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Hydrographic properties and ventilation of the Black Sea

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Abstract—Using hydrographic data collected by CTD during five cruises of the 1988 Black Sea Oceanographic Expedition, from 16 April to 29 July 1988, we describe the distribution of potential temperature (θ), salinity (S), and potential density (σ_θ) throughout the water column. The salinity and density increase rapidly with depth, while temperature decreases to a minimum at 50 m in the cold intermediate layer (CIL). All three variables increase slowly with depth in the deep water. The hydrographic properties of the upper 200 m varied little over the duration of the 1988 expedition. Significant differences are observed when the 1988 data are compared with the 1969 *Atlantis II* data set. All of the 1969 data are warmer at a given salinity than the 1988 data to a depth with a salinity of about 21.0‰. Possible causes for these changes are increased heat loss to the atmosphere and decreased freshwater input. The most distinctive feature in the deep water is a homogeneous benthic bottom layer that extends from about 1700 m to the bottom. There is a single pronounced step in all hydrographic properties at the top of this layer. Vertical transport across the upper boundary may be controlled by double diffusion driven by geothermal heat flow. The predicted double-diffusive heat flux agrees with geothermal heat flow to within a factor of 5. A simple box model with surface, entrainment and deep-water reservoirs is used to model the entrainment process and the residence time of deep water in the Black Sea. The results suggest that the Bosporus inflow entrains water with properties of the CIL. The ratio of entrainment to Bosporus inflow is 3.3. Assuming a Bosporus inflow of 312 $km^3\ y^{-1}$, the resulting residence time of the deep water is 387 years. A total CO_2 balance is used to calculate the flux of carbon into the deep water and a ^{14}C balance is used to calculate the pre-nuclear value of $\Delta^{14}C = -200‰$ in the entrainment water. This highly depleted value would have resulted in an apparent age of 1400 years for the CIL and, probably, the surface water as well. If the carbon flux of biological origin was depleted to the same extent this may account for some of the differences in sedimentary chronology based on ^{14}C dates and varve counts.

INTRODUCTION

THE Black Sea is anoxic because of its strong vertical salinity stratification (CASPERS, 1957; SOROKIN, 1983) caused by excess of precipitation and river run-off over evaporation (TOLMAZIN, 1985a). The deep water has a higher salinity due to the inflow of Mediterranean water which enters through the Bosporus. The depth of the halocline in the Black Sea reflects a balance between the freshwater and seawater inflows. This density gradient inhibits mixing and is the origin of the stability of the anoxic (oxygen–hydrogen sulfide) interface. The overall halo-circulation is estuarine in nature, which is the reverse of that for

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the Mediterranean. Based on a preliminary data set from the 1988 U.S.–Turkish Black Sea Expedition, MURRAY *et al.* (1989) suggested that there may have recently been an upward displacement of the constant density (isopycnal) surfaces due to an increase in salinity at a given potential temperature. These changes could be due to either natural or man-made variations in climate and river run-off. FASHCHUK and AYZATULLIN (1986) also have suggested that a recent decrease in freshwater input is causing a vertical smoothing of the salinity gradient.

In this paper we examine the temperature and salinity relationships in the Black Sea using the complete data set collected during the five cruises of the 1988 expedition on the R.V. *Knorr* (MURRAY and IZDAR, 1989). Specifically we examine the temperature and salinity relationships in the upper layer and evaluate the question of systematic changes. We discuss the hydrographic structure of the deep water including the benthic bottom layer. Finally, we present simple box model calculations that give new insights into the ventilation and residence time of the deep water of the Black Sea.

BACKGROUND

The early hydrographic data of the Black Sea were summarized by NEUMANN (1944) and CASPERS (1957). The detailed 1969 data from the R.V. *Atlantis II* (AII-49) are the most useful reference data set (BREWER, 1971; SPENCER and BREWER, 1971) because of their high quality, regional coverage and careful documentation.

The surface mixed layer has a relatively low salinity that varies from 17.5 to 18.5‰ depending on the season and the proximity to river input (especially in the northwestern region). The temperature varies seasonally in the surface layer due to solar heating and decreases with depth to a minimum located at a depth of approximately 50 m in the central basin and as deep as 100 m near the margins (OGUZ *et al.*, in press). This temperature minimum is identifiable throughout the Black Sea and has been called the cold intermediate layer (CIL). Below the CIL is the permanent halocline (50–200 m) which separates the surface water from the deep water. The isopycnal surfaces above 300 m are dome-shaped and shallower in the central parts of the Black Sea reflecting the gyre-like circulation. In the deep water the vertical salinity and potential temperature gradients are small, but both properties increase continuously to maximum values of about 22.33‰ and 8.904°C, respectively, at the bottom (Fig. 1).

The CIL is a major feature of the upper water column and deserves further discussion (FILIPPOV, 1965; GEORGIEV, 1967; TOLMAZIN, 1985a). The 8°C isothermal surfaces are the commonly accepted upper and lower boundaries of the CIL, and the layer is deeper and thicker near the margin of the Black Sea than in the center. This cold water is apparently not a remnant of locally produced winter water because at most locations the surface water does not get sufficiently cold (especially in the eastern half of the sea). TOLMAZIN (1985a) summarized evidence suggesting that the water in the CIL originates in an area of intense cooling in the northwestern shelf (NWS) region and spreads horizontally throughout the Black Sea on an isopycnal surface. OVCHINNIKOV and POPOV (1987) have recently argued that the waters of the CIL also form in the winter in the central cyclonic eddies. Spiral outflow of the newly generated CIL water occurs along the dome-shaped isopycnal surfaces. For both mechanisms of formation the severity of winter conditions determines the volume of CIL formed. Recent data by OGUZ *et al.* (in press) suggest that both mechanisms are probably important.

