the continental margin areas in the SW, NW and NE regions. The good spatial resolution in the SW region allowed us to investigate the effect of intrusion of the Bosporus plume waters from the Mediterranean on biogeochemical properties of the Black Sea.

Hydrographic data were obtained by standard CTD procedures using SeaBird equipment. Oxygen and sulfide were determined by both wet chemical (volumetric) and electrochemical (voltametric) techniques. All data are available on the Knorr2001 web site at oceanweb.ocean.washington.edu/cruises/Knorr2001. The vertical distribution of oxygen in the study area determined by volumetric titration (after the Winkler analysis) and pump profiling with flow cell voltammetry (Codispoti, et al., 1991; Luther, et al., 2002) are compared in Fig. 2. Data from the northern, central and southern regions are indicated separately. Generally, the voltametric and volumetric oxygen data are in good agreement. The voltametric data has better vertical resolution, 0.8 to 1.5 meter, because it was collected with the pump profiling system. This provides precise tracing and quantitative characteristics of the distribution of oxygen in layered intrusions of the Bosporus plume. Volumetric titration of a limited number of samples does not provide good resolution of these intrusions, as they are usually only 1 to <5 meter thick (Konovalov et al, this volume; Luther et al, this volume).

The vertical distribution of oxygen in the layer above σ_t ~15.0 does not show any distinctive variations over the Black Sea. Oxygen containing intrusions from the Bosporus plume (deeper than σ_t = 15.0) are easily seen in the profiles from the southern stations of the 2001 KNORR cruise (especially in Fig. 2b).

Data on sulfide (not shown here) reveal a systematic difference between the volumetric and voltametric results from the upper anoxic zone. Volumetric results are usually higher by a few μM and the onset of sulfide determined from voltametric data is usually located about $\Delta\sigma_t = 0.1$ deeper, as compared to the volumetric data. Luther (unpublished data) has recently demonstrated the presence of elemental sulfur around the onset of sulfide. Elemental sulfide is probably detected by the volumetric method, which is a determination of all reduced substances (primarily HS^-, $S_2O_3^{2-}$, S_8^o) by excess I_2. If elemental sulfur exists in an electrochemically inactive form, this may explain the systematic difference. The difference may also be due to the presence of organic S.

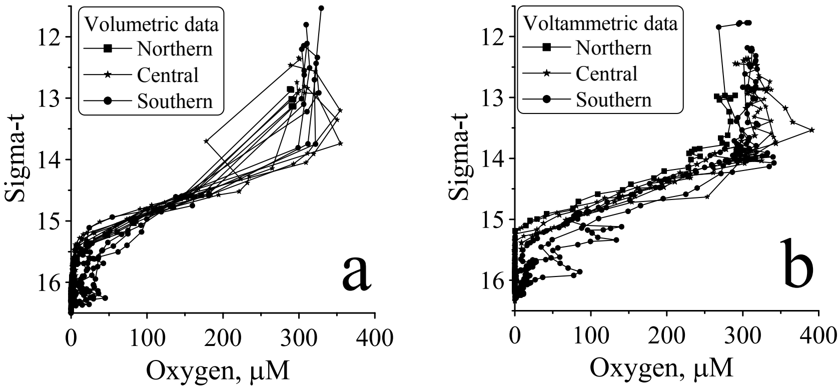

Fig. 2. Comparison of oxygen data determined by the volumetric (a) and voltametric (b) methods.

Does the suboxic zone exist everywhere?

There is spatial variability in the characteristics of the suboxic zone. A high resolution examination of the oxygen data (versus σ_t) from different parts of the Black Sea is shown in Fig. 3. The data are divided into two parts to highlight the effect of ventilation from the Bosporus plume. Horizontal dashed lines indicate the "suboxic zone" defined as < 10 μM O_2 and < 10 nM H_2S.

The SW part of the Black Sea is under direct influence of the oxygenated intrusions of the Bosporus plume (Fig. 3b). The onset of sulfide in the SW can be suppressed to $\sigma_t \approx 16.4$, while this onset in the central and NW is located on average at $\sigma_t \approx 16.2$. The suboxic zone as traditionally defined does not exist in the SW region, but at the same time there is never any overlap of oxygen and sulfide (C-Layer).

