



Stability of the oxic–anoxic interface in the Black Sea

K. O. BUESSELER,* H. D. LIVINGSTON,* L. IVANOV† and A. ROMANOV†

(Received 1 December 1992; in revised form 4 June 1993; accepted 4 June 1993)

Abstract—We have examined the position of the oxic, suboxic and anoxic interfaces in the Black Sea between 1965–1992. It appears as if the suboxic zone (i.e. depths where DO and $\text{H}_2\text{S} < 5 \mu\text{M}$) has been a common feature throughout the Black Sea, and only recently been observed due to advances in sampling and analytical procedures. The upper boundary of the suboxic zone is identified based upon a minimum in the PO_4 profile at a density of $15.95 \sigma_t$. The lower boundary at $16.20 \sigma_t$ is identified by the onset of H_2S . These densities show seasonal and interannual variations of the order of $0.05\text{--}0.10 \sigma_t$, but no directional trend over the past 2–3 decades. The position of the suboxic zone is consistent with $T\text{--}S$ data. Large variations in $T\text{--}S$ characteristics are seen between years and seasons above the suboxic layer, as ventilation is quite rapid. Below the $\text{DO} < 5 \mu\text{M}$ horizon, entrainment processes bring surface water to depth, thus forming a suboxic layer as DO and H_2S are consumed. $T\text{--}S$ characteristics vary slightly below $16.2 \sigma_t$, and are constant below $17.0 \sigma_t$, indicating that these waters are ventilated less frequently.

INTRODUCTION

MANY recent studies of the Black Sea conclude that there have been systematic changes in recent decades in the depth and structure of the boundary between oxic and anoxic waters (TOLMAZIN, 1985; FASHCHUK and AYZATULLIN, 1986; BRYANTSEV *et al.*, 1988; MURRAY *et al.*, 1989; MURRAY and IZDAR, 1989). These reports have received considerable attention, as it is primarily the unique biological and geochemical processes which occur at such an interface, which draw oceanographers to this basin. In order to interpret new findings, in particular those which are based upon comparisons to previous data, one needs at least some understanding of temporal changes and stability of the Black Sea chemocline. Furthermore, for the countries surrounding the Black Sea, any shoaling in the depth of anoxia (currently at approximately 100 m in the central gyres) might have a dramatic impact on fisheries and other activities in the surface waters (MEE, 1992).

In this paper, we focus on two recent claims: first, that there has been a shoaling of the oxic–anoxic interface (FASHCHUK and AYZATULLIN, 1986; BRYANTSEV *et al.*, 1988; MURRAY *et al.*, 1989), or at least a change in the temperature and salinity balance in the upper waters; and secondly, whether or not the “suboxic zone” [i.e. the depth interval between the depletion of dissolved oxygen (DO) and the onset of hydrogen sulfide (H_2S)], is a new feature in the Black Sea (MURRAY *et al.*, 1989). We use a combination of historical data and new results to examine these issues. We take a similar approach to TUGRUL *et al.* (1992) and

*Woods Hole Oceanographic Institution, Woods Hole, MA 02543, U.S.A.

†Marine Hydrophysical Institute of Ukrainian Academy of Science, Sevastopol, Ukraine.

SAYDAM *et al.* (1993) by using nutrient profiles for the identification of the density of the oxic–anoxic interface. Ultimately, we feel that both the structure and depth of the chemocline are largely determined by physical processes which transport surface waters to depth. Changes in the chemocline are therefore linked to ventilation rates and the balance of salt and water in the Black Sea.

To begin this discussion, some background on previous studies is needed, and the sampling and analytical methods used. We choose to present the data on the suboxic zone first, as our discussion on the separation in the depth of oxygen depletion and sulfide onset provides background information for examining historical data on the depth and density of the Black Sea chemocline.

BACKGROUND

Anoxia in Black Sea deep waters is thought to be maintained by restricted mixing across a shallow density gradient, and oxidative consumption of organic matter derived from surface waters. A first order deep water residence time of approximately 1500 years can be calculated, based upon a simple balance between the inflow of Mediterranean water through the Bosphorus ($312 \text{ km}^3 \text{ y}^{-1}$; LATIF *et al.*, 1991) and the volume of the anoxic deep waters ($4.65 \times 10^5 \text{ km}^3$ —below 100 m). These long apparent residence times, coupled with a relatively linear *T–S* gradient across the pycnocline, have led many previous researchers to treat the pycnocline as a stable diffusive boundary between surface oxic and deep anoxic waters. For example, steady state, vertical advection diffusion models have been applied to quantify the redox coupled fluxes of dissolved Fe and Mn across the oxic–anoxic boundary in the Black Sea (SPENCER and BREWER, 1971; BREWER and SPENCER, 1974; LEWIS and LANDING, 1991).

Accompanying the sharp pycnocline in the Black Sea is a strong chemocline. The chemocline is most often defined by a decrease in oxygen concentration below detection, and the onset of increasing hydrogen sulfide concentrations at depth, i.e., the oxic–anoxic interface. In much of the earlier literature, scientists reported that a stable region existed at depth where oxygen and sulfide overlapped by as much as 10–50 m (for example, FASHCHUK and AYZATULLIN, 1986). Given that reduced sulfide is unstable in the presence of oxygen, this so-called “*S*-layer” (also translated from Russian as “*C*-layer”) suggested relatively long residence times (days) for *in situ* sulfide oxidation rates, and/or extremely rapid mixing across the pycnocline. Many reports can also be found however where the depth of oxygen zero and sulfide onset were found to be identical (for example, SPENCER and BREWER, 1971), suggesting that the “*S*-layer” was not a common feature.

Oceanographic water sampling techniques have made great strides over the past 3 decades. Much of the data to be compared here was obtained using either discrete bottle casts using wire mounted samplers (pre-1980), or sampling casts made using Rosette mounted bottles in conjunction with CTDs (1980s), or most recently, using high resolution pumping systems (late 1980s). All discrete water samplers are limited somewhat in vertical resolution by ship’s motion and bottle design. Sample resolution of less than 5 m is difficult using wire mounted bottles, but more commonly, earlier Black Sea studies (for example, R.V. *Atlantis II*, 1969) used sample spacings of 20–50 m across the chemocline. Rosette–CTD based sampling systems allow for the collection of essentially continuous profiles of salinity, temperature and pressure, as well as the collection of water samples from bottles, limited again by the flushing characteristics of the bottles and the number of depths chosen

to sample. Finally, high resolution water sampling for chemical or biological measurements has now been reported using a deck mounted pumping system (± 1 m in calm weather; FRIEDERICH *et al.*, 1990; CODISPOTI *et al.*, 1991).

When comparing the depth of a given chemical feature using modern and older data, one must be careful to consider vertical sample resolution in addition to analytical detection capability. For example, the depth of sulfide onset was determined to within 1–2 m in 1988, above a detection limit of $1 \mu\text{M}$ sulfide (FRIEDERICH *et al.*, 1990). Earlier data from 1969 had a sample resolution between the last bottle with zero sulfide and the first bottle with detectable sulfide of tens of meters. In this manner, if one looks at earlier data and plots only the depth or density of H_2S onset, it is necessarily deeper than modern data where one has higher resolution and better analytical sensitivity.

