

Oxic, Suboxic and Anoxic Conditions in the Black Sea

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Abstract

The Black Sea is the classic marine anoxic basin. It has an oxygenated surface layer overlying a sulfide containing (anoxic) deep layer. This condition has evolved because of the strong density stratification on the water column. The density stratification is strong because water with high salinity enters from the Bosphorus Strait and mixes with overlying cold intermediate layer (CIL) water that forms in the winter on the northwest shelf and in the western gyre. The rate of CIL formation is variable in response to changing climate. This mixture of Bosphorus outflow and CIL forms the Bosphorus Plume which ventilates the deep layers of the Black Sea. New data about the biogeochemical distributions (oxygen, sulfide, nitrate and ammonium) were obtained during R/V Knorr research cruises in 2001 and 2003. The distributions in the upper layers reflect a classic example of the connection between climate forcing, physical regime, chemical fluxes and biological response.

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

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1. Introduction

The Black Sea is located between latitudes 40° 55'N to 46° 32'N and longitudes 27° 27'E to 41° 42'E in the east-west depression between two alpine fold belts, the Pontic Mountains to the south and the Caucasus Mountains to the northeast.. The topography of the north western coast (except for Crimea) is relatively low. This is the world's largest semi-enclosed marginal sea with a physical and chemical structure that is determined by its hydrological balance (Caspers, 1957; Sorokin, 1983). Values for area, volume and depth are summarized in Table 1. The continental shelf is widest in the northwest but the rest of the Black Sea is surprisingly deep for a marginal sea.

The narrow (0.76 – 3.60 km) and shallow (<93 m) Bosphorus Strait provides the only pathway of water exchange between the Black Sea and the Mediterranean. The sill depths of the Bosphorus are 32-34 m at the southern end and 60 m at the northern end (Gunnerson and Ozturgut, 1974; Latif et al., 1991). The seawater that flows out of the Bosphorus Strait is the only source of salty water to the basin. Deep-water salinity values increase to $S = 22.33$. Freshwater inflow from several European rivers (especially the Danube, Dniester, Dnieper, Don and Kuban) keeps the salinity low in the surface layer ($S \approx 18.0$ to 18.5 in the central region). As a result, the water column is strongly stratified with respect to salinity, and thus density. The main water fluxes are summarized in Table 2. These values show that evaporation exceeds precipitation and that the surface outflow is about twice as large as the deep inflow through the Bosphorus. The currents in both directions are very strong.

A consequence of the vertical stratification is that the surface layer (about 0 to 50m) is well oxygenated while the deep layer (100m to 2000m) is anoxic and contains high sulfide concentrations. At the boundary between the oxic surface and anoxic deep layers, there is a suboxic zone (at approximately 50 to 100 m depth) where the concentrations of both O_2 and H_2S are extremely low and do not exhibit any perceptible vertical or horizontal gradients (Murray *et al.*, 1989; Codispoti et al, 1991).

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 layer, where O_2 and H_2S do not overlap, was first observed during the 1988 Knorr Black Sea Expedition (Murray and Izdar, 1989; Murray, 1991). Its boundaries were chosen from the vertical distribution of oxygen and sulfide observed in the central gyre. After its discovery, these distributions were confirmed by others and the processes controlling its origin and variability have been extensively discussed. When the suboxic zone was first observed Murray et al., (1989) suggested that it might be a new feature resulting from reduced fresh water input from rivers. Subsequent research has demonstrated that it is most likely a permanent feature of the Black Sea (at least since the early 1960s) (Buesseler, et al., 1994; Murray, et al., 1995) The average thickness of this zone varies several-fold on a time scale of decades (Konovalov and Murray, 2001) and this variability appears to be driven by variability in climate (Oguz and Dippner, in

press). The balance between oxygen injected due to ventilation of the thermocline with surface water 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 water of Bosporus origin is also an important control for the depth of the first appearance of sulfide (Konovalov and Murray, 2001). Redox processes involving nitrate-manganese-sulfur are important for cycling of those elements in the lower part of the suboxic zone (Oguz et al, 2001).

The Black Sea is important for geochemists for several reasons.

1. It is the classic anoxic ocean basin and is considered a prototype for the earth's ancient ocean. The ocean was considered to be initially totally anoxic. As atmospheric oxygen increased the ocean contained an oxic surface layer and anoxic deep water from about 2.5 b.y. to 0.6 b.y. (Holland, 1984; Berner and Canfield, 1989).
2. It has a well developed suboxic zone at the interface between the oxic and sulfidic layers where many important redox reactions involving Fe, Mn, N and other intermediate redox elements occur.
3. Similar redox reactions take place in sediments throughout the world's oceans but they are easier to study in the Black Sea because they are spread out over a depth scale of 10s of meters (rather than cm or mm as in sediments). The various reactions have been shown to occur on similar density (or depth) horizons from year to year, making them easy to study on repeated cruises.
4. The Black Sea is an ideal site to study the effect of climate on ocean distributions. It is of small enough scale that variability in climate can vary physical forcing and thus chemical fluxes and biological processes.

2. New data sets for the Black Sea

New hydrographic (T, S and density) and oxygen/sulfide data were collected during two R/V Knorr research cruises to the Black Sea in 2001 and 2003. The cruises were divided into multiple legs which allowed participation by 48 scientists from US, Turkey, Ukraine, Russia and Romania. One goal of these cruises was to analyze spatial and temporal variability in the suboxic zone in the southwestern part of the Black Sea in order to determine the effect of intrusion of the high salinity waters from the Bosporus on biogeochemical properties of the Black Sea (Konovalov et al., 2003). At 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) (Yakushev et al., in press). The station locations were well situated to study the continental margin areas in the SW, NW and NE regions.

Hydrographic data were obtained by standard CTD procedures using SeaBird sensors. Oxygen and sulfide were determined by both wet chemical (volumetric) and electrochemical (voltametric) techniques (Luther et al. 2002, Konovalov et al. 2003). Nutrients were analyzed using standard

autoanalyzer techniques. The vertical distribution of properties were sampled with rosette-CTD and pump profiling techniques (Codispoti, et al., 1991; Konovalov et al., 2003) Charts of station locations, tables of participants, the analyses and all data are available on the Knorr2001 and Knorr2003 web sites at

www.ocean.washington.edu/cruises/Knorr2001

and

www.ocean.washington.edu/cruises/Knorr2003 .