In the central and NW parts of the Black Sea we observe the "classic" suboxic zone as defined by the 1988 data (Fig. 3a). The SBSIO data from the NE margin are similar to the NW region. This "classic" suboxic zone has steep vertical gradients of oxygen at the upper boundary and a well-resolved layer of low concentrations and little or no gradients of oxygen within the zone. Thus, the first main point of this presentation is that the suboxic zone does not exist in the SW region of the Black Sea where the water column is affected directly by oxygenated intrusions of the Bosporus plume. It does appear to be present throughout the rest of the Black Sea.

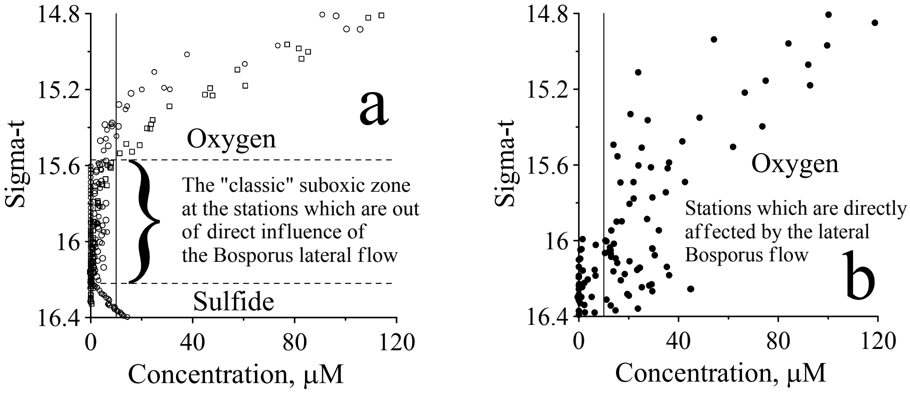

Fig.3 The vertical distribution of oxygen in the (a) central (◦) and northern (□) part and (b) southern part as see in the Knorr 2001 data.

Are there regional variations in the suboxic zone?

There are significant differences in the thickness of the suboxic zone in different regions. Representative profiles from the central gyre (Stn 2), NW margin (Stn 12) and NE margin (SBSIO) are shown in Fig. 4. These data show that the density values of the upper and lower boundaries of the suboxic zone vary from the central to the NW and NE regions. Variations in the density of the lower boundary of the suboxic zone are minor but there are significant differences in the density of the upper boundary. In any given region the vertical profiles of oxygen are very similar but they vary on a sub-basin scale. The spatial variations in the location of the upper boundary are due to variations in the oxygen content at the upper boundary. This value reflects variations in the rate of ventilation of the water in the pycnocline and the oxygen consumption capacity of the rain rate of particulate organic carbon. The thickness of the oxic surface layer and the Cold Intermediate Layer (CIL) is smaller in the central part of the Black Sea because of the dome shape structure of the pycnocline. As a result there is a smaller inventory of oxygen in the upper water column. Thus, an equal flux of sinking organic matter moves the oxycline and the upper boundary of the suboxic zone upward more effectively in the central part of the Black Sea. In addition, the central part of the Black Sea is considered to be more biologically productive, as compared to the periphery of the deep part of the sea, especially in the early spring when blooms occur. This is another factor that results in a thicker suboxic zone in the central gyre area. We hypothesize that the thickness of the suboxic zone is larger in the central area because the exported carbon flux has a greater impact in that region.

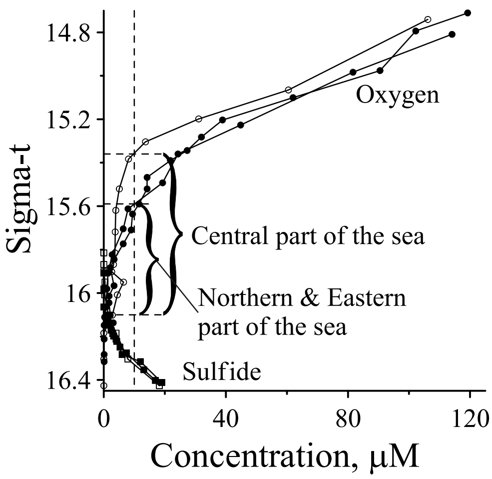

Fig 4. The suboxic zone in the central, northwestern and northeastern parts of the Black Sea

Are there other differences between these regions?