One way to successfully increase relative vertical resolution using earlier data sets, is to compare a given property at multiple sites vs density, or relative to the depth of oxygen zero (BREWER and SPENCER, 1974; CODISPOTI *et al.*, 1991; TUGRUL *et al.*, 1992). While the Black Sea pycnocline is generally dome shaped, and deeper at the margins, many features show quite strong lateral homogeneity along isopycnal surfaces (CODISPOTI *et al.*, 1991; LEWIS and LANDING, 1991; TUGRUL *et al.*, 1992; MURRAY *et al.*, 1993). Thus, combining data from many sites along isopycnal surfaces allows refinement of the shape of a given profile or density of a given feature.

Finally, when comparing historical and more recent data, the different analytical techniques must be taken into account. In our analysis, we will focus on historical measurements of sulfide, and on the correlation between nutrient profiles and precisely determined low oxygen levels. With regard to the measurement of oxygen, most of the earlier data were gathered from discrete bottle samples using the Winkler method. While this method is adequate in most oceanic environments, at low oxygen concentrations ($< 20 \mu\text{M}$) alternative procedures, such as the method of BROENKOW and CLINE (1969), are generally preferred. As suggested by GRASSHOFF (1975) and more recently by CODISPOTI *et al.* (1991), the greatest problem with much of the earlier oxygen data is that water samples collected from the anoxic zone are easily contaminated with atmospheric oxygen upon retrieval. This will tend to produce low oxygen artifacts in waters that were initially anoxic. This artifact is most likely to be seen in the oxygen data from the suboxic zone, because in more highly sulfidic deep waters, small amounts of atmospheric oxygen entering the sampling bottle would be consumed by the oxidation of the more abundant sulfide.

SUBOXIC ZONE

The suboxic zone was clearly evident in 1988, when CODISPOTI *et al.* (1991) used a continuous pumping sampler and low oxygen techniques to sample across the Black Sea chemocline. The data shown here [Fig. 1(a)] are for a central basin site sampled in July. This station had the highest resolution oxygen data for the R.V. *Knorr* cruises in 1988. At a density around $15.5 \sigma_t$, oxygen decreases dramatically [see break in oxygen scale—Fig. 1(a)], and waters above this isopycnal surface are thought to be ventilated on at least an annual basis (BUESSELER *et al.*, 1991). Given the definition of the suboxic zone first proposed by MURRAY *et al.* (1989), being those waters where both oxygen and sulfide are present at concentrations $< 5 \mu\text{M}$, the data suggest an upper boundary of $15.9 \sigma_t$ and a lower boundary of $16.3 \sigma_t$ for the suboxic zone at this site in 1988. This is equivalent to a separation of 30–45 m in the central Black Sea. When comparing this work to other

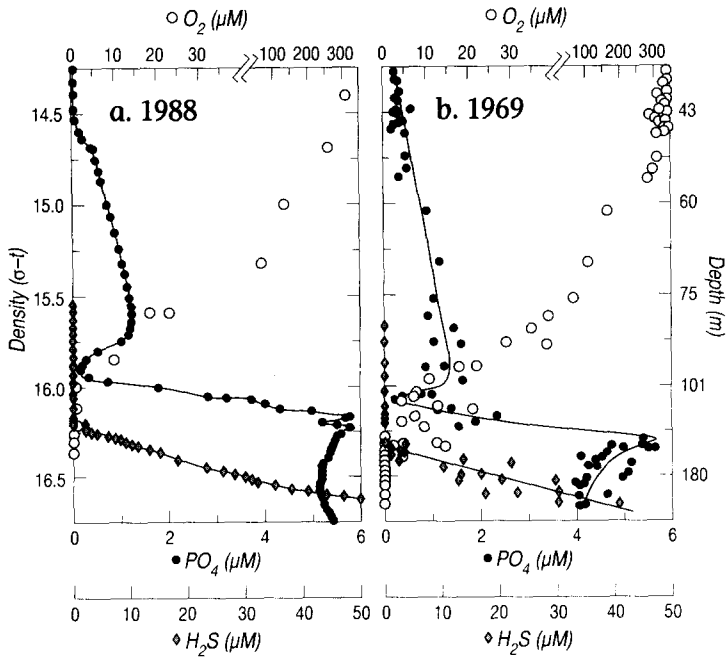


Fig. 1. Profiles of oxygen (O_2 —open circles), phosphate (PO_4 —solid circles) and sulfide (H_2S —gray diamonds), all in units of μM and plotted relative to density (σ_t). (a) Is from a single central basin site sampled on 18 July 1988 ($43\ 05^\circ N$, $34\ 00^\circ E$; R.V. *Knorr* cruise 5, Sta. 2, pumpcast 2). (b) Is a composite profile from mid basin sites ($z > 2000$ m) sampled in April 1969 (Stas 1444, 1445, 1446, 1461, 1462, 1464, 1474 and 1480; R.V. *Atlantis II*). Original data and methods can be found in FRIEDERICH *et al.* (1990) for (a) and BREWER (1971) for (b).

discussions on the suboxic zone and density of these boundaries (such as VINOGRADOV and NALBANDOV, 1990; TUGRUL *et al.*, 1992; MURRAY *et al.*, 1993), it is important to keep the detection limit used to define these boundaries in mind, as a shift in $5\ \mu M$ concentration in DO or H_2S is equivalent to $0.1\ \sigma_t$, or 10–20 m in the central gyres.

All of the profiles in Fig. 1 are plotted vs density rather than depth, and focus on densities below the seasonally stratified mixed layer, down to the base of the permanent pycnocline (14.75 – $16.75\ \sigma_t$, or approximately 30–300 m). This scaling relative to density allows one to clearly see the sharp vertical chemical gradients across the pycnocline. More importantly, since sulfide, oxygen, and the nutrients exhibit strong homogeneity along isopycnal surfaces, this plot is thus characteristic of all R.V. *Knorr* deep water stations (water depths > 2000 m). For example, the standard deviation in the σ_t of H_2S onset during the 1988 R.V. *Knorr* cruises is only $0.035\ \sigma_t$ ($n = 16$; Table 1).