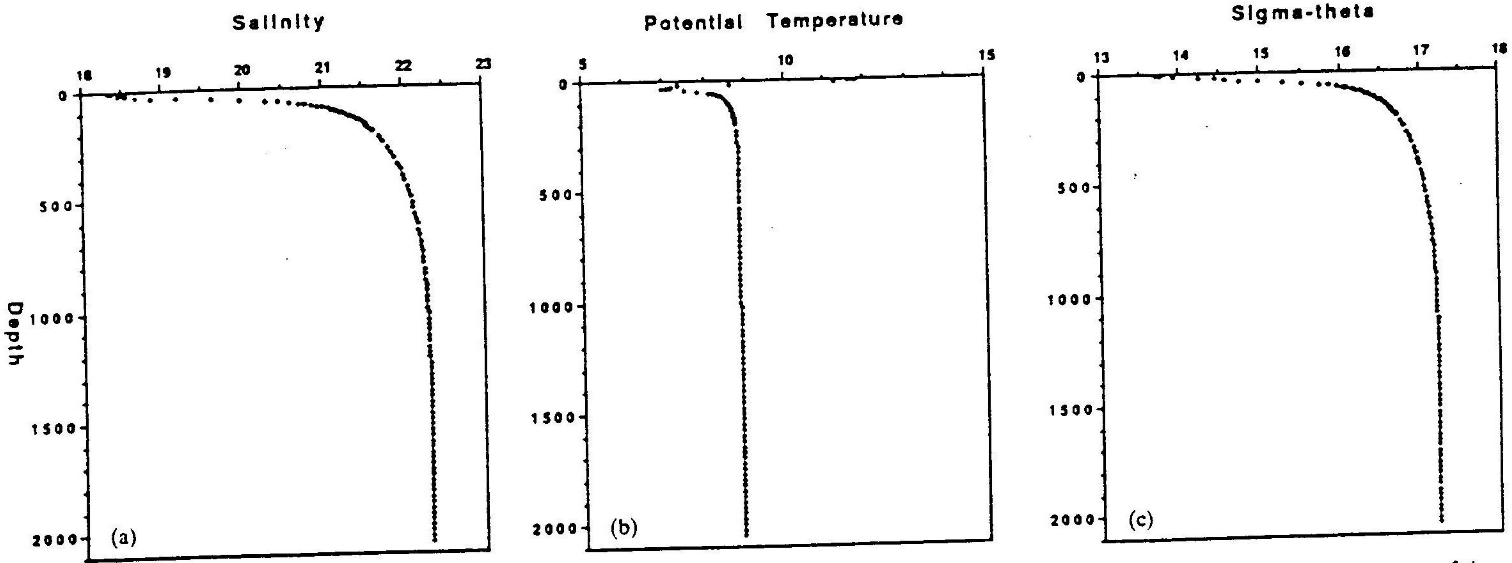


Fig. 1 Complete water column vertical profiles of (a) salinity, (b) potential temperature and (c) σ_θ at Sta. BS3-2 HC-20 which is in the center of the western gyre of the Black Sea.

One of the major new observations made during the 1988 expedition was a suboxic zone where oxygen and sulfide exist at near-zero concentrations (MURRAY *et al.*, 1989; CODISPOTI *et al.*, 1991; JORGENSEN *et al.*, 1991). It has been hypothesized that the origin of this suboxic zone may be due to either variations in the rate of formation of the CIL (MURRAY *et al.*, 1989) or plumes of Bosporus inflow (BUESSELER *et al.*, 1991).

The temperature and salinity distributions in the deep Black Sea, below the halocline, have not previously received much scrutiny, in part because the variations are small and because of a general lack of detailed hydrographic data (especially by CTD). SPENCER and BREWER (1971) combined data from several stations collected during the 1969 *Atlantis II* cruise and concluded that there was a linear salinity–potential temperature relationship from a salinity of about 20.0‰ to a salinity of 21.9‰ and potential temperature of 8.83°C, a depth range of about 75–400 m. Below this depth the waters were almost isothermal to about 900 m where the properties were 8.84°C and 22.24‰. In the deep water from 900 to 2100 m there was another linear θ–S relationship, with values increasing to bottom water values of 8.91°C and 22.41‰. Both SOROKIN (1983) and TOP and CLARKE (1983) have proposed that the increase in potential temperature below 400 m could be accounted for by geothermal heat flow. SPENCER and BREWER (1971) argued that the homogeneous water from 400 to 900 m represented the main horizontally advective deep-water input of Bosporus origin. They proposed that the deep water below 1000 m was renewed only by eddy diffusion.

Radiocarbon analyses by OSTLUND (1974) on samples collected in 1965 suggested that the deep water from 300 to 1700 m had a uniform ^{14}C age of about 1000 y supporting the notion that Mediterranean source water penetrates at this depth. Water below 2000 m had an age of about 2000 y, inferring that it was renewed less frequently during times of abnormal climate conditions. Carbon-14 analyses of samples collected in 1984 (OSTLUND and DYRSSEN, 1986) indicated that all deep waters below about 1400 m have an apparent age of 2000 y. The apparent age gradually decreases to about 1470 y at 600 m. The tritium (TOP and CLARKE, 1983) and chlorofluorocarbon (J. BULLISTER, personal communication) distributions suggest that samples shallower than about 500 m have been contaminated by ^{14}C from atmospheric nuclear weapons testing. OSTLUND and DYRSSEN (1986) suggested that some of the OSTLUND (1974) ^{14}C samples may have been contaminated during collection and thus some of the ages appeared young.