The profiles for dissolved and particulate manganese (together with oxygen and sulfide) for the central, northwest and southwest regions are shown for comparison in Figs. 5 and 6. These plots demonstrate that there are other variations in the structure of the oxic/anoxic transition layer and the suboxic zone. The southeastern part of the sea (Fig. 6) is the area of intensive redox processes in a multi-layered oxic/anoxic transition zone. The suboxic zone cannot be traced into this region because of the intrusion of the oxygenated Bosporus plume waters. In this region, dissolved manganese is actively oxidized by the injected oxygen. Maximum particulate manganese concentrations are 3- to 7-times larger than those in the central and northwestern parts of the sea (Fig. 5). The onset of dissolved manganese in the SW region is moved deeper from its usual density of σ_t = 15.8 – 15.9 to a density of about σ_t = 16.2. The onset of sulfide is moved deeper from σ_t = 16.1-16.2 to about σ_t = 16.4 and it usually exhibits an interleaved, multi-layered oxic-suboxic-sulfidic structure.

The suboxic layer of the central part of the sea (Plot 5a) suggests an example of a stagnant biogeochemical structure. The oxygen concentration remains at the level of 5 μM throughout the upper and middle part of the suboxic zone and decreases to the analytical detection limit below σ_t = 15.9. The maximum of particulate manganese is smaller than observed in the NW and SW parts of the sea, and seems to be disconnected from the onset of sulfide. The onset of dissolved manganese starts far below the upper boundary of the suboxic zone suggesting that redox transformations of manganese cannot generate a significant flux of electron-acceptors through the suboxic zone. The suboxic zone of the central area seems to illustrate a relaxation stage of biogeochemical redox transformations that may have occurred primarily elsewhere (such as the SW region) in the Black Sea.

The structure of the suboxic zone of the northwestern part of the Black Sea (Fig. 5b) is well defined and reproducible. Three maxima of particulate manganese are detected there. The upper maximum of particulate manganese at σ_t = 15.4 appears to not be related to Mn(II) – Mn(III,IV) redox transformations in the suboxic zone but probably corresponds to a bacterial pool of manganese (see also Tebo, 1991). The main peak of particulate manganese inside the suboxic zone, which is composed of Mn(III,IV) oxides (Stewart et al, 2002), has concentrations about two times higher than in the central part of the sea. The lower peak of particulate manganese within the sulfide zone has never been previously reported. This feature of particulate manganese, which exists in the layer of 20 – 40 meters below the onset of sulfide at σ_t = 16.2, is probably not an oxidized form of manganese, but it remains to be investigated to determine what is its form.

The overall structure of the suboxic zone indicates more active redox processes are occurring in the NW region, compared to the central gyre area. A smooth logarithmic profile of oxygen makes localization of the upper boundary of the suboxic zone formal. The suboxic zone of the northern part of the sea might correspond to an intermediate state, when (a) the flux of organic matter is not enough to compensate the vertical flux of oxygen, (b) the lateral flux of oxygen due to intrusion of the Bosporus plume does not exist, (c) the vertical flux of oxygen across the upper boundary of the suboxic layer is enough to affect the redox budget of this zone. The form and superposition of the vertical profiles of oxygen, dissolved and particulate manganese suggest that manganese involved redox processes can intensify redox fluxes through the suboxic zone (Murray, et al., 1995). Still, the intensity of these fluxes is not enough to compensate the upward flux of sulfide and the onset of sulfide progressively moves up from 16.3 to 16.4 in the southern area, to about 16.25 in the central part, and further to 16.1 to 16.15 in the northern part (Plot 5, 6, and 7a).

A hypothesis can be made that the most intensive redox reactions occur in the SW region downstream from the Bosporus plume. These reactions occur at the other boundaries (e.g. NE and NW) as well, but with greatly reduced intensity. The distributions in the central gyres may be relict features that are the remnants of these reactions.