The corresponding temperature and salinity data for this station are plotted in Fig. 2(a) vs density and in Fig. 2(b) vs depth. Also plotted in Fig. 2(a) is the Brunt Väisälä frequency. The Brunt Väisälä frequency is related to the strength of vertical density stratification ($\partial\rho/\partial z$), and is calculated from

$$N^2 = \frac{g}{\rho} \cdot \frac{\partial\rho}{\partial z}$$

A minima in N^2 is seen at $14.7\ \sigma_t$ at the temperature minima which forms the core of the

Table 1. Densities of the phosphate minimum and sulfide boundary in the Black Sea

| Date | σ_t for PO ₄ min | | | σ_t for H ₂ S > 0 | | | $\Delta\sigma_t$ | Source |
|------------------|------------------------------------|------------|-----|-------------------------------------|------------|-----|------------------|--|
| | X | σ_n | n | X | σ_n | n | | |
| March–April 1969 | 16.05 | 0.05 | 8 | 16.30 | 0.05 | 8 | 0.25 | R.V. <i>Atlantis II</i> |
| October 1985 | 16.07 | 0.09 | 15 | 16.30 | 0.10 | 15 | 0.23 | R.V. <i>M. Lomonosov</i> , Cruise 44 |
| April–May 1988 | 15.92 | 0.15 | 23 | 16.21 | 0.09 | 23 | 0.29 | R.V. <i>Prof. Kolesnikov</i> , Cruise 18 |
| May 1988 | 15.87 | 0.05 | 4 | ND | ND | | | R.V. <i>Knorr</i> , Cruise 2 |
| June 1988 | 15.89 | 0.03 | 10 | 16.16 | 0.03 | 10 | 0.27 | R.V. <i>Knorr</i> , Cruise 3 |
| June 1988 | 15.93 | 0.04 | 2 | 16.12 | 0.03 | 2 | 0.19 | R.V. <i>Knorr</i> , Cruise 4 |
| July 1988 | 15.84 | 0.05 | 3 | 16.19 | 0.03 | 4 | 0.35 | R.V. <i>Knorr</i> , Cruise 5 |
| Nov.–Dec. 1989 | 16.01 | 0.14 | 29 | 16.21 | 0.12 | 29 | 0.20 | R.V. <i>M. Lomonosov</i> , Cruise 51 |
| Sept.–Oct. 1990 | 15.98 | 0.15 | 10 | 16.19 | 0.09 | 10 | 0.21 | R.V. <i>M. Lomonosov</i> , Cruise 53a |
| Nov.–Dec. 1991 | 15.92 | 0.10 | 31 | 16.27 | 0.05 | 31 | 0.34 | R.V. <i>M. Lomonosov</i> , Cruise 54 |
| July 1992 | 15.93 | 0.10 | 54 | 16.19 | 0.05 | 54 | 0.26 | R.V. <i>Prof. Kolesnikov</i> , Cruise 29 |
| October 1992 | 15.95 | 0.05 | 16 | 16.16 | 0.05 | 16 | 0.21 | R.V. <i>M. Lomonosov</i> , Cruise 55 |

σ_t = sigma t ; X = mean σ_t value; σ_n = standard deviation; n = number of stations; $\Delta\sigma_t$ = density difference between PO₄ minimum and H₂S > 0 boundaries.

Cold Intermediate Layer (CIL). The maxima in N^2 below the CIL is related to the upper boundary of the pycnocline around $14.8 \sigma_t$. These values and the shape of the Brunt Väisälä frequency curve are typical of the Black Sea, and similar to values reported by BREWER (1971) and MURRAY *et al.* (1991).

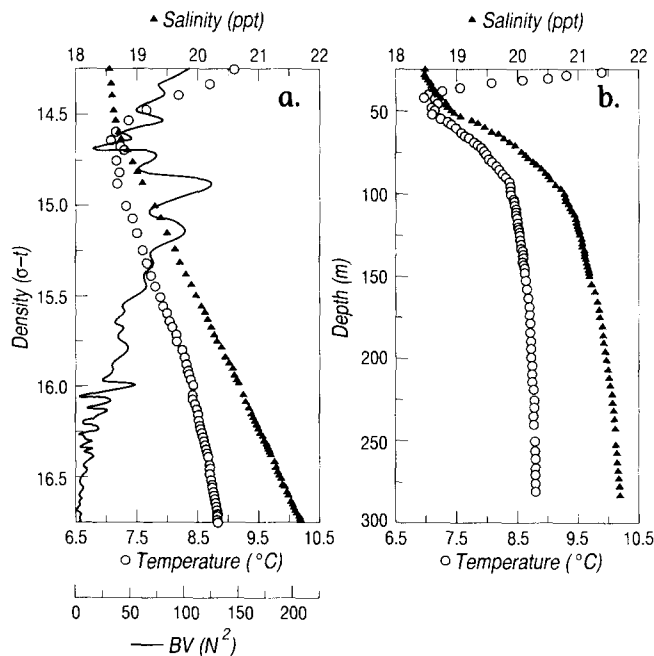


Fig. 2. Profiles of temperature (open circles), salinity (filled triangles) and the Brunt Väisälä frequency [solid line; plotted as N^2 (h^{-1})—see text] relative to density (a) and depth [T – S only—(b)]. Data are for the same site as in Fig. 1(a) (1988 R.V. *Knorr* cruise 5, pumpcast 2).

Returning to the DO and H₂S profiles, a comparison with the profile of PO₄ can be made [Fig. 1(a)]. Phosphate is low in surface waters, increases to a weak maximum around σ_t 15.7, drops to a sharp minimum at 15.9, and peaks again just above the onset of sulfide. The PO₄ minima is thought to be formed due to PO₄ removal which accompanies the formation of insoluble oxides of Mn and Fe just above oxygen zero (SHAFFER, 1986; CODISPOTI *et al.*, 1991). Using the dissolved Mn and Fe concentration data from 1988 (found in LEWIS and LANDING, 1991), it has been shown that both Mn and Fe are highly correlated in the suboxic zone (SHOLKOVITZ, 1992). As such, it is difficult to separate the formation of Mn or Fe oxides as the controlling mechanism for the removal of PO₄. Both dissolved Mn and Fe increase below 15.9 σ_t in the central gyres of the Black Sea (LEWIS and LANDING, 1991) and the PO₄ minimum at this interface is clearly linked to this same redox boundary. This PO₄ minimum is sometimes absent in coastal regions, and high vertical resolution sampling around 16.0 σ_t is required to see this sharp PO₄ minimum.

TUGRUL *et al.* (1992) and SAYDAM *et al.* (1993), used a similar approach to show that the nitrate maximum at 15.4 σ_t corresponds quite well with the depth of DO = 10–20 μ M throughout the R.V. *Knorr* data set as well as during recent Soviet and Turkish cruises in 1987–1991. We have chosen to focus on the PO₄ minima as a proxy for the oxygen interface, rather than the nitrate maxima, as the PO₄ minima coincides more closely with the definition MURRAY *et al.* (1989) originally proposed for the upper boundary of the suboxic zone (i.e. DO < 5 μ M). By using the PO₄ minimum as an indicator of the anoxic boundary, we can ignore the less reliable oxygen data sets, when comparing the 1988 results to other Black Sea data.