3. How does the Black Sea Work?

Like the open oceans the Black Sea has wind driven circulation with gyres, eddies, deep water thermohaline circulation and shallower ventilation into the thermocline. Neuman (1942) described the surface circulation of the Black Sea as consisting of two large cyclonic (counterclockwise) central gyres that define the eastern and western basins. These gyres are bounded by the wind-driven Rim Current (Oguz et al., 1998) which flows along the abruptly varying continental slope all the way around the basin. The Rim Current exhibits large meanders and filaments that protrude into the regions of the central gyres. The geostrophically calculated currents typically have speeds of 25 m s^{-1} along the axis of the Rim Current. Inshore or coastal of the Rim Current there are several anticyclonic (clockwise currents) eddies (Oguz, 2002)(**Fig. 1**). Some of these eddies are permanently controlled by topography (e.g. the Sakarya Eddy located over the Sakaraya submarine canyon) while others are more temporally and spatially variable (e.g. the Sevastopol Eddy).

The Bosphorus Strait is the only connection of the Black Sea with the Marmara Sea and the Mediterranean Sea making it the only source of salt water to the Black Sea. This salty water is also relatively warm ($\sim 15^\circ\text{C}$). The rivers are the main source of fresh water ($300 \text{ km}^3 \text{ y}^{-1}$) and mostly drain onto the NW shelf. The surface water can get relatively cold in the winter, especially on the NW shelf. On average the lower layer inflow from the Bosphorus to the Black Sea is about $300 \text{ km}^3 \text{ y}^{-1}$ and the upper layer outflow is about $600 \text{ km}^3 \text{ y}^{-1}$ which gives $300 \text{ km}^3 \text{ y}^{-1}$ for the vertically integrated transport driven by the Bosphorus inflow (Table 2).

These inputs result in strong vertical stratification with a fresh, lower density layer at the surface and a salty higher density layer in the deep water. The keys for understanding the distributions are to remember that the only source of salt (and warm) water is through the Bosphorus and the only source for cold (and fresh) water is from the surface.

The Black Sea has an estuarine type circulation which means the water flows in at depth and out at the surface. Full scale (0-2200m) salinity, potential temperature and density (σ_{θ}) are shown in **Figs. 2a, b, c**. These CTD data were obtained during a research cruise on the R/V Knorr in the center of the western gyre in May 1988 (Murray et al., 1991). Salinity increases continuously from low values of about $S = 18$ at the surface to deepwater values of over $S = 22.33$. Density (σ_{θ}) is controlled primarily by the salinity, and increases similarly. Temperature is seasonally variable at the surface and decreases with depth to a feature called the cold-intermediate layer (CIL) with a temperature minimum at about 50m (Fig. 2b). The water in this layer forms in the winter on the NW shelf and in the center of the western gyre. Its extent of replenishment varies from year to year depending on the climate (Oguz and Dippner, in press). Below the CIL the temperature increases continuously all the way to the bottom. The properties of salinity, temperature and density are extremely uniform in the deep water from about 1700m to the bottom and form a homogeneous bottom boundary layer (**Fig. 2d,e,f**) (Murray et al., 1991). The top of the layer can be identified by a sharp density step. This layer appears to be formed due to bottom heating of the Black Sea by the upward flux of geothermal heat flow (which destabilizes density) superimposed on the downward increasing salinity (which stabilizes density). The situation when the gradients of temperature and salinity have the same sign and thus opposite effects on density results in a transport process called double diffusion (Imboden and Wuest, 1995).

A temperature-salinity diagram can be used to illustrate the relationships between the distributions of temperature and salinity. The data from **Fig. 2a** are shown as a T-S plot in **Fig. 3**. The high temperature and low salinity data on the left are from water near the surface. Temperature decreases to a minimum of about 7°C in the cold intermediate layer and then both salinity and temperature increase continuously into the deep water.

When the T-S data from the Black Sea is plotted with data from the Bosphorus (which has maximum values of about $T = 15^{\circ}\text{C}$ and $S = 36$) it is apparent that, to a first approximation, the deep water of the Black Sea forms from linear two-end member mixing of the Bosphorus inflow with the cold intermediate layer. The magnitude of the Bosphorus inflow averages $350 \text{ km}^3 \text{ y}^{-1}$ but current measurements suggest large variability in response to changing local wind conditions. This implies that local synoptic meteorological conditions exert strong controls on the magnitude of transport. Numerical model results have been used to estimate short term (Oguz et al., 1990)

and longer term, decadal time scale (Stanev and Peneva, 2002) variability in transport through the Bosphorus. The net transport varies from 200 to 350 km³ y⁻¹ over decadal time scales. The cold intermediate layer has two sources that are highly variable in intensity depending on climate. The first is the shallow northwest shelf where the water gets very cold (<5.5°C) in the winter (Fig. 5)(Tolmazin, 1985a). The second site is in the central western gyre region. An example of rejuvenation of the CIL in the western gyre was observed during a series of R/V Knorr cruises from March to May, 2003. The distribution of temperature versus depth for this period of time is shown in **Fig. 6**. During the cruise in March the water had uniformly cold temperature (T = 6.1°C) from the surface to the depth (density σ_{θ} = 14.5) of the CIL (Gregg and Yakushev, in press). The relative intensity of the NW shelf and central gyre sources is probably variable on a year to year basis depending on climatic conditions.