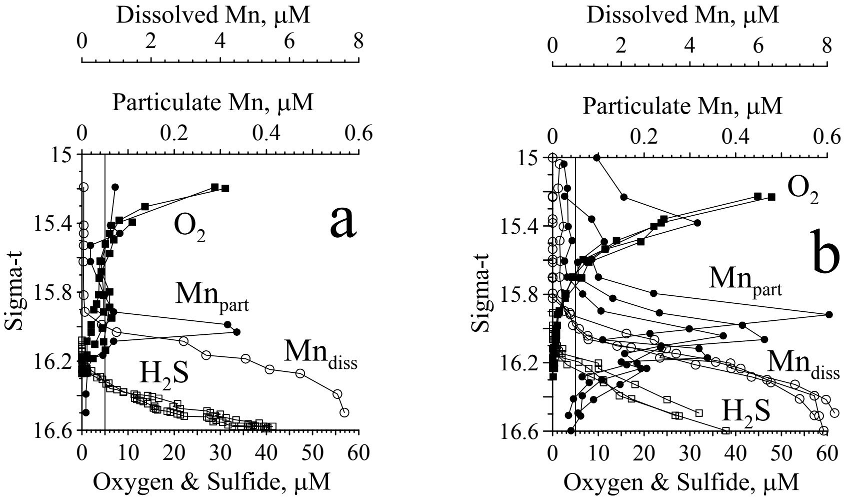

Fig. 5. The vertical distribution of oxygen, sulfide and dissolved and particulate manganese in the central gyre (a) and northeastern (b) parts of the Black Sea.

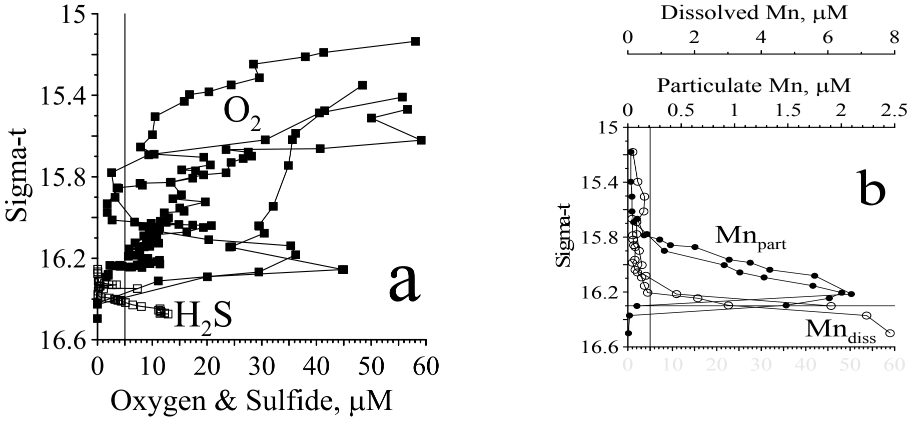

Fig. 6. The vertical distribution of oxygen, sulfide and dissolved and particulate manganese in the southwestern part of the Black Sea.

The cause of these temporal and spatial variations**.**

The distributions of sulfide versus density are shown in Fig. 7. Spatial variability for Knorr 2001 is shown in Fig. 7a and temporal variability from the 1969 Atlantis II to Knorr 1988 to Knorr 2002 is shown in Fig. 7b. We believe that the flux of organic matter increased during the 1980's due to increased eutrophication resulting from increases in the nitrate inventory (e.g. Codispoti et al., 1991) and this resulted in a systematic increase in the concentration of sulfide inside the anoxic zone (Konovalov, et al., 1997; Konovalov and Murray, 2001).

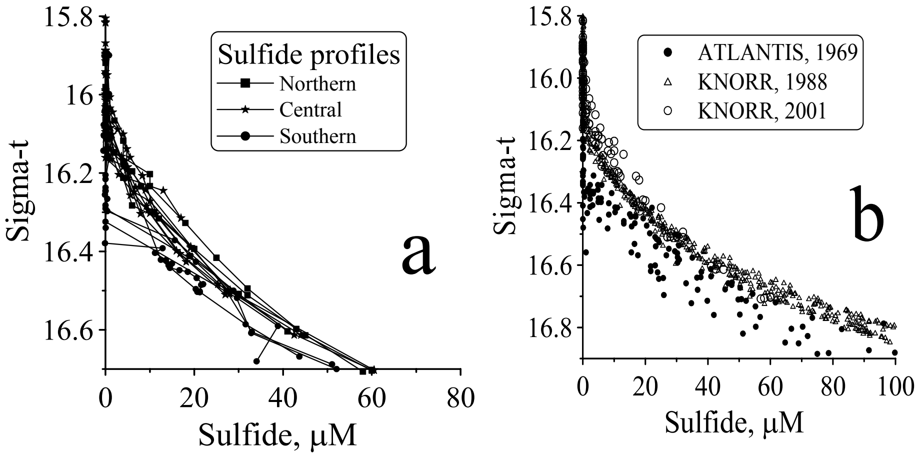

Fig. 7. Spatial and Temporal Sulfide Variations

The data in Fig. 7a demonstrate that for a range of locations during Knorr 2001 the onset of sulfide from about 16.0 to 16.4. The data in Fig. 7b reveals that the onset of sulfide has varied temporally from 16.0 to 16.5 for the period from the 1969 ATLANTIS II cruise to the 2001 KNORR cruise (profiles for the southern stations are eliminated). The average value of σ_t for first appearance of sulfide progressively shoaled from 1969 to 2001. The means are about the same but in detail there are differences. The spatial and temporal variabilities are about the same and both are tied to the mechanism and intensity of ventilation.