We use the results from the 1969 cruise of the R.V. *Atlantis II* [Fig. 1(b)] to provide evidence for the existence of a suboxic zone 20 years prior to the R.V. *Knorr* cruises. For this analysis, we have combined data along isopycnal surfaces from several central basin sites in order to better define the shape of the vertical profiles (see Background section). As pointed out by TUGRUL *et al.* (1992), we have also corrected the R.V. *Atlantis II* salinity data by –0.065 psu, and recalculated the R.V. *Atlantis II*'s σ_t values. This offset is relatively constant between the suboxic zone and deep waters, and was suggested by TUGRUL *et al.* (1992) since R.V. *Atlantis II* bottom water densities were systematically denser than all other modern data sets. Even without this correction, the arguments presented below would suggest a relative separation of 0.25 σ_t units between the isopycnal surfaces where O₂ and H₂S concentrations are < 5 μ M.

In 1969, considerably more scatter in all of the concentration profiles can be seen relative to more recent studies [compare Fig. 1(a) and (b)]. This is due to analytical limitations at the time, as well as to the uncertainty generated by combining data from different stations along isopycnal surfaces. Since the density gradient is still quite sharp in the lower part of the pycnocline, any error in *T* or *S* in these earlier data sets will create additional scatter when concentration data from different stations are plotted vs density.

In the 1969 data, sulfide concentrations increase above 5 μ M below a density surface of approximately 16.30. Oxygen concentrations decrease sharply below 15.5 σ_t . A steep oxygen gradient is seen between 30 and 10 μ M, below which the oxygen data begin to scatter (at concentrations between 5 and 15 μ M) until the H₂S zone is reached. An earlier interpretation of this data was that the depth of sulfide onset and oxygen zero coincided, at a density of 16.30 (corresponding to uncorrected σ_t units of 16.4 in earlier literature, e.g. BREWER, 1971). In contrast, we would argue that the scatter in DO below 10–20 μ M is due to sampling and analytical artifacts, and that by following the decreasing trend in O₂

concentration between $30\ \mu\text{M}$ and $10\ \mu\text{M}$, one would place the true $\text{DO} < 5\ \mu\text{M}$ boundary at $16.1\ \sigma_t$.

As suggested from the 1988 data, we can also ignore the R.V. *Atlantis II* oxygen data completely, and use the PO_4 minima to define the $\text{DO} < 5\ \mu\text{M}$ boundary. In 1969 a PO_4 minimum is seen at a density of $16.05\ \sigma_t$, well above the onset of H_2S [Fig. 1(b)]. As stated above, if Fe and Mn oxide precipitation above oxygen zero control the PO_4 minimum, then the suboxic zone can thus be postulated to exist between 16.05 and $16.3\ \sigma_t$ in 1969. This corresponds to a vertical displacement of 35 – 45 m in the central Black Sea.

In Table 1, we summarize selected US and Soviet data collected at over 200 stations between 1985 and 1992, as well as the R.V. *Atlantis II* data from 1969, where both the density of H_2S onset and the PO_4 minima could be determined. The PO_4 minima is found at an average density of 15.95 (within a range of $0.17\ \sigma_t$ for all sources and seasons). The density of H_2S onset is consistently greater, averaging 16.20 (within a range of $0.10\ \sigma_t$). The density difference between the PO_4 minima and H_2S onset, $\Delta\sigma_t$, averages $0.25\ \sigma_t$ (Table 1). Note that we use here $\text{H}_2\text{S} > 0$ as the lower boundary for the suboxic zone (rather than $\text{H}_2\text{S} > 5\ \mu\text{M}$) as the first sample with detectable H_2S was easier to identify in every data set. In fact, $\Delta\sigma_t$ using $\text{H}_2\text{S} > 5\ \mu\text{M}$ would be $\sim 0.05\ \sigma_t$ larger, or $0.30\ \sigma_t$. We use these data to conclude that the suboxic zone has been a universal feature of the central Black Sea for the past 2–3 decades, with an absolute thickness of 30 – 50 m in the central gyres.

There is no apparent trend in $\Delta\sigma_t$ with time or season in the data in Table 1, although variations from 0.19 to $0.35\ \sigma_t$ are seen (mean of all data = $0.25\ \sigma_t$). We therefore disagree with TUGRUL *et al.* (1992) who concluded that the suboxic zone has spread towards the surface by approximately $0.3\ \sigma_t$ in the late 1980s relative to 1969. These authors use 1969 DO and nitrate (NO_3) data to support their hypothesis of a rising upper boundary for the suboxic zone. We would agree that NO_3 concentrations have apparently increased in the past decades (CODISPOLI *et al.*, 1991), but we do not feel that the evidence for a shoaling of NO_3 maximum is clear. Using a much larger historical data set than in TUGRUL *et al.* (1992), we will now examine in more detail long term variations in the position of the H_2S boundary at the base of the suboxic zone.

SHOALING OF OXIC–ANOXIC INTERFACE

Many different investigators have recently supported the view that the oxic/anoxic interface has been shoaling in the Black Sea over the past 2–3 decades (FASHCHUK and AYZATULLIN, 1986; BRYANTSEV *et al.*, 1988; MURRAY *et al.*, 1989). This view is easily taken, as man's impact on the Black Sea during this time frame includes a reduction in fresh water input, and an increase in nutrient loading (TOLMAZIN, 1985), both of which could lead to a shoaling of the oxygen zero boundary. The question to be addressed here is not whether man has had an impact, but whether or not we can see any measurable trend in the depth or density of the Black Sea chemocline.

Previous comparisons of historical data on the onset of anoxia in the Black Sea have been based primarily upon the depth of oxygen zero or the depth of sulfide onset. BEZBORODOV (1990) thoroughly reviewed the Soviet literature on this subject, as well as the recent R.V. *Knorr* studies. By analyzing sulfide data from hundreds of stations throughout the Black Sea, Bezborodov concludes that there has been no systematic change in the depth of sulfide onset between 1926 and 1990 in the central western gyre. He does point out however, that 30 m seasonal and annual variations in the depth of sulfide onset are