Most of the mixing between the Bosphorus outflow and the cold intermediate layer occurs on the continental shelf just north of the Bosphorus (Tolmazin, 1985b). This can be seen in the salinity and temperature sections that extend along the axis of the Bosphorus from the Marmara Sea to the continental shelf of the Black Sea (**Fig. 7**)(Gregg and Ozsoy, 1999). Salinity and temperature is plotted versus thalweg distance which is the distance along the axis of the Bosphorus. It is measured relative to the southern entrance. The southern and northern sills are located at ~3 km and ~34 km respectively. The bottom layer with high salinity water from the Marmara Sea comes in from the south and thins as it enters the Black Sea. Salinity gradients are sharp at its upper boundary indicating mixing with overlying water. The overlying water is characterized by the temperature minimum characteristic of the CIL. This mixing results in the linear, two end-member mixing characteristics for T and S discussed earlier (Fig. 4). Most mixing occurs before the Bosphorus outflow reaches the shelf break. The resulting Bosphorus plume ventilates the interior of the Black Sea at the depth represented by its density when it reaches the shelf break (Ozsoy et al., 1993; Stanev et al., 2004). The most common mixing conditions result in ventilation of the upper 500m but there must be occasional rare ventilation events that reach the bottom. We know this because the only source for relatively warm and salty water is the Bosphorus Plume and S and T increase continuously all the way to the bottom. From the salinity balance of the deep Black Sea (50m to 2200m) the ventilating water is composed of an average CIL to Bosphorus entrainment ratio of ~ 4:1 (Murray et al., 1991). Thus, the average

composition of the Bosphorus Plume consists of a mixture of 4 parts CIL with 1 part high salinity Bosphorus inflow from the Mediterranean.

In detail this ratio must vary with depth and is higher in the upper few 100m and lower in the deeper water. Buesseler et al (1991) used Cs isotope data to estimate an entrainment ratio of 10 for depths shallower than 200m. Lee et al (2002) used chlorofluorocarbon (CFC) data to model the decrease in ventilation and increase in residence time with depth over the upper 500m. The residence times of water in different layers calculated from CFC data is shown in **Table 3**. Zone 1 includes the suboxic zone. The lower boundary of zone 10 is at about 500m. The entrainment ratio of CIL to Bosphorus inflow decreases from 9.95 in Zone 1 to 3.78 for Zone 10. The CFC residence time increases from 4.8 y to 625 y over the same interval.

The residence time of the deep water has been a subject of debate. If the Bosphorus inflow ($313 \text{ km}^3 \text{ y}^{-1}$) was the only source of water to the deep Black Sea (volume $>50\text{m} = 5.20 \times 10^5 \text{ km}^3$) the residence time would be 1,661 yr. But as the Bosphorus inflow entrains cold intermediate water in a ratio of 4:1 the correct inflow to the deep water is $313 \times 5 = 1565 \text{ km}^3 \text{ y}^{-1}$ with a corresponding average residence time for all water $>50\text{m}$ of 332 yr. A salinity balance gives the same answer (Murray et al., 1991). In detail the residence time varies with depth so this value is not incompatible with the values calculated from CFC given in **Table 3**.

^{14}C has been used to calculate an “age” of ~ 2000 yr for the deep water of the Black Sea (Ostlund and Dyrssen, 1986). The difficulty with this approach is that the age was calculated relative to an input value that was assumed to be $\Delta^{14}\text{C} = -50\text{‰}$. This is the value expected for surface seawater in equilibrium with the atmosphere in pre-nuclear times (before about 1950). Atmospheric equilibration of new surface water with ^{14}C takes on the order of 10 yrs (Broecker and Peng, 1974). If the residence time is really close to 330 yrs as calculated above and the ventilating water was composed in part of Bosphorus inflow with $\Delta^{14}\text{C} = -50\text{‰}$, the value of the ^{14}C for the CIL water entrained would have to be $\Delta^{14}\text{C} = -200\text{‰}$. In other words, The CIL would have had a $\Delta^{14}\text{C}$ value much older than expected for atmospheric equilibrium. This could occur if “old” deep water was upwelled, cooled at the surface during the winter to make CIL which was then sent back down to the deep Black Sea without coming to equilibrium with the atmosphere.

4. Biogeochemical Distributions

Because of the strong vertical stratification, the deep water is not replenished fast enough to replace the oxygen consumed by respiration of organic matter. Thus the Black Sea has an oxygen containing surface layer and a sulfide containing deep layer. An example of the oxygen and sulfide distributions versus depth and density in the center of the western gyre is shown in **Fig. 8** (R/V Knorr 2003 Leg #7, Stn #12). Oxygen is at atmospheric saturation in the upper 40m then decreases sharply to near zero by 60m. The same profiles are shown versus density in the figure on the right. Because of the surface circulation patterns discussed earlier, density surfaces are deeper around the margins and dome in the central regions. The shorthand notation is to express density as $\sigma = (\rho - 1) \times 1000$ where ρ is the density. For water with a density of $\rho = 1.016 \text{ kg m}^{-3}$ the value of $\sigma = 16.0$. Thus density is usually used as a depth coordinate in the Black Sea. All characteristic features tend to be deeper near the margins and shallower in the central gyres but almost always they fall on specific density levels. For this reason, plotting against depth in the Black Sea produces a scatter of data, but when plotted against density, the same data shows much less variability. (e.g. Codispoti et al., 1991).

The first appearance of sulfide occurs at about 90m or $\sigma = 16.15$ (**Fig. 8**) and then sulfide increases continuously to maximum values of about $380 \mu\text{M}$ by 2200m. One of the intriguing questions for the Black Sea is what is the sink for the upward flux of sulfide? Sulfide decreases to zero before the first appearance of oxygen thus sulfide is apparently not oxidized by the downward flux of oxygen. Several hypotheses have been made to explain the removal of sulfide. Millero (1991) and Luther et al (1991) suggested that Mn cycling plays an important role and that the upward flux of sulfide is oxidized by a downward flux of oxidized Mn (III, IV). Konovalov and Murray (2001) estimated that a significant amount of upward flux of sulfide is oxidized by O_2 injected horizontally by the Bosphorus Plume. Oxygen containing intrusions from the Bosphorus plume (deeper than $\sigma_t = 15.0$) are easily seen in profiles from the stations of the 2001 and 2003 KNORR cruises in the southwestern part of the sea, close to the Bosphorus (Konovalov et al, 2003).