Tritium analyses on samples collected in 1975 (TOP and CLARKE, 1983) decrease to below detection (<0.2 TU) at 900 m and then increased to above zero in the two deepest samples at 1745 and 1939 m. The presence of tritium below 1500 m inferred that Black Sea surface water is entrained by the sinking Mediterranean plume and that at least some of this water penetrates all the way to the bottom. The 1988 tritium distribution was similar to that of 1975 except that no anomalies were detected in the deep water (OSTLUND, 1990). TOP and CLARKE (1983) constructed a three box model for the Black Sea using tritium and ^{3}He data and geothermal heatflow. They calculated that the deep box (1000–2000 m) and middle box (<400–1000 m) had residence times of 400 and 125 y, respectively. This approach was probably not valid, however, because they did not take heat input associated with the Bosporus inflow into account. The tritium and ^{14}C analyses appear to suggest different rates of deep-water renewal, and these inconsistencies have not yet been reconciled. TOP and CLARKE (1983) concluded that the "old" radiocarbon ages may be due to redissolution of "dead" carbonate carbon from the sediments.

TOP *et al.* (1990) recently used a calculated ^4He sediment flux and water column ^4He analysis to estimate that the water column of the Black Sea has a residence time of 850 ± 300 y. They regarded this as an upper limit.

The major uncertainty for understanding the ventilation of the Black Sea is with regard to the degree of entrainment by the Mediterranean plume and its depth of injection (FILIPPOV, 1968; FRIEDRICH and STANEV, 1989). Here we define entrainment as the mixing of Mediterranean water of Bosporus origin with near-surface Black Sea water to produce the hydrographic properties of the new Black Sea deep water. At a rate of Mediterranean water input of about 190 $km^3\ y^{-1}$ (SPENCER and BREWER, 1971) it would take about 2700 y to displace the deep volume (>50 m) ($5.20 \times 10^5\ km^3$) of the Black Sea (SVERDRUP *et al.*, 1942). There are two main problems with this simple approach. The first is that significant entrainment must occur to modify the high salinity Bosporus input. The potential temperature of the Black Sea deep water is 8.9°C, and the inflowing Mediterranean water in the Bosporus has a year-around temperature of about 14°C (GUNNERSON and OZTURGUT, 1974). The high salinity (35‰) Mediterranean inflow must entrain cold surface or near-surface Black Sea water to form Black Sea deep water. OSTLUND (1974) used a salinity balance to estimate that the ratio of entrained water to new inflow was 4:1. BOUDREAU and LEBLOND (1989) constructed a model of the evolution of the salinity of the Black Sea. They used entrainment theory, which assumes that the entrainment coefficient at a given location is a function of the slope, to estimate that this ratio was 1:4. Entrainment will decrease the deep-water residence time if all the water flows into the deep Black Sea, and thus it is important to understand the rates and dynamics of this process.

The second problem is that after entrainment the Bosporus inflow may not necessarily sink to the bottom (FILIPPOV, 1968; ROOTH, 1986). Instead it may sink to an intermediate depth dictated by the conditions of interior stability and buoyancy flux and spread horizontally on the isopycnal surface appropriate to its density (ÖZSOY *et al.*, in press). TOLMAZIN (1985b) has shown that traces of Mediterranean water can be found near the Bosporus at various depths from 200 to 1000 m. TOP and CLARKE (1983) used helium and neon analyses as tracers to show that these plumes exist. BUESSELER *et al.* (1991) have used cesium isotopes to describe shallow ventilation of the Black Sea.

METHODS

Hydrographic data were collected during all five cruises of the 1988 Black Sea Oceanographic Expedition (MURRAY and IZDAR, 1989). These cruises were conducted from 16 April to 29 July 1988. The data were collected using a rosette-CTD package equipped with 30 or 5 l Go-Flo Niskin bottles. The rosette also contained a SeaTech transmissometer and fluorometer. The pressure, temperature and conductivity data were acquired using a Seabird SBE-9/11 CTD. Calibrations of the three sensors were done in March and September 1988, before and after the expedition. Salinities were analysed manually during the expedition using an inductive salinometer and agreed with the CTD values to within 0.003‰. The data were processed following the procedures and recommendations given in UNESCO (1988). The raw data were edited, filtered and then compacted and interpolated to the nearest 1 m bin. Values of depth, salinity, potential temperature, sigma-t and sigma-θ were calculated using the equations given in UNESCO

(1983). A hydrographic data report has been published (White et al., 1989) that gives data for every 2 m from 6 to 100 m, every 5 m from 100 to 250 m and then every 25 m from 250 m to the maximum depth. There were 221 CTD casts conducted over the 3½ month period. These data are available from the University of Washington and through the National Oceanographic Data Center (NODC). The overall precision of the hydrographic data set, based on repeated casts into the benthic boundary layer, was about 0.001°C and 0.002‰. The accuracy of the temperature and salinity data, as determined by the difference in the calibration of the sensors before and after the expedition, was better than 0.001°C and 0.001‰, respectively.

RESULTS

Representative complete water column profiles of salinity, potential temperature, and potential density (σ_θ) are shown in Fig. 1. The corresponding potential temperature vs salinity diagram is shown in Fig. 2. These data are from Black Sea cruise 3 (Sta. 2) Hydrocast 21 on 7 June 1988 at 42°50.53'N and 31°58.85'E and are representative of the central western basin. This location is in the center of the western gyre near the long-term sediment trap station BSKI. At this location salinity increases rapidly with depth from a surface value of 18.289‰ to a value of 22.091‰ at 500 m. It continues to increase with depth to a maximum value at the bottom of 22.321‰. The potential temperature decreases sharply from a surface value of 16.664°C to a minimum value of 6.970°C at 44 m in the CIL, and then increases to 8.773°C at 200 m. Over the rest of the water column potential temperature increases slowly to a maximum value at the bottom of 8.906°C. The potential density (σ_T) increases smoothly with depth from 12.804 at the surface to 17.223 at the bottom. Overall, potential density is primarily controlled by the salinity.