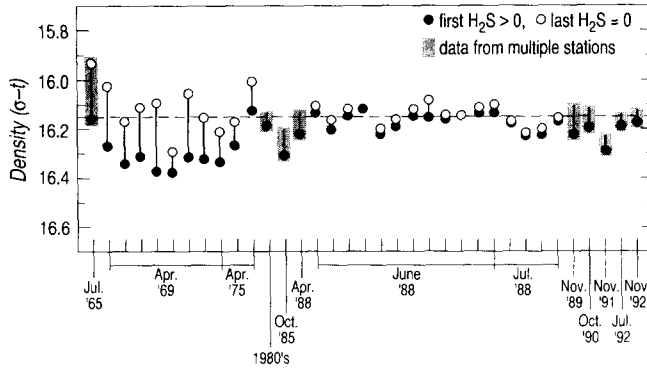


Fig. 3. Data on the historical density of the H_2S interface. When available, the density of the deepest sample with zero H_2S is shown (open circle), and the density for the shallowest sample with $\text{H}_2\text{S} > 0$ (solid circle). Data representing multiple stations are shown (shaded), as well as values from individual sites. For the Soviet studies, data are shown as the average density of the shallowest sample with $\text{H}_2\text{S} > 0$ for a given source (i.e. solid circle), and the vertical error bar represents the standard deviation of that estimate. Sources for the data from each year are as follows: 1965—R.V. *J.E. Pillsbury*, $n = 30$, GUPTA (1971); 1969—R.V. *Atlantis II*, $n = 8$, BREWER (1971) with salinity adjustment -0.065 psu (see text); 1975—R.V. *Chain*, $n = 2$, GAGOSIAN (1975) and GAGOSIAN and HEINZER (1979); 1980s—summary of $n = 600$, BEZBORODOV (1990); October 1985—R.V. *M. Lomonosov*, $n = 15$, unpublished data MHI, see Table 1; April 1988—R.V. *P. Kolesnikov*, $n = 23$, MHI; June–July 1988—R.V. *Knorr*, $n = 16$ ($z > 2000$ only), FRIEDERICH *et al.* (1990); November 1989—R.V. *M. Lomonosov*, $n = 29$, MHI; September 1990—R.V. *M. Lomonosov*, $n = 10$, MHI; November 1991—R.V. *M. Lomonosov*, $n = 31$, MHI; July 1992—R.V. *P. Kolesnikov*, $n = 54$, MHI; October 1992—R.V. *M. Lomonosov*, $n = 16$, MHI.

common. Also, he suggests that some of the earlier Soviet data are not reliable (such as FASCHUK *et al.*, 1987), and that multi-year data were not adequately considered in many of the studies (such as JOROV and BOGUSLAVSKY, 1985; BOGUSLAVSKY *et al.*, 1985). In any case, as pointed out by BEZBORODOV (1990) and others (KEMPE *et al.*, 1990), given the strongly domed shape of the Black Sea pycnocline, small variations in position and season can produce large variations in the depth of a given feature.

The most appropriate question is therefore whether the *density*, not depth, of the pycnocline has changed in the past decades, and secondarily, whether or not the isopycnal surfaces themselves have shoaled. We will attempt to answer these questions based upon the position of the sulfide interface, as sulfide measurements are abundant and relatively consistent between data sets, and less prone to analytical artifacts which plague oxygen measurements (see Background).

We have summarized in Fig. 3, many of the US and Soviet data collected between 1965 and 1990 where the density of sulfide onset could be determined. In total, these data represent over 800 H_2S and density determinations (see Fig. 3 caption for data sources). If available, we plot both the density corresponding to the deepest sample with undetectable sulfide, and the shallowest sample with a positive sulfide concentration. In this manner, the true density of sulfide onset (assuming the original data are valid) must lie between these two samples/densities. From this figure, it can be seen that there is no systematic increase or decrease in the density of the sulfide interface. Increased sensitivity and sample resolution causes the depth of first detectable sulfide to be systematically shallower in more recent studies (Fig. 3). This “shoaling” of the density of first detectable sulfide must not be

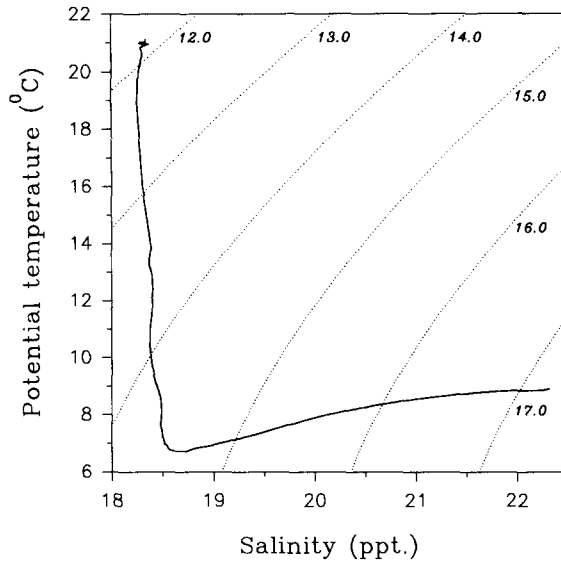


Fig. 4. Potential temperature vs salinity plot from June 1988 (R.V. *Knorr* cruise 4, Sta. 9 H1; data taken from WHITE *et al.*, 1989). Isopycnal surfaces from 12.0–17.0 σ_t are shown as dotted lines.

confused with long term changes in the absolute depth of the sulfide interface. While short-term variations between individual stations as large as 0.05–0.1 σ_t can be seen (for example Fig. 3, June 1988), there is no obvious long term trend in the density of the sulfide boundary, and this interface ($\text{H}_2\text{S} > 0 \mu\text{M}$) is generally found between 16.1 and 16.2 σ_t during the last 25 years.

Given that there is no evidence for a historical trend in the density of sulfide onset, a possible shoaling of the interface is still possible if the density surfaces themselves are now at shallower depths overall. To compare historical trends in hydrographic properties, T – S plots can be quite useful. A typical summer time T – S plot for the Black Sea is shown in Fig. 4. Surface water temperature and salinity fluctuations can be quite dramatic, causing the upper portion of the T – S curve ($\sigma_t < 14.0$) to vary considerably between season and location. Temperature and salinity decrease systematically down to the depth of the Cold Intermediate Layer ($t < 8^\circ\text{C}$, $\sigma_t = 14.5$). Below this depth, temperatures begin to increase, with the bulk of the water column below 200 m in the central Black Sea having a salinity > 21.5 and a temperature $> 8.5^\circ\text{C}$ ($\sigma_t > 17.0$).

MURRAY *et al.* (1991) used T – S data to argue that the waters sampled during the R.V. *Knorr* cruise in 1988 were systematically saltier and/or cooler than found in 1969 (R.V. *Atlantis II*) or 1975 (R.V. *Chain*). This increase in density was originally proposed to be due to either recent reductions in freshwater input to the Black Sea, and/or decadal climatic trends. We expand here upon this comparison, using data from a larger data base, and focus on the region of the T – S curve between 7 and 9°C , and 19 and 22 ppt, corresponding to waters below the CIL.