The suboxic zone is defined as the region between where oxygen decreases to near zero ($\text{O}_2 < 10 \mu\text{M}$) and where sulfide first appears ($\text{H}_2\text{S} > 10 \mu\text{M}$) (Murray et al., 1989; 1995). This layer varies in thickness from year to year (**Fig. 9**) mostly due to climate driven variability in the

depth of complete oxygen depletion (Konovalov and Murray, 2001; Oguz and Dippner, in press). The distribution of O_2 is determined by a balance between the oxygen sink due to respiration of sinking particulate organic matter (enhanced by increasing eutrophication during the 1970s and 1980s) and the input of O_2 by ventilation of the CIL (Konovalov and Murray, 2001). Ventilation of the CIL sets the upper oxygen concentration and fundamentally determines the steepness of the vertical gradient and thus the downward flux of oxygen. The first appearance in sulfide has been much less variable with time. There was a period of the late 1980's and early 1990's, when the oxycline moved deeper (**Fig. 9**) because a series of severe winters produced favorable climate conditions (cold) for ventilating the CIL. The thickness of the suboxic zone decreased as oxygen penetrated deeper. During this period the temperature minimum (T_{min}) of the CIL was low and it moved to deeper density layers. Ventilation of the CIL was enhanced and oxygen concentrations on $\sigma_t = 15.4$ were higher. The periods of 1987 and 2001 had lower oxygen concentrations on the $\sigma_t = 15.4$ density surface and followed warm periods with less CIL formation and resulted in higher temperatures. As a result the suboxic layer became thicker. Data from the 2001 KNORR cruise (**Fig. 9**) demonstrate that the Black Sea remains highly eutrophic and will undergo further perturbations during the anticipated future warming climate conditions.

The distributions of nitrate and ammonium in the center of the western gyre (Knorr 2003; Leg #7; Stn #12) are shown versus depth and density in **Fig. 10**. Nitrate is depleted in the surface due to biological uptake. It starts to increase at 40m and reaches a maximum at 65m ($\sigma_t = 15.5$) (approximately where O_2 decreases to 0). After oxygen has decreased to zero nitrification of ammonium released from organic matter does no longer occur. Nitrate then decreases to zero at 75m ($\sigma_t = 15.95$). Ammonium starts to increase at the same depth (density) and increases progressively into the deep water. The disappearance of NO_3 and NH_4 at the same depth is consistent with a downward flux of NO_3 and an upward flux of NH_4 that are consumed over a narrow depth interval by the anammox reaction ($NO_2^- + NH_4^+ = N_2 + 2H_2O$). Note that the anammox reaction reduces NO_2^- , not NO_3^- , so there must be some denitrification that also occurs that reduces NO_3^- to NO_2^- in order for anammox to occur. Kuipers et al (2003) used 16S RNA gene sequences, RNA probes, ^{15}N label experiments and ladderane membrane lipids to show that anammox bacteria are indeed present at this level in the Black Sea. This reaction where ammonium is oxidized anaerobically to N_2 is important in the nitrogen cycle of the Black Sea

(Fuchsman et al., in press). Such a reaction has been long inferred from chemical distributions (Richards, 1965; Brewer and Murray, 1973) and is now confirmed.

The suboxic zone has interesting distributions of many other elements with redox chemistry intermediate between oxygen and sulfide. Examples include Mn, Fe (Spencer and Brewer, 1971; Spencer et al., 1972; Lewis and Landing, 1991; Tebo, 1991), arsenic and antimony (Cutter, 1991) rare earth elements (Schijf et al., 1991) and iodine (Luther and Campbell, 1991; Truesdale et al., 2001).

Methane (CH₄), which is produced after sulfate has been totally reduced in the classic redox sequence, is also high in the deep Black Sea. Initial studies of rates by Reeburgh et al. (1991) could only detect anaerobic methane consumption and the source of methane was uncertain. Recent studies have discovered numerous cold seeps of CH₄ on the NW shelf and slope that result in large plumes of CH₄ rich bubbles (C. Schubert, EAWAG, Switzerland, personal communication, 2003). The source must be CH₄ production deep in the sediments of the Danube Fan after sulfate has been reduced to zero.

Most of these redox reactions are mediated by bacteria resulting in *in situ* consumption of CO₂ (Brewer and Murray., 1973; Yilmaz et al., in press)). Chemosynthetic bacteria that grow on carbon dioxide and water get their energy from reduced compounds like H₂S, NH₄, Mn(II), Fe(II) and CH₄. In addition, the discovery by Repeta et al, (1989) of high concentrations of bacteriochlorophyll (BChl) e in the suboxic zone suggests that anoxygenic photosynthesis occurs (Jorgensen et al., 1991). This is surprising because the light availability at these depths (<4 mEinst m⁻² s⁻¹) is equal to between 0.0005% to 0.00005% of the surface irradiance (Overmann et al., 1992). The BChl e is associated with brown phototrophic *Chlorobium* bacteria. These bacteria are obligate phototrophs and compete with other bacteria under conditions of severe light limitation. They require light and sulfur. Their growth rates are extremely slow and their calculated doubling times are on the order of 2.8 yrs but somehow they maintain their existence. The role these bacteria play in elemental cycling is still unclear.

The density values that were characteristic of many water column features during the 1988 Knorr Expedition are shown in **Table 4**. These values have served as a benchmark for subsequent cruises to evaluate the stability of the redox features. There has been some variability from place to place and time to time but the general picture has remained the same.

5. Organic matter preservation

The conditions that control the preservation, accumulation and burial of organic matter has been the focus of considerable debate. Central to this controversy is whether there is enhanced preservation of organic matter under oxic versus anoxic conditions. One theory is that anoxic decomposition of organic matter is intrinsically slower than oxic decomposition. Lee (1992) conducted lab experiments that showed there was little difference in the rates of decomposition of specific types of organic compounds (e.g. amino acids, carbohydrates) under oxic versus anoxic conditions. Several geochemical studies (e.g. Pederson and Calvert, 1990; Calvert et al., 1992; Ganeshram et al., 1999) have argued that organic matter preservation is not enhanced by anaerobic conditions. Hartnett et al (1998) suggested that the organic matter preservation efficiency is inversely correlated with the length of time organic matter is exposed to O₂ before burial under anoxic conditions. In the Black Sea oxygen exposure time is minimal as sinking particles reach anoxic conditions just below the euphotic zone. Finally, a comparison of organic carbon preservation in sediments off Washington State and off Mexico led to the conclusion that oxygen rather than carbon input controls the extent of preservation (Hartnett and Devol, 2003). So this debate continues but we do know from observations that wooden ship wrecks are better preserved in the anoxic layer than the oxic layer of the Black Sea (Ballard et al., 2001). The anoxic conditions in the Black Sea do enhance the preservation of archaeological remains.