The temporal variability of oxygen and sulfide is also shown in Fig. 8. This Fig. is similar to that presented by Konovalov and Murray, (2001) but is extended to 2001 to include the new data from Knorr 2001. This Fig. shows that the oxycline and the upper boundary of the suboxic zone generally moved upward relative to density (shoaled) after the 1960s and 1970s. Individual deepenings of the oxygen contours correspond to the colder winters that occurred in 1978, 1984, 1988 and 1993. As salinity plays a more important role that temperature for controlling the density it usually requires a sequence of more than one cold winter to make an impact. After these cold weather periods the cold intermediate layer is better ventilated and its oxygen content is higher. From 1995 to 2001 the thickness of the suboxic zone increased and reached the thickness observed during the 1988 KNORR cruise, while the concentrations of oxygen in the upper oxycline (above σ_t = 15.0) and in the core of the CIL (around σ_t = 14.5) decreased to values that have never previously been observed in the Black Sea.

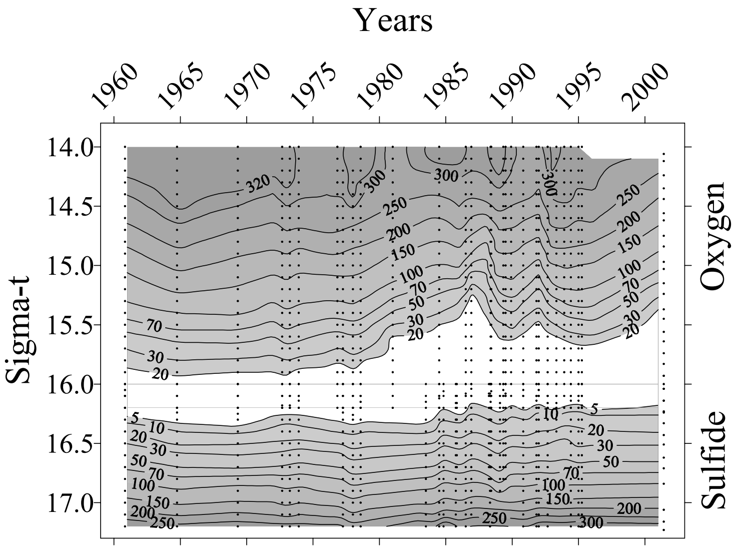

Fig. 8. Temporal variability in suboxic zone thickness from 1960 to 2001

The period of mild winter conditions, which started in 1994-1995, resulted in extremely weak ventilation of the CIL. This intensity of this hydrological structure has been greatly reduced as shown by the mean T-S diagrams from 1969 to 2001 (Fig. 9). The minimum temperature reached only 7.8ºC in 2001, while it usually varies from 7.0º to 7.2º and drops to about 6.5ºC after extremely cold periods.

The question can be poised whether the recent warming and decreased ventilation of the CIL is tied to global warming. To evaluate this we prepared a plot of the temperature minimum in the CIL and the density of this temperature minimum in the historical record (Fig. 10a). We also plotted the temperature at a constant density of σ_t = 14.5 which is characteristic of the CIL (see Fig. 9). These data show that there have been warm CIL periods in the past and thus the current values are not unprecedented. In fact the CIL was even warmer during several years in the early 1980s.

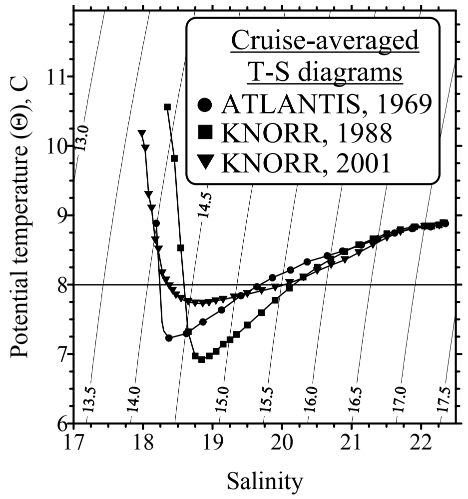

Fig. 9 Mean T-S diagram for Atlantis II 1969; Knorr 1988 and Knorr 2001 cruises.