The T – S data shown in Fig. 5(a)–(e) support the conclusion that the 1988 R.V. *Knorr* samples were generally denser than average, however there is no historical trend in T – S properties. The consistency in deep water T – S properties lends support to the reliability of this comparison. For instance, data from 1991 are warmer and/or fresher than in 1988,

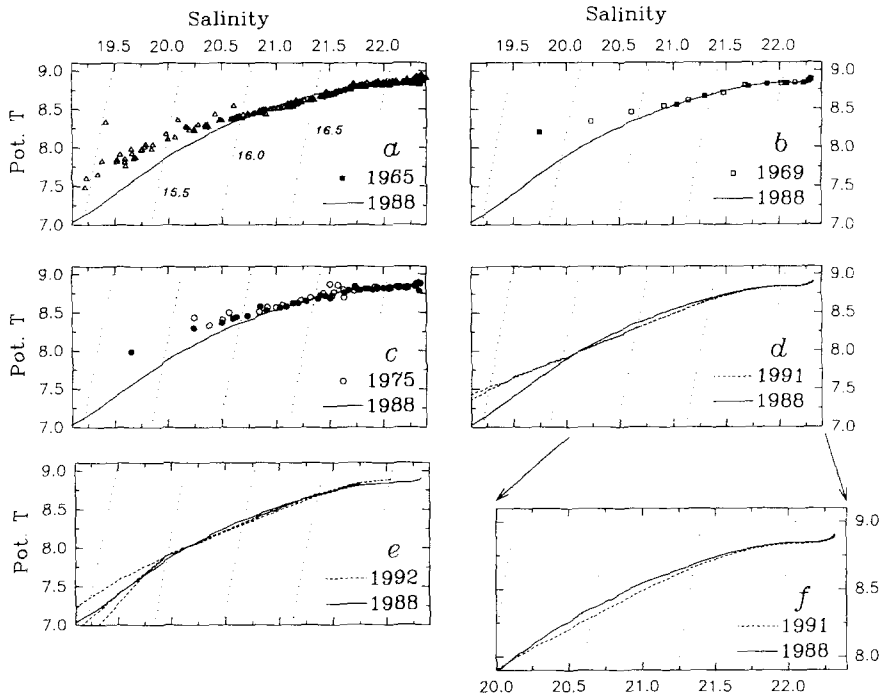


Fig. 5. Potential temperature vs salinity plots comparing data from 1988 (solid line in all figures; same 1988 station as in Fig. 4), with other cruises. Isopycnal surfaces are plotted as dotted lines every $0.5 \sigma_t$ between 15.0 – $17.0 \sigma_t$ [see (a) for σ_t values]. (a) 1988 and 1965 (open triangles from R.V. *J.E. Pillsbury*—July); (b) 1988 and 1969 (R.V. *Atlantis II*—April, open squares—Sta. 1444; filled squares—Sta. 1445). (c) 1988 and 1975 (R.V. *Chain*—April, open circles—Sta. 1355; filled circles—Sta. 1356). (d) 1988 and 1991 (R.V. *Bilim*—August, HYDROBLACK Stas 71 and 72). (e) 1988 and 1992 [R.V. *M. Lomonosov*—March (Sta. 1), July (Sta. 5287) and August (Sta. 15)]. (f) 1988 and 1991 [same data as (d) plotted on expanded scale].

similar to 1969 [Fig. 5(b) and (d)]. Also, T – S data from 1992 lie both above and below the 1988 curve at densities below $15.5 \sigma_t$ [Fig. 5(e)]. Overall the various data sets show large T – S variations between years, and even within a given year, down to temperatures of at least 8 – 8.5°C and salinities of 20 – 20.5 ppt (Fig. 5). This corresponds to a density of 15.5 – $16.0 \sigma_t$. As seen from the DO and H_2S profiles (Fig. 1), Black Sea waters are ventilated regularly down to these isopycnal surfaces. The relatively cooler and/or saltier waters in 1988 above these densities are therefore most likely a reflection of the severe winter of 1987 (SIMONOV and ALTMAN, 1991), and not a long-term change in the water or heat balance.

In the region of the suboxic zone and below ($>16.0 \sigma_t$), one can observe small T – S variations between different years down to temperatures as high as 8.8°C , and salinities of 22 ppt. This corresponds to a maximum density of $17.0 \sigma_t$ and a depth of close to 500 m in the central gyres. For example, when the T – S plots of 1991 and 1988 are compared in detail [Fig. 5(f)], the 1988 data are found to be slightly warmer or fresher in the region of the suboxic zone and lower pycnocline (15.8 – $16.5 \sigma_t$). While the data from the 1960s and 1970s are not of sufficient accuracy and resolution to examine small T – S variations in these

intermediate depths, dramatic long term changes in the hydrographic properties of the pycnocline below $\sigma_t = 16.0$ are not evident here.

VENTILATION OF THE PYCNOCLINE

We have seen from the DO and T – S curves that direct ventilation of the upper waters occurs down to at least the 15.5 σ_t surface (below which DO decreases rapidly). The source region for these newly formed waters is thought to be the area of cyclonic circulation where density interfaces are close to the sea surface, especially during winter. It is possible that winter storms contribute significantly in the raising of the level of turbulent energy above 15.5 σ_t , and thus in setting the T – S characteristics of these waters. The energy for mixing is likely due to internal waves, and from seiche movements which are very energetic in winter (BLATOV *et al.*, 1984), as well as from inertia-gravity waves.

Below the 15.5 density surface, mixing is slower and less regular. Data from the Chernobyl cesium isotopes (BUESSELER *et al.*, 1991) suggested that significant ventilation of intermediate depths occurs as the outflowing Black Sea waters are entrained with the inflowing Mediterranean waters. Within 2 years after the 1986 accident, waters down to 16.5 σ_t in the central western basin had been tagged with the surface derived Chernobyl water mass tracers. Evidence for this entrainment process was also found by ÖZSOY *et al.* (1991), when they examined the composite R.V. *Knorr* T – S curve in detail. These researchers found quite clearly anomalous T – S properties in selected lenses of water as deep as 500 m. This was not evident at every station, but primarily at margin stations along the Turkish coast and near the mouth of the Bosphorus. In a similar fashion, CODISPOTI *et al.* (1991) find sharp nutrient and sulfide anomalies from these same stations and depths, which they attribute to entrainment processes. ÖZSOY *et al.* (1991) postulate that the spreading plumes of entrained water result from the double diffusive ambient conditions. The entrainment process is not a newly discovered feature, as sub-surface oxygen anomalies along the southern coast of the Black Sea were found in 1969, as well (GRASSHOFF, 1975).

It is evident from the T – S and geochemical data that intermittent injections of surface derived waters at densities corresponding to the suboxic zone occur (16.0–16.5 σ_t). These events provide a mechanism for separating the DO and H_2S boundaries. The injection of DO into sulfidic waters would result in the consumption of both DO and H_2S in the oxidation of sulfide to sulfate (MILLERO, 1991). Below the suboxic zone, this same ventilation process could lead to the differences in the T – S characteristics seen down to 16.5–17.0 σ_t ; however, at these depths, the intensity of entrainment is reduced, and likely varies from year to year. The suboxic zone thus becomes a boundary between the rapidly mixed surface waters ($\sigma_t < 15.5$ –15.9), and the more irregularly ventilated intermediate depths ($\sigma_t > 16.2$ –16.5). Direct injection of surface waters below about 500 m ($\sigma_t = 17.0$) in the central basin is rare, and cannot be found in any of the recent freon (J. Bullister, personal communication) or tritium data sets (TOP *et al.*, 1991). Below this depth, T – S characteristics are constant, and residence times are expected to be quite long.