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Table 1 Physical characteristics of the Black Sea

Total area	423,000 km ²
Area of Northwest Shelf	101,600 km ²
Total volume	534,000 km ³
Deep water volume (>50 m)	520,000 km ³
Depth of Permanent Halocline	50 to 200 m
Maximum Depth	2243 m

Table 2 Present Day Water Fluxes of the Black Sea

River input	350 km ³ y ⁻¹
Danube River	250 km ³ y ⁻¹
Dniester	8
Dnieper	51
Don	28
Kuban	12
Precipitation	300 km ³ y ⁻¹
Evaporation	353 km ³ y ⁻¹
Bosporus outflow to Black Sea	313 km ³ y ⁻¹
Average Salinity = 34.9	
Temperature = 14.5° C - 15.0° C in summer	
= 12.5° C – 13.5° C in winter	
Bosporus outflow to Marmara Sea	610 km ³ y ⁻¹
Slope of water surface along the Bosporus from north to south	35 cm
Current Velocities (surface)	~ 2 m s ⁻¹
(deep)	~0.5 ms ⁻¹ (but reaching ~1.5 m s ⁻¹ over sills)

Table 3 Entrainment ratios (CIL/Bosporus outflow) and Residence times of water in different density intervals determined using CFC data (from Lee et al., 2002)

Zone	Density Interval	Entrainment Ratio	Residence Time (y)
1	15.450 – 16.178	9.95	4.8
2	16.178 – 16.451	5.73	12.5
3	16.451 – 16.610	4.93	21.1
4	16.610 – 16.717	4.55	30.8
5	16.717 – 16.799	4.32	44.4
6	16.799 – 16.858	4.10	59.7
7	16.858 – 16.910	4.03	85.1
8	16.910 – 16.950	3.91	129
9	16.950 – 16.986	3.84	235
10	16.986 – 17.016	3.78	625

Table 4 Characteristic density values of features associated with the biogeochemistry of the Black Sea. The uncertainty of each value is about 0.05 density units.

Feature	Density (σ_{θ})
PO₄ shallow maximum	15.50
O₂ < 10 μM	15.70
NO₃ maximum	15.40
Mn_d < 200 nM	15.85
Mn_p maximum	15.85
PO₄ minimum	15.85
NO₂ maximum	15.85
NO₃ < 0.2 μM	15.95
NH₄ > 0.2 μM	15.95
Fe_d < 10 nM	16.00
H₂S > 1 μM	16.15
PO₄ deep maximum	16.20

Figure 1 Chart of the Black Sea showing the wind-driven counter clockwise (cyclonic) Rim Current and several of the main anticyclonic gyres. The northwest shelf and Rim Current are indicated.

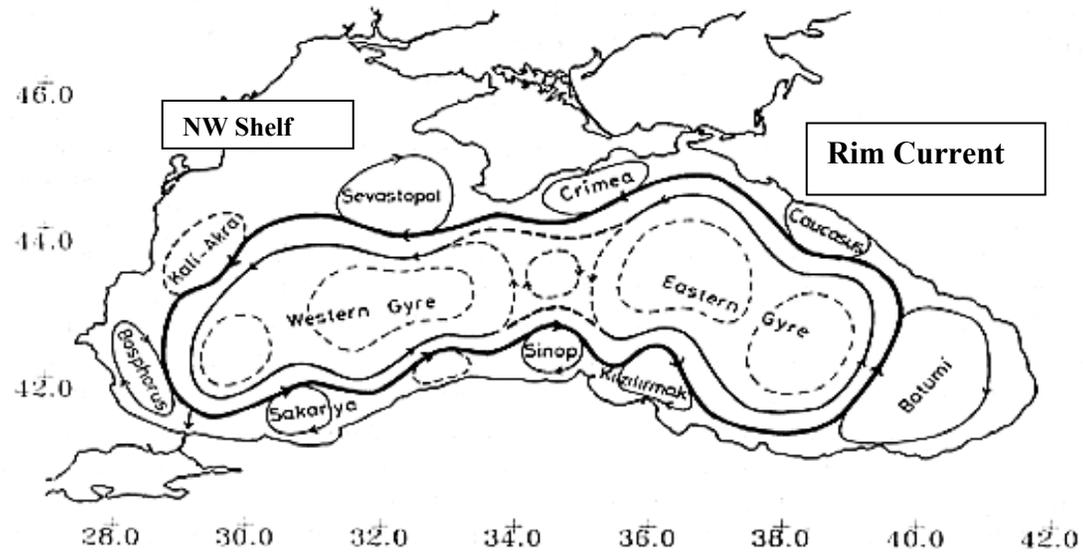


Figure 2 Salinity, potential temperature and density (sigma-theta) from R/V Knorr 1988 Stn# BS3-2 HC-20 the Black Sea.
a, b, c) Full scale water column 0 – 2200m **d,e,f)** Expanded scale to illustrate bottom boundary layer
 (from Murray et al., 1991)