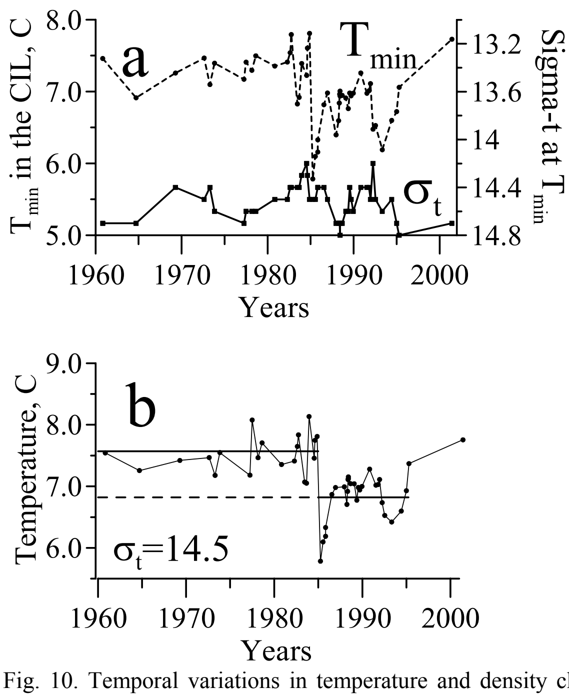

Fig. 10. Temporal variations in temperature and density characteristics of the CIL. a) The temperature minimum and its density, b) temperature on σ_t = 14.5.

Summary and Conclusions

Two basic processes are proposed (Konovalov and Murray, 2001) to govern the upper boundary of the suboxic zone. The first is ventilation of the overlying CIL layer, which sets the upper oxygen concentration and fundamentally determines the steepness of the vertical gradient and thus the downward flux of oxygen. The second is the export flux of organic matter, which is mostly responsible for driving the consumption of oxygen in and below the surface oxic layer. Two periods in the recent history of the Black Sea are illustrated in Fig. 11. For each of these periods, the concentration of oxygen in the middle pycnocline (σ_t = 15.4) just above the suboxic zone varied along an average line (see dashed lines) reflecting variations in the intensity of ventilation. There was a period from the late 1970's to early 1980's, when the concentration of oxygen decreased due to increasing export production due to eutrophication.

There was a period of the late 1980's and early 1990's, when the oxycline moved down (Fig. 8) because of favorable climate conditions (a series of severe winters) and the thickness of the suboxic zone decreased. The T_{min} of the CIL was low (Fig. 10a) and the temperature minimum moved to deeper density layers during this period. Ventilation of the CIL was enhanced and oxygen on σ_t = 15.4 was higher. The periods of 1987 and 2001 followed warm periods and resulted in higher temperatures and lower oxygen concentrations on the σ_t = 15.4 density surface. The suboxic layer was thicker. Data from the 2001 KNORR cruise (Fig. 11) demonstrate that the Black Sea remains highly eutrophic and will undergo further perturbations during the anticipated future warming climate conditions.

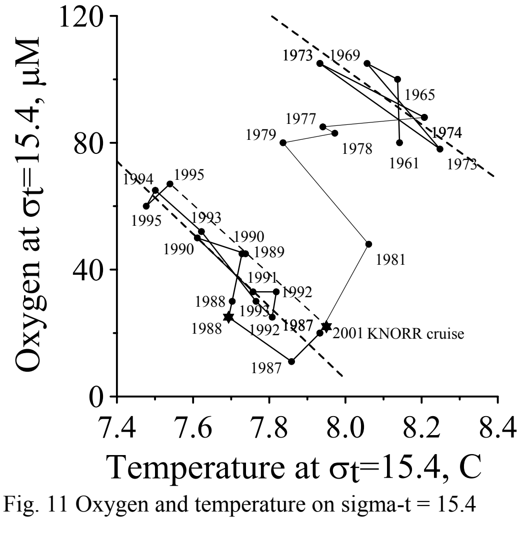

Fig. 11 Oxygen and temperature on sigma-t = 15.4

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