CONCLUSIONS

Since the original hypothesis of a possible shoaling of the Black Sea chemocline (FASHCHUK and AYZATULLIN, 1986; MURRAY *et al.*, 1989), interest in the stability of this

interface has grown. A variety of authors have now re-evaluated historical and recent water column data and come to the opposite conclusion, i.e., that the boundary between surface oxic and deep anoxic waters is not changing (BEZBORODOV, 1990; TUGRUL *et al.*, 1992; SAYDAM *et al.*, 1993). We would agree with this latter group. Using data collected between 1965 and 1992 by a variety of US and former USSR sources, and relying on H₂S data and the PO₄ minima as tracers of this boundary, we find that the oxic and anoxic interfaces have been relatively stable with respect to isopycnal surfaces over the past 2–3 decades. In addition, we also feel that the suboxic zone (where DO and H₂S < 5 μM) is not a new feature, but rather has only recently been seen due to advances in our sampling and analytical capabilities.

Our conclusions are also consistent with the general pattern of the *T-S* curves, which show large annual and interannual variability above the suboxic zone ($\sigma_t < 15.9$) where ventilation is rapid, and slight *T-S* variations as deep as 17.0 σ_t . The oxic–anoxic boundary is thus not a simple diffusive boundary. Horizontal transport along isopycnal surfaces must be considered at depths which include the suboxic zone (15.9–16.2 σ_t) and the lower pycnocline.

Our analysis considers only evidence for relatively large scale changes and trends in the densities of chemical interfaces in the Black Sea. In particular, we have not addressed mesoscale variability, nor short term variations in the structure of the chemocline within a range of 0.05–0.1 σ_t . This would require a more detailed study with high resolution hydrographic and chemical data in both space and time. Such data sets are just beginning to emerge.

When comparing earlier to more modern data sets, questions of data quality are of great concern. Fortunately in the Black Sea, the constancy of *T-S* properties below about 500 m allows for a check on earlier density estimates. Also, since we can define the suboxic zone boundaries based upon the PO₄ minimum and onset of H₂S, the absolute values of these concentration measurements are not absolutely critical. Due to the sharp chemical gradients across the chemocline, perhaps the biggest limitation in earlier data sets was the generally wide vertical sampling resolution.

Independent from analyses such as ours which are based upon water column data, ANDERSON *et al.* (1991) have examined Black Sea sediments for evidence of a change in redox conditions. They studied five cores along a 10 km transect spanning oxic to anoxic waters in the Bay of Sinop. The cores thus examined show no evidence for a change in redox conditions (visible from color, laminations and bioturbation features) over time-scales within the range of ²¹⁰Pb dating, or approximately 150 years.

The implications for a non-changing redox boundary in the Black Sea are important. Many of the post-*Knorr* research papers assume *a priori* that the oxic–anoxic interface has shoaled, and interpret their findings based upon what is emerging to be a false assumption. As just two examples, the new finding of anoxygenic photosynthesis (REPETA and SIMPSON, 1991) and the apparent decrease in the maximum of microbial biomass (BIRD and KARL, 1991) are attributed to be initiated by, or at least consistent with a shoaling of the interface. This does not mean that there have been no changes to the Black Sea's biology and chemistry in the past decades. There is strong evidence for increasing concentrations of nitrate (CODISPOTI *et al.*, 1991), as well as decreases in ²²⁶Ra and Ba (FALKNER *et al.*, 1991), and a decrease in the depth of light penetration (MEE, 1992). All of these changes may be induced by human impact, however they should be viewed within the context of a relatively stable Black Sea pycnocline and oxic–suboxic–anoxic boundary. Long term

studies using high resolution sampling and high quality hydrographic techniques combined with moored instrumentation to obtain increased temporal information are required to monitor this basin for further changes.

Acknowledgements—It is a pleasure to acknowledge the assistance we obtained in locating both published and unpublished data for the comparative analyses which went into this publication. Special thanks go to G. Heimerdinger, D. Aubrey and co-workers in the CoMSBlack program. P. Brewer and R. Gagolian. Editorial comments by L. Codispoti, J. Murray, O. Gustafsson, N. Stokosov and one anonymous reviewer are highly appreciated. Translations from Russian literature by S. Livingston and A. Karachintsev are kindly acknowledged, as well as the secretarial assistance of M. Lumping and S. Clifford. This work was supported under NSF grant OCE-8917465 and EPA Assistance ID No. R817047-01-3 to K.O.B. and H.D.L., as well as support from Marine Hydrophysical Institute and the Ukrainian Academy of Sciences for L.I. and A.R. This is contribution no. 8400 from the Woods Hole Oceanographic Institution.

REFERENCES

- ANDERSON R. F., M. Q. FLEISHER, T. LYONS and G. COWIE (1991) Sedimentary record of a shoaling of the oxic/anoxic interface in the Black Sea. *Eos, Transactions, American Geophysical Union*, **72**, 36.
- BEZBORODOV A. A. (1990) Variability in position of the onset of anaerobic waters in the Black Sea as based on data of the past years. In: *Complex oceanographic investigations of the Black Sea (hydrology, hydrophysics, hydrochemistry)*, Academy of Science of Ukraine, Marine Hydrophysical Institute, Sevastopol, 76–114, V. E. ZAIKA, editor, [in Russian].
- BIRD D. F. and D. M. KARL (1991) Microbial biomass and population diversity in the upper water column of the Black Sea. *Deep-Sea Research*, **38**(S2A), S1069–S1082.
- BLATOV A. S., N. P. BULGAKOV, V. A. IVANOV, A. N. KOSAREV and V. S. TUZHILKIN (1984) Variability of hydrophysical fields of the Black Sea. Leningrad, Hydrometeoizdat, pp. 240 [in Russian].
- BOGUSLAVSKY S. G., V. A. JOROV and A. A. NOVOSIOLOV (1985) On the problem of the hydrogen sulfide zone of the Black Sea. *Marine Hydrophysical Journal*, **1**, 54–58 [in Russian].
- BREWER P. (1971) *Hydrographic and chemical data from the Black Sea*. Woods Hole Oceanographic Institute Technical Report, Reference No. 71-65.
- BREWER P. G. and D. W. SPENCER (1974) Distribution of some trace elements in Black Sea and their flux between dissolved and particulate phases. In: *The Black Sea—geology, chemistry and biology*, E. T. DEGENS and D. A. ROSS, editors, Memoir 20, American Association of Petroleum Geologists, Tulsa, OK, pp. 137–143.
- BRONKOW W. W. and J. D. CLINE (1969) Colorimetric determination of dissolved oxygen at low concentrations. *Limnology and Oceanography*, **14**, 450–454.
- BRYANTSEV V. A., D. YA FASHCHUK, T. A. AYZATULLIN, S. V. BAGOTSKIY and A. V. LEONNOV (1988) Variation in the upper boundary of the hydrogen sulfide zone in the Black Sea: analysis of field observations and modeling results. *Oceanology*, **28**, 180–185.
- BUESSELER K. O., H. D. LIVINGSTON and S. A. CASSO (1991) Mixing between oxic and anoxic waters of the Black Sea as traced by Chernobyl cesium isotopes. *Deep-Sea Research*, **38**(S2A), S725–S745.
- CODISPOTI L. A., G. E. FRIEDERICH, J. W. MURRAY and C. SAKAMOTO (1991) Chemical variability in the Black Sea: implications of data obtained with a continuous vertical profiling system that penetrated the oxic/anoxic interface. *Deep-Sea Research*, **38**(S2A), S691–S710.
- FASCHUK D. YA. and T. A. AYZATULLIN (1986) A possible transformation of the anaerobic zone of the Black Sea. *Oceanology*, **26**, 171–178.
- FASCHUK D. YA., T. A. AYZATULLIN and L. K. SEBAH (1987) The specifics of the contemporary state of the layer of coexistence of oxygen and hydrogen sulphide in the Black Sea. *Contemporary State of the Ecosystem of the Black Sea*. Moscow Science, pp. 29–41 [in Russian].
- FALKNER K. K., D. J. O'NEILL, J. F. TODD, W. S. MOORE and J. M. EDMOND (1991) Depletion of barium and radium-226 in Black Sea surface waters over the past thirty years. *Nature*, **350**(6318), 491–494.
- FRIEDERICH G. E., L. A. CODISPOTI and C. M. SAKAMOTO (1990) *Bottle and pumpcast data from the 1988 Black Sea expedition*. Monterey Bay Aquarium Research Institute Technical Report 90-3, pp. 224.
- GAGOLIAN R. B. (1975) Hydrographic data from the Black Sea, R.V. *Chain* Cruise 120, Leg 1, April 15–30, 1975. WHOI Report.