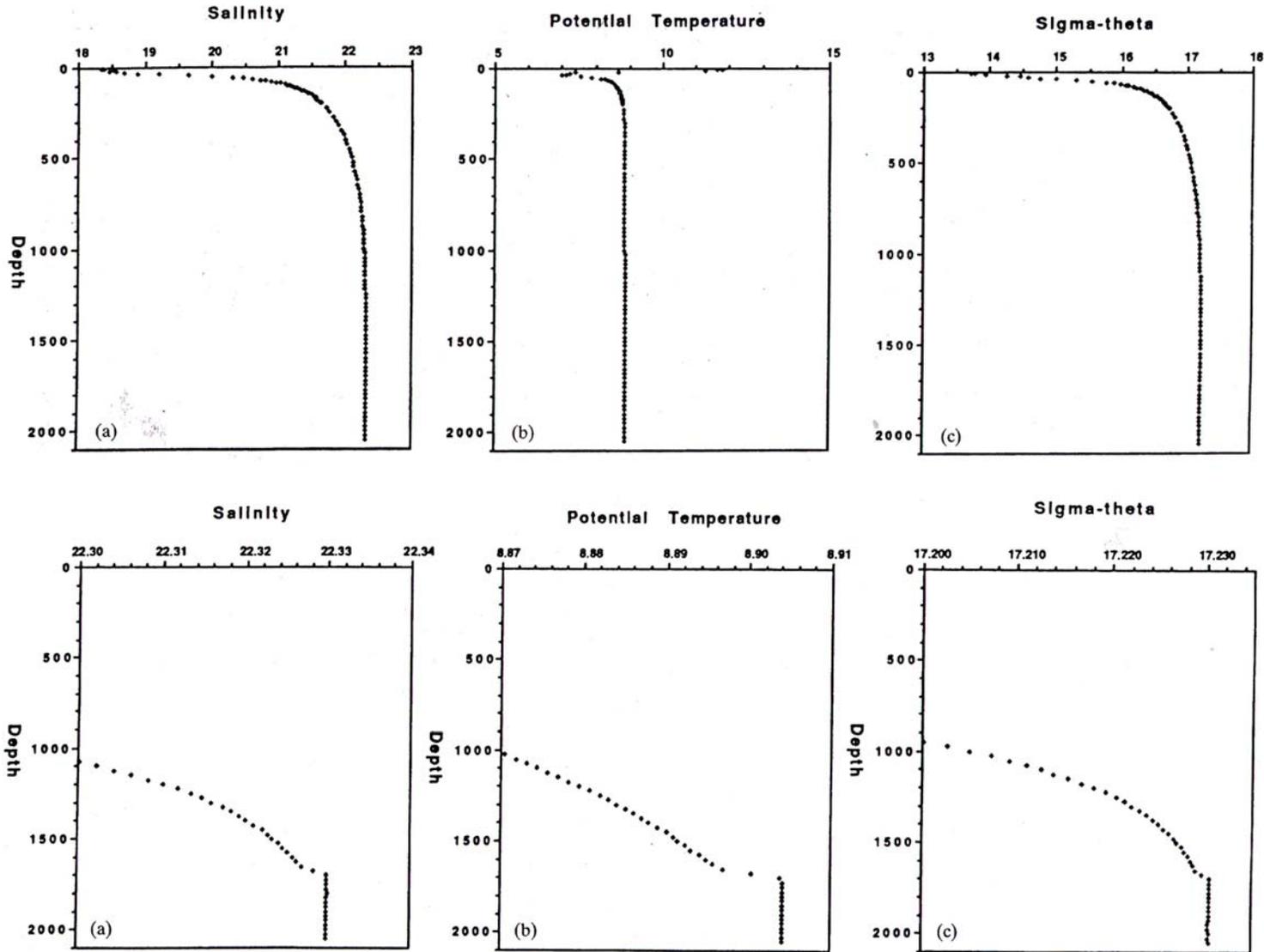


Figure 3 Potential temperature-salinity diagram for the center of the western basin (R/V Knorr 1988 Stn# BS3-2 HC-20)(from Murray et al., 1991)

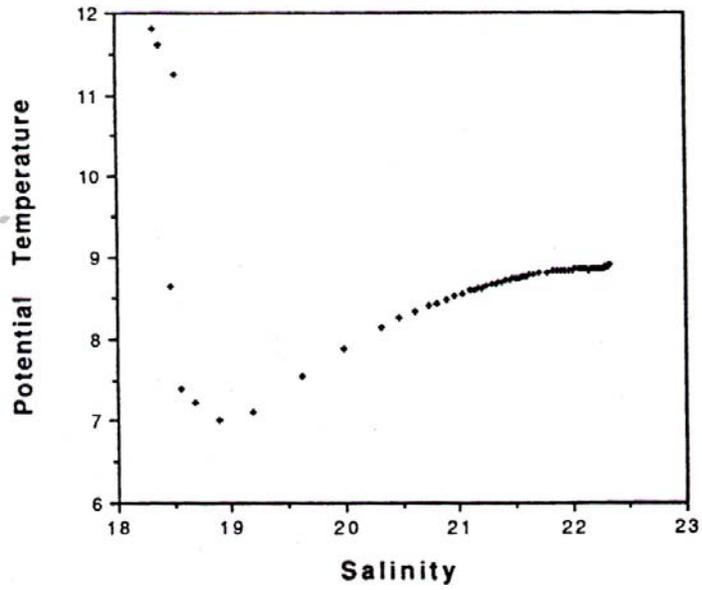


Figure 4 T-S data from the Black Sea and the Bosphorus plotted together (from Murray et al., 1991)

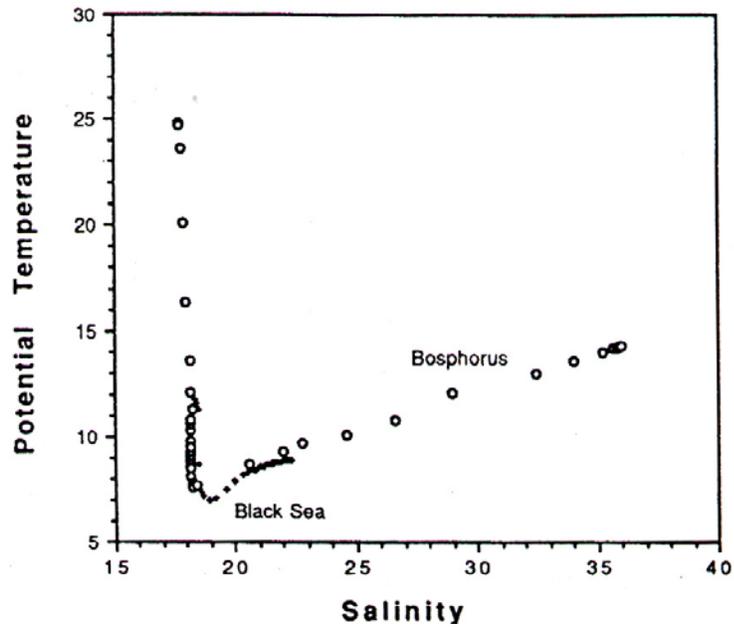


Figure 5 Isotherms in the cold intermediate layer for spring (from Tolmazin, 1985a). The lowest temperatures are in source area on the NW shelf.