The strength of the vertical density stratification ($d\rho/dz$) is commonly expressed as the square of the Brunt–Väisälä frequency, N, calculated as

$$N^2 = -g/\rho \, d\rho/dz. \tag{1}$$

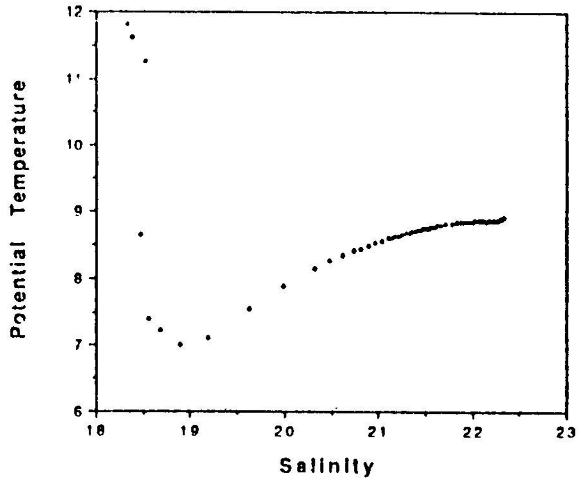


Fig. 2. Potential temperature–salinity diagram for Sta. BS3-2 HC-20.

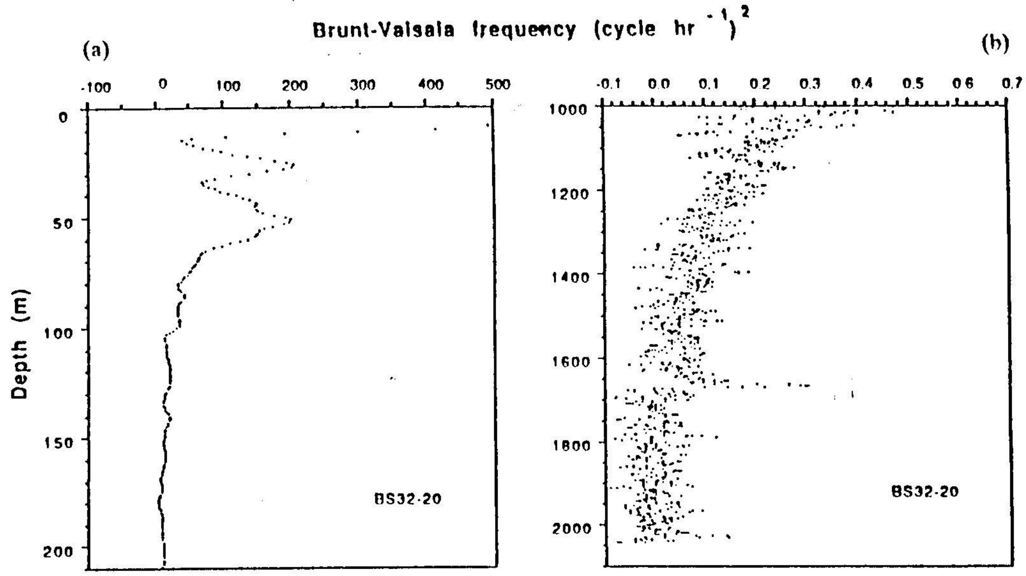


Fig. 3. The Brunt–Väisälä frequency plotted as N^2 in $(h^{-1})^2$ for the (a) upper 200 m and (b) the region (1000–2000 m) across the benthic bottom layer.

The stability is very large in the upper 200 m, and N^2 ranges from 50 to $>200\ h^{-2}$, then decreases to low values (<1) in the deep water (Fig. 3). Similar values of about 100 h^{-2} at the oxygen zero horizon were calculated by BREWER (1971).

The θ–S relationship is similar to that shown by SPENCER and BREWER (1971); however, linear regions are less evident, especially from salinities of 20.0 to 22.0‰. In full-scale plots (Figs 1 and 2) the θ and S distributions look similar to previous data, and deep-water variations are small.

We attempted to use our data to dermine the origin of the CIL. BOGUSLAVSKIY *et al.* (1976) presented a chart of isotherms of the CIL using a synoptic data set collected in May 1973. Their results suggested that the origin of the CIL is in the northwest shelf region. Using a similar approach we plotted in map view the lowest temperature recorded at each location during the 1988 expedition. We also examined the temperature on the characteristic density surface of the CIL (σ_θ = 14.6–14.7). Using our data set we could discern no systematic regional variation in the temperature of the CIL. The explanation for this is probably because the temperature at the minimum tended to increase with time at some locations during our sampling period (April to July). In addition, no stations were occupied in the Exclusive Economic Zones of the U.S.S.R., Romania or Bulgaria. There were not enough stations occupied during any of the five individual cruises to obtain sufficiently detailed resolution to address this problem.

Depth profiles of S, θ and σ_θ, using enlarged vertical scales, are shown in Figs 4 and 5 to illustrate features in the mid-water and deep-water column. Potential temperature increases to a maximum of 8.849 at 475 m (Fig. 4). It then decreases to a slight minimum of 8.845 at 600 m followed by further increase with depth. Salinity and σ_θ increase smoothly with depth through this region with only a hint of a slight inflection. The prominent feature below 1000 m is a homogeneous benthic bottom layer (Fig. 5). The depth of the top of this benthic bottom layer, defined as where θ deviates from the mean value by greater than

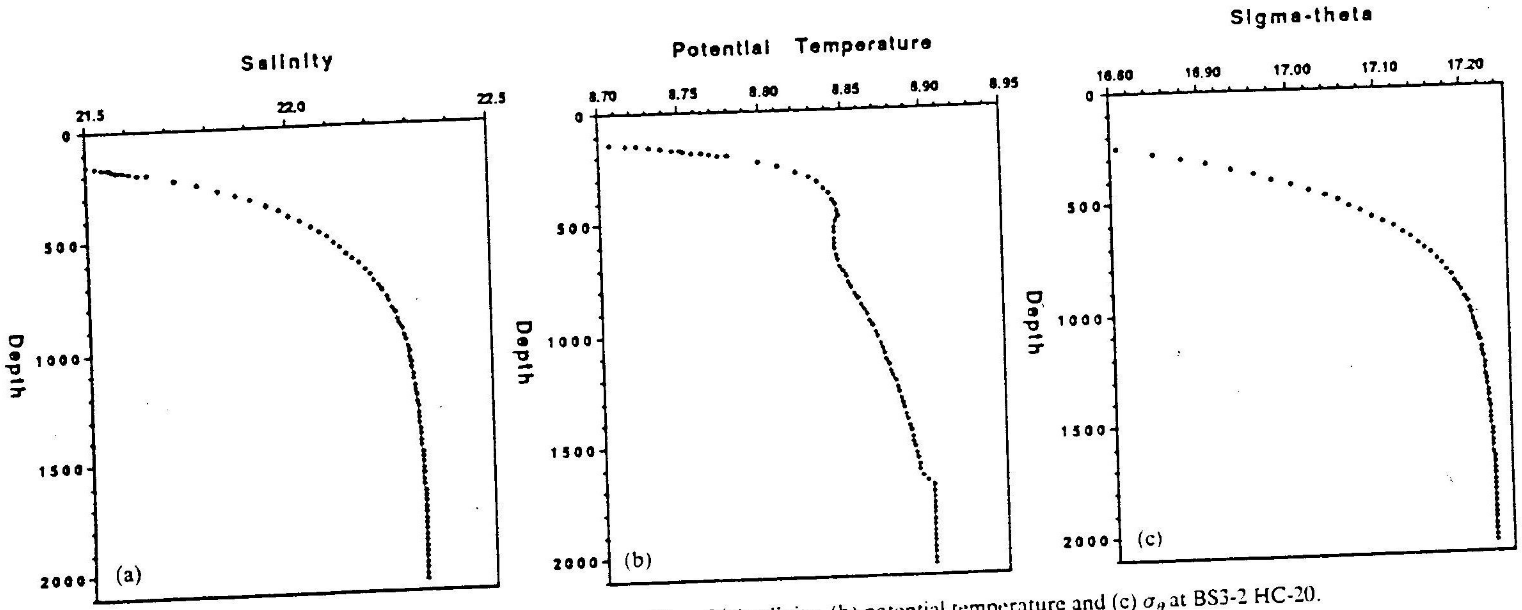


Fig. 4. Deep water (>200 m) vertical profiles of (a) salinity, (b) potential temperature and (c) σ_θ at BS3-2 HC-20.

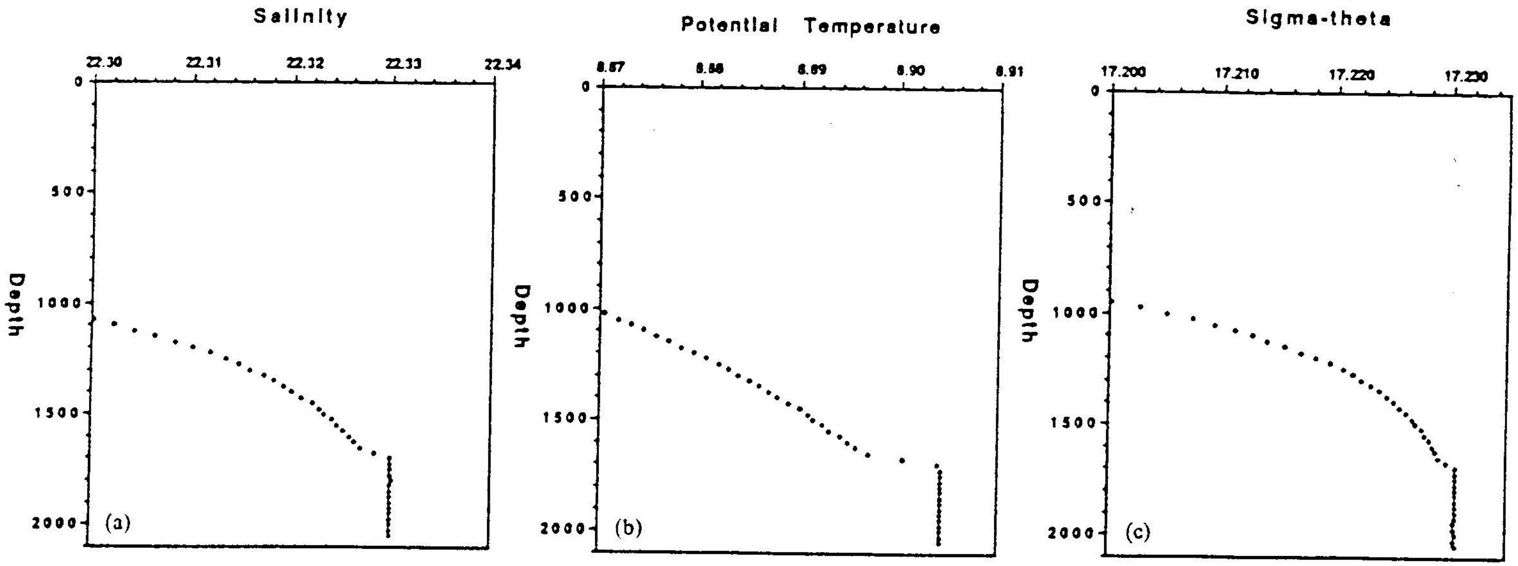


Fig. 5 Nearbottom (1000–2000 m) vertical profiles of (a) salinity, (b) potential temperature and (c) σ_θ at BS3-2 HC-20.

0.002°, is about 1740 m and varies little with time or space (Table 1). Similarly the average properties of the benthic bottom layer (determined from 25 casts at different times and locations) show very small variation and no horizontal gradients (Table 2), i.e. the 1σ standard deviations for potential temperature and salinity are 0.0012°C and 0.0020‰, respectively.

An enlargement of the θ–S diagram (Fig. 6) is especially intriguing because it is evident that there are no linear θ–S regions in the deep water. On the contrary, the values below 500 m (S = 22.1‰, θ = 8.845) vary continuously with depth and could not be formed by simple two end-member mixing. The nature of the curvature suggests an additional source of heat. Because of its uniform θ and S values, the benthic bottom layer appears only as the last data point in this plot.

One station (BS5-HC51) was occupied in the Bosporus near the northern sill (60 m sill depth) and the vertical profiles of θ and S are shown in Fig. 7. The inflowing Mediterranean water at the bottom has values of θ = 14.2 and S = 36.7‰ which are within the range of values reported by GUNNERSON and OZTURGUT (1974). The inflowing Mediterranean water is the only source of salt in the Black Sea, and this is an important constraint on the box model calculations that follow.

DISCUSSION

Ventilation of the upper 200 m

MURRAY *et al.* (1989) suggested that CIL water formed during the past 10–20 y with a higher salinity (and density) than in the past, perhaps due to annual or decadal-scale variations in climate and river run-off. Variability on these scales was also emphasized by KEMPE *et al.* (1990). Decreased run-off from Soviet rivers (TOLMAZIN, 1985a) would be an additional effect superimposed on the natural variability. The changes reported by MURRAY *et al.* (1989) were based on comparison of θ, S and σ_θ data from a station occupied in 1988 in the center of the western gyre (BS3-2) with data collected in 1969 at a nearby station (AII-1445). There was little difference between the potential temperature profiles; however, the salinity in 1988 was higher by about 0.1‰ over the 50–200 m depth range. Evaluation of possible hydrographic changes requires a more detailed examination of the complete 1988 Black Sea data set from all five cruises including variability on different time scales. In order to conclude that comparisons over a multi-year period are valid we first must evaluate the regional variability over daily and monthly time scales. Factors that can

Table 1. Depth of the top of the benthic boundary layer determined using the data in 25 m bins as presented in White et al. (1989). *Average depths determined using all the casts at each location during the 1988 expedition*

Station	Depth (m)	
BSK I (western gyre)	1739 ± 52	(n = 7)
BSK II (center)	1796 ± 33	(n = 12)
BSK III (eastern gyre)	1738	(n = 2)
BSC (near Bosporus)	1738 ± 25	(n = 4)

Table 2. Average values of potential temperature, salinity and potential density in the bottom boundary layer of the Black Sea. Also given are the 1σ standard deviations. These values were determined using data obtained from 25 CTD casts spread throughout the Turkish Exclusive Economic Zone of the Black Sea

Parameter	Value
Potential temperature (θ)	8.9057 ± 0.0012°C
Salinity (S)	22.3212 ± 0.0020‰
Potential density (σ_θ)	17.2233 ± 0.0015

introduce variability on these time scales include internal waves, mesoscale processes (e.g. eddies) and variable horizontal and vertical transport.

Murray (in press) analysed the variability in hydrographic parameters at two stations repeatedly occupied during the 4-month 1988 expedition (center of the western gyre at BSK I; 32°E, 40°50′N and between the eastern and western gyres at BSK II; 34°E, 43°00′N). The depths studied were the center of the CIL and a depth in about the middle of the suboxic zone. The depth of the CIL was chosen because this is a depth where lateral injection is thought to be important and the potential for variability is large. The middle of the suboxic zone was picked because it is in the middle of the pycnocline where internal waves might be important and because of the geochemical importance of that zone. During the time interval of a typical 3- to 4-day station occupation, during which multiple hydrocasts were taken, the variations in depth, temperature and salinity of the CIL were ≤2 m, <0.03°C and <0.03‰, respectively. The characteristic minimum time constant for internal waves ($= 2\pi N^{-1}$), calculated using the density gradient at this depth, ranges from 0.5 to 0.9 h, and no systematic variability was seen at these, or any other, frequencies. From April to the end of July there was no systematic variation with time in any of these properties in the CIL (depth range 38–42 m) at BSK I. At BSK II, however, the depth

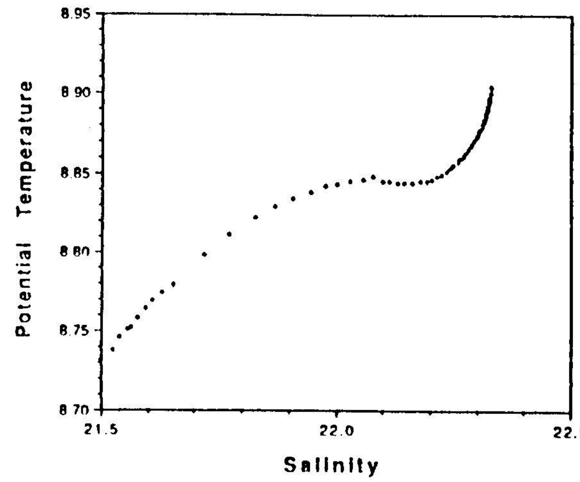


Fig. 6. Blow up of the potential temperature–salinity diagram for the deep water below about 200 m.

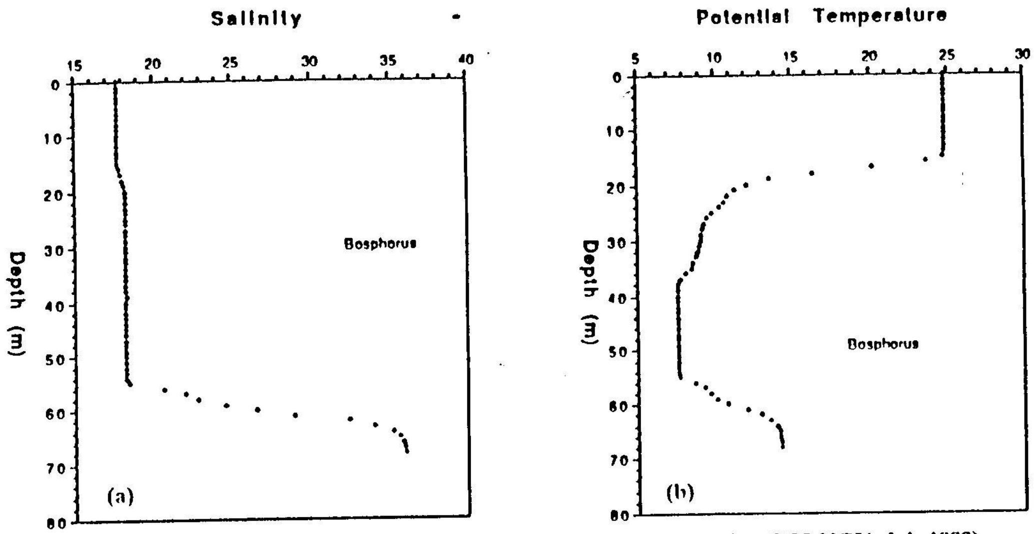


Fig. 7. Profiles of (a) salinity and (b) potential temperature from a station (BS5-HC51; July 1988) located in the northeastern end of the Bosporus.

range of the CIL was slightly deeper (45–51 m) and the potential temperature increased progressively by 0.5°C from April to July. In the middle of the suboxic zone at both locations, 72 m at BSK I and 76 m at BSK II, the variability in θ and S was less than that in the CIL and no systematic changes were observed with time. The rapid migrations, by several tens of meters, in the depth of the pycnocline at nearshore station locations reported by KEMPE *et al.* (1990) were not observed in any of our nearshore or offshore data. We also conducted yo-yo-type repeat CTD casts over periods of 3–4 h at nearshore stations (e.g. BS3-3) and observed only small variability (≤2 m). In the absence of good winter hydrographic data it is not possible to conclude whether the small variability documented above holds for an annual basis.

Multi-year variability also requires careful examination. Stations AII-1445 and AII-1463 were occupied in 1969 and are located near our 1988 sites BSK I and BSK II, respectively. At BSK I the temperatures are in excellent agreement with the 1969 values. The salinity (and density) were higher by 0.2 and 0.4‰ in all 1988 samples than 1969 as reported by MURRAY *et al.* (1989). At BSK II, however, the comparison is different. The temperature, salinity and density at a given depth were all higher in 1969 than at any time sampled during 1988, and by large amounts (0.4°C and 0.7‰). The systematic differences can be illustrated by comparing the upper 200 m salinity profiles at BSK I (BS3-2 with AII-1445) (Fig. 8a) and BSK II (BS3-6 with AII-1463) (Fig. 8b).

In addition to these two sets of comparisons, six more 1969 AII stations can be compared with 1988 *Knorr* stations. Of these, three are near the Turkish coast and three are in the eastern gyre region. The three comparisons near the Turkish coast all had a higher salinity at a given depth in 1988 than 1969, while the comparisons in the eastern gyre showed the reverse. KEMPE *et al.* (1990) have also pointed out the difficulty in comparing salinity vs depth profiles from different years. The problem with this approach is that depth profiles are a function of local currents and mixing and eddy fields and are thus highly dependent on the time of observation. The appropriate way to evaluate whether there have been large-scale hydrographic changes is to compare data at a given density or in the form of θ–S diagrams. All of the stations occupied at similar sites in 1969 and 1988 and suitable for comparison are included in the θ–S diagram in Fig. 9. Even though comparisons of the salinity vs depth profiles suggest much variability, when viewed as a θ–S diagram the data present a consistent pattern. All of the 1969 data are warmer at a given salinity than the 1988 data down to a salinity of about 21.0, which corresponds to a depth of about 100 m in the central Black Sea. Such differences could not be due to changes in surface currents or internal waves as suggested by KEMPE *et al.* (1990).

There are two possible explanations for the change in the θ–S relationships. The first is that the upper layers of the Black Sea are significantly colder in 1988, except perhaps for the core of the CIL (6.75°C; 18.5‰) which appears to be unchanged. Over the upper 200 m the average temperature decrease of 0.5°C yields an integrated heat loss of about 8.2×10^3 cal cm^{-2} or 34×10^3 J cm^{-2}. Over 19 y this corresponds to an average annual cooling rate of 432 cal cm^{-2} y^{-1} (or 1800 J cm^{-2} y^{-1}). Typical values of the net annual heat flux between the ocean and atmosphere at mid to high latitudes range from 20 to 100 kcal cm^{-2} y^{-1} (BUDYKO, 1963; WORTHINGTON, 1972). It is certainly plausible that the heat loss needed to explain the changes in the θ–S distributions could be due to a small but consistent variation in the natural annual heat flux; however, calculations to test this hypothesis are beyond the scope of this paper.

The second explanation is that for the depths below the CIL (about 45 m) the salinity at a given temperature was higher in 1988 than it was in 1969. For depths above the CIL the temperature is controlled by seasonal solar radiation. This alternative could be due to increased Mediterranean input as a result of decreased river outflow (TOLMAZIN, 1985a). The integrated salinity difference, times the volume of the upper 200 m, is equivalent to an additional influx of Mediterranean water of about 20 km^3 y^{-1} since 1969. This volume is of the same order of magnitude as the decrease in river input estimated by TOLMAZIN (1985a). The best estimates of the Bosporus input range from 180 to 312 km^3 y^{-1} (SPENCER and

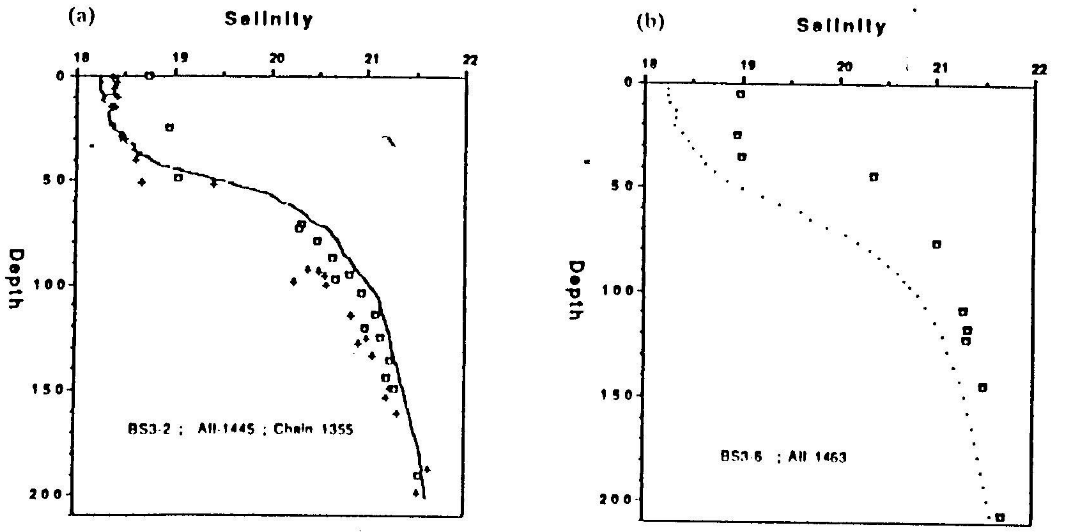


Fig. 8. Comparison of 1969, 1975 and 1988 salinity–depth profiles in the upper 200 m: (a) BS3-2, AII 1445 and Chain 1355, (b) BS3-6, AII 1463.

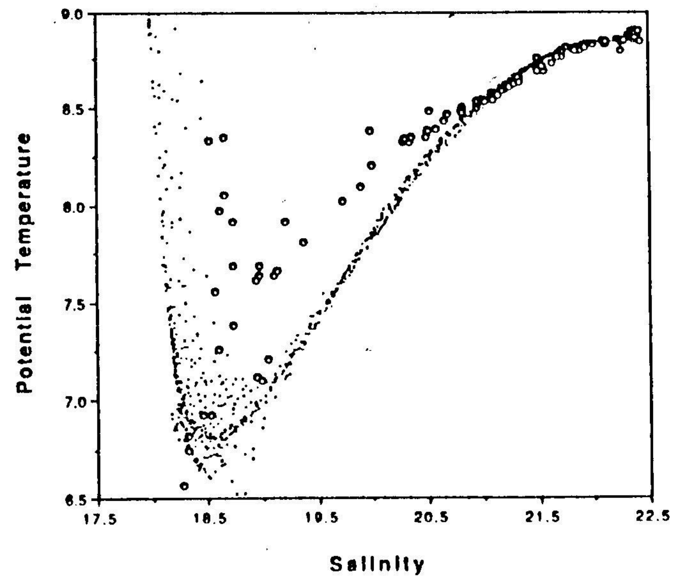


Fig. 9. Potential temperature–salinity diagram including data from six pairs of 1988 and 1969 stations in close proximity. The open circles are the 1969 data.

BREWER, 1971; GUNNERSON and OZTURGUT, 1974; SOROKIN, 1983; UNLUATA *et al.*, 1989). Such a change in Mediterranean input could have easily gone unnoticed.

The ventilation of the upper layer (e.g. 50 to at least 150 m) of the Black Sea appears to occur very rapidly. BUESSELER *et al.* (1991) have used the pulse-like input of Chernobyl cesium isotopes (^{134}Cs and ^{137}Cs) to show that ventilation of the upper layers occurs by the lateral injection of a 1:10 mixture of inflowing Mediterranean water and CIL water. The entrainment process is thought to occur near the Bosporus followed by isopycnal transport. Multiple interleaving layers of water masses with differing histories therefore must be considered in the interpretation of any vertical profile. The chemocline thus should be viewed as a region of strong lateral ventilation, with small variations easily accounting for the changes in the θ–S relationships described here.

It is clear that changes have occurred in the temperature and salinity relationships in the upper 200 m of the Black Sea