- GAGOSIAN R. B. and F. HEINZER (1979) Stenols and stanols in the oxic and anoxic waters of the Black Sea. *Geochimica et Cosmochimica Acta*, **43**, 471–486.
- GRASSHOFF K. (1975) The hydrochemistry of landlocked basins and fjords. Chapter 15 in: *Chemical oceanography*, Vol. 2, J. P. RILEY and G. SKIRROW, editors, Academic Press, New York, pp. 455–597.
- GUPTA R. S. (1971) Oceanography of the Black Sea: Inorganic nitrogen compounds. *Deep-Sea Research*, **18**, 457–475.
- JOROV B. A. and S. G. BOGUSLAVSKY (1985) Trends of some hydrological and hydrochemical processes of the Black Sea. *Meteorology and Hydrology*, **11**, 63–69 [in Russian].
- KEMPE S., G. LIEBEZETT and A.-R. DIERCKS (1990) Water balance in the Black Sea. *Nature*, **346**, 419.
- LATIF M. A., E. ÖZSOY, T. OGUZ and U. ÜNLÜATA (1991) Observations of the Mediterranean inflow into the Black Sea. *Deep-Sea Research*, **38**(S2A), S711–S723.
- LEWIS B. L. and W. M. LANDING (1991) The biogeochemistry of manganese and iron in the Black Sea. *Deep-Sea Research*, **38**(S2A), S773–S804.
- MEE L. (1992) The Black Sea in crisis: The need for concerted international action. *Ambio*, **21**(4), 278–286.
- MILLERO F. J. (1991) The oxidation of H₂S in Black Sea waters. *Deep-Sea Research*, **38**(S2A), S1139–S1150.
- MURRAY J. W., L. A. CODISPOTI and G. E. FRIEDERICH (1993) Redox Environments: The suboxic zone in the Black Sea. In: *Aquatic chemistry*, C. P. HUANG, C. R. O'MELIA and J. J. MORGAN, editors, American Chemical Society, in press.
- MURRAY J. W. and E. IZDAR (1989) The 1988 Black Sea Oceanographic Expedition: overview and new discoveries. *Oceanography*, **2**, 15–21.
- MURRAY J. W., H. W. JANNASCH, S. HONJO, R. F. ANDERSON, W. S. REEBURGH, Z. TOP, G. E. FRIEDERICH, L. A. CODISPOTI and E. IZDAR (1989) Unexpected changes in the oxic/anoxic interface in the Black Sea. *Nature*, **338**, 411–413.
- MURRAY J. M., Z. TOP and E. ÖZSOY (1991) Hydrographic properties and ventilation of the Black Sea. *Deep-Sea Research*, **38**(S2A), S663–S690.
- ÖZSOY E., Z. TOP, G. WHITE and J. W. MURRAY (1991) Double diffusive intrusions, mixing and deep-sea convection processes in the Black Sea. In: *Black Sea oceanography*, E. IZDAR and J. M. MURRAY, editors, Kluwer Academic Publishers, The Netherlands, pp. 17–42.
- REPETA D. J. and D. J. SIMPSON (1991) The distribution and recycling of chlorophyll, bacteriochlorophyll and carotenoids in the Black Sea. *Deep-Sea Research*, **38**(S2A), S969–S984.
- SAYDAM C., S. TUGRUL, O. BASTURK and T. OGUZ (1993) Identification of the oxic/anoxic interface by isopycnal surfaces in the Black Sea. *Deep-Sea Research I*, **40**, 1405–1412.
- SHAFFER G. (1986) Phosphate pumps and shuttles in the Black Sea. *Nature*, **321**, 515–517.
- SHOLKOVITZ E. R. (1992) Comments on: "Redox cycling of rare earth elements in the suboxic zone of the Black Sea" by C. R. GERMAN *et al.* (1991), *Geochimica et Cosmochimica Acta*, **55**, 3553–3558.
- SIMONOV A. I. and A. N. ALTMAN (1991) Hydrometeorology and hydrochemistry of the USSR seas. Vol. 4: *The Black Sea*. 1 issue: Hydrometeorological conditions. St Petersburg, Hydrometeoizdat, 429 pp. [in Russian].
- SPENCER D. W. and P. G. BREWER (1971) Vertical advection diffusion and redox potentials as controls on the distribution of manganese and other trace metals dissolved in waters of the Black Sea. *Journal of Geophysical Research*, **76**(24), 5877–5892.
- TOLMAZIN D. (1985) Changing coastal oceanography of the Black Sea. I. Northwestern Shelf. *Progress in Oceanography*, **15**, 217–276.
- TOP Z., G. ÖSTLUND, L. POPE and C. GRALL (1991) Helium isotopes, neon and tritium in the Black Sea: a comparison with the 1975 observations. *Deep-Sea Research*, **38**(S2A), S747–S760.
- TUGRUL S., O. BASTURK, C. SAYDAM and A. YILMAZ (1992) Changes in the hydrochemistry of the Black Sea inferred from water density profiles. *Nature*, **359**, 137–139.
- VINOGRADOV M. YE. and YU. R. NALBANDOV (1990) Effect of changes in water density on the profiles of physiochemical and biological characteristics in the pelagic ecosystem on the Black Sea. *Oceanology*, **30**(5), 567–573.
- WHITE G., M. RELANDER, J. POSTAL and J. W. MURRAY (1989) Hydrographic Data from the 1988 Black Sea Oceanographic Expedition. University of Washington, School of Oceanography Special Report No. 109.