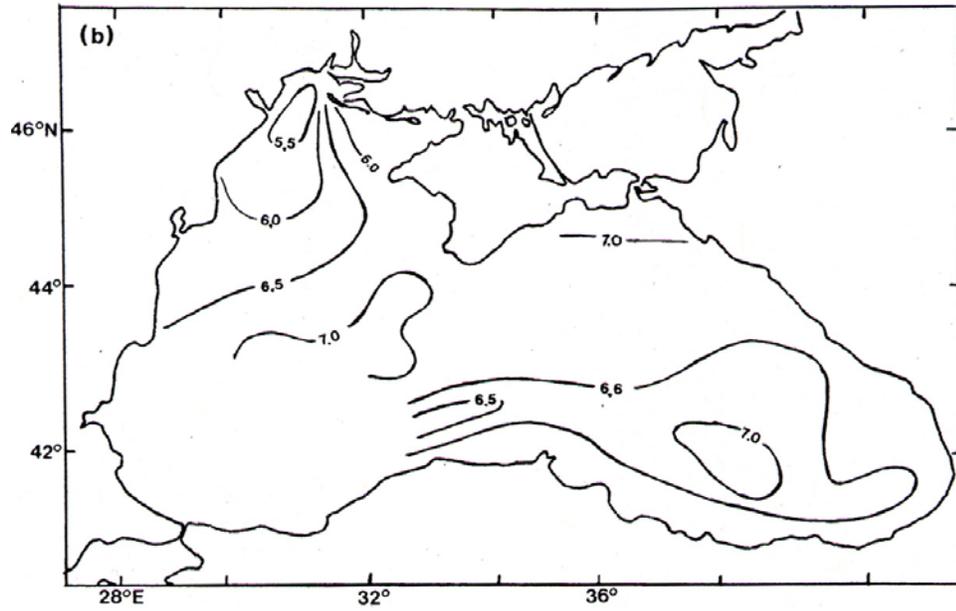


Figure 6 Temperature versus depth at the same location in the center of the western gyre of the Black Sea in March-May 2003. The legend gives the R/V Knorr Leg and date of the CTD casts. The chief scientists were Mike Gregg (UW) for Leg 5, James Murray for Leg 7 and George Luther for Legs 8 and 9.

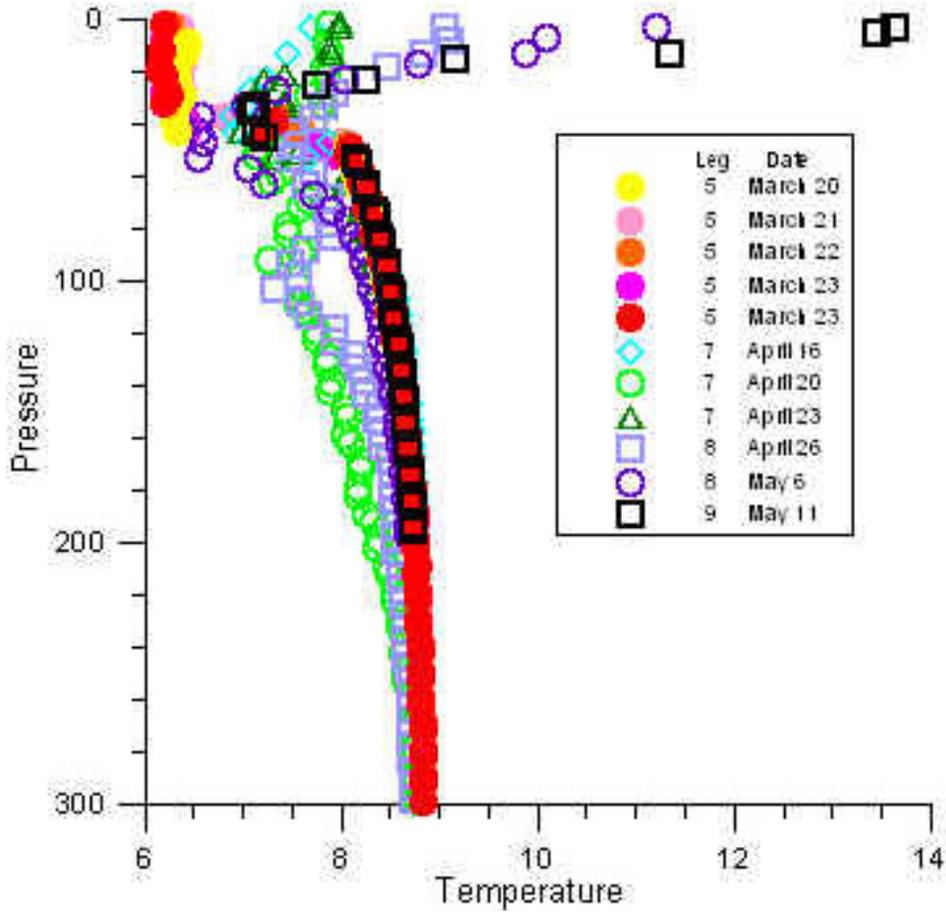


Figure 7 Section of salinity (left) and temperature (right) along the axis of the Bosphorus. The bottom topography is shown. The depth scale is from 0 to 100m. The southern entrance of the Bosphorus is at a thalweg distance of 0. The outflow into the Black Sea occurs at 34km. the southern and northern sills are seen at 4 km and 34km, respectively. The high salinity water from the Marmara Sea ($S > 37$) comes in from the south at the bottom. The temperature minimum of the CIL can be seen at about 40m north of the Bosphorus on the shelf of the Black Sea. From Gregg and Ozsoy (1999)

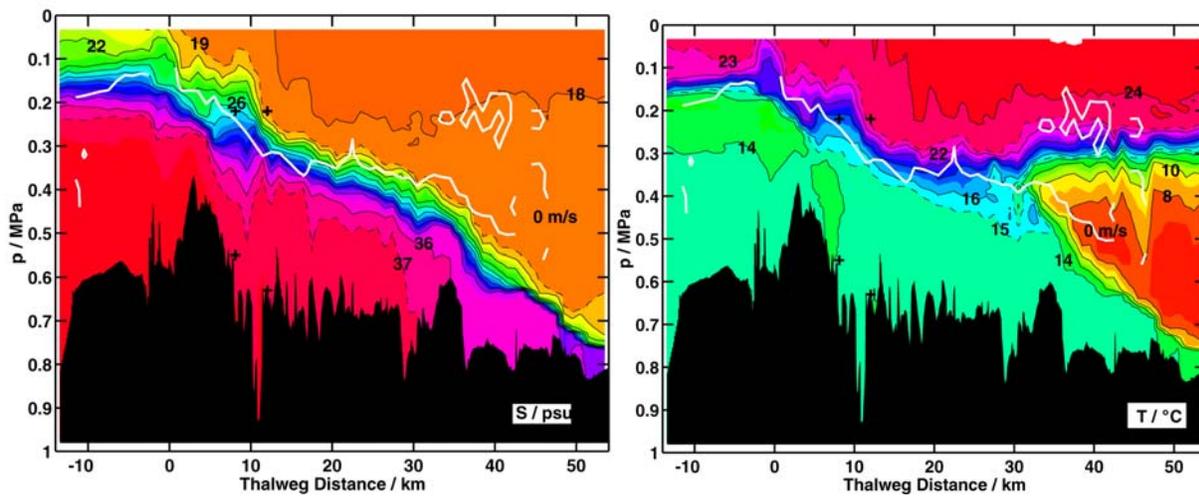


Figure 8 Oxygen and sulfide data from the center of the western gyre (Leg 7; Stn 12) during R/V Knorr 2003. The data are courtesy of G. Luther (U. Delaware) and S. Konovalov (MHI, Sevastopol, Ukraine). Depth on the left and density on the right.

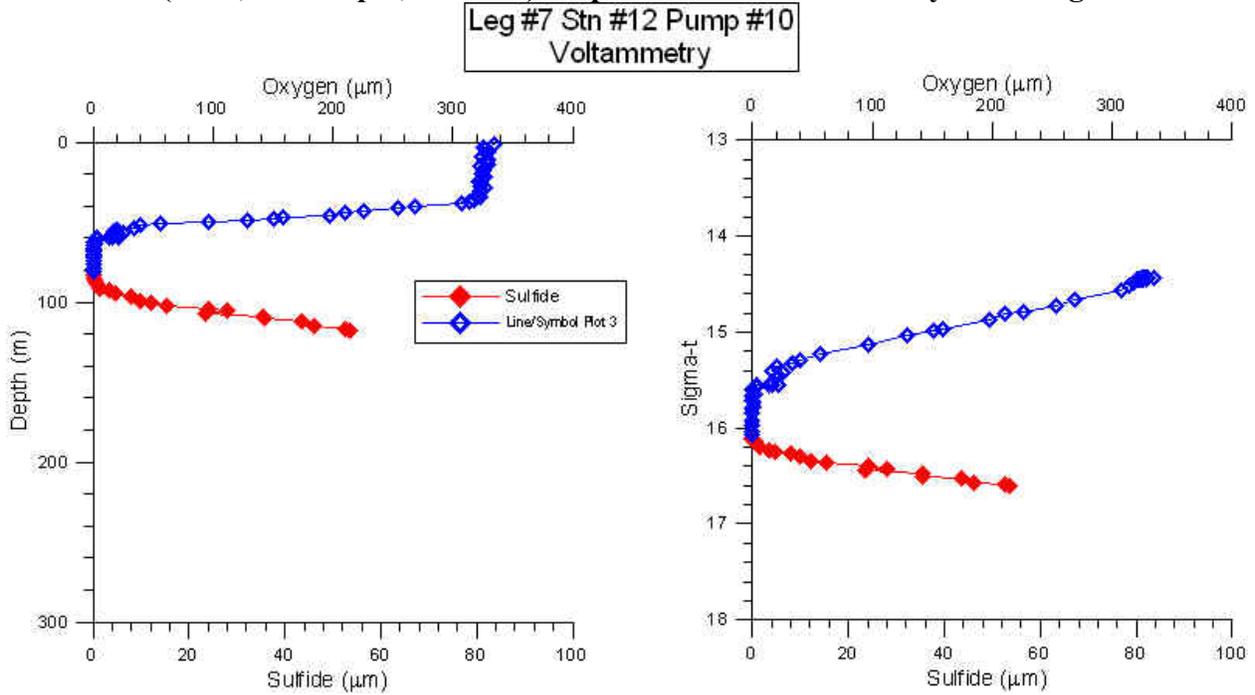


Figure 9 Temporal variability in the distribution of oxygen and sulfide versus sigma-t from 1961 to the present (from Konovalov and Murray, 2001). In this example the suboxic zone is the region between $\text{O}_2 < 10\mu\text{M}$ and $\text{H}_2\text{S} < 5\mu\text{M}$.

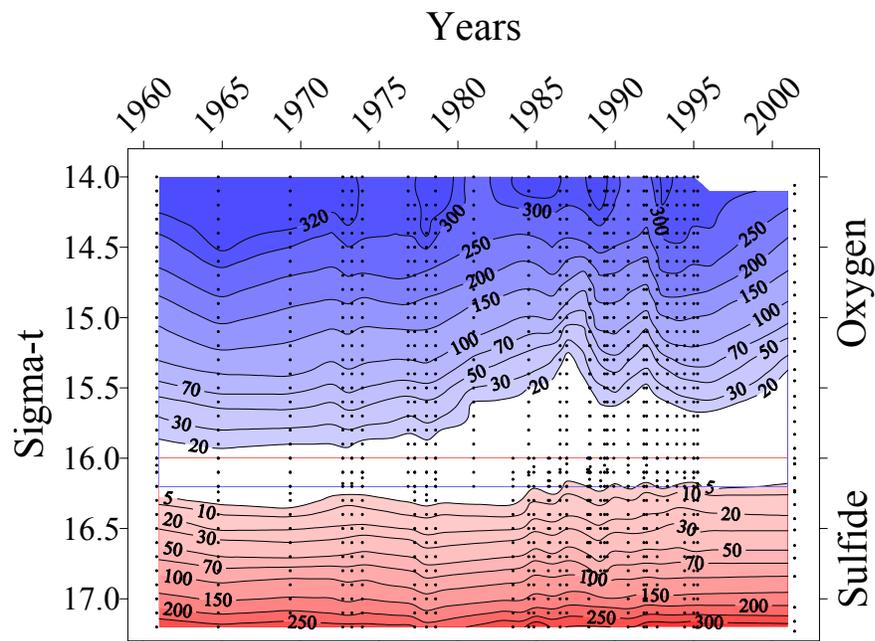


Figure 10 Nitrate and ammonium from the center of the western gyre (Leg 7; Stn 12) during R/V Knorr 2003. Depth on the left and density on the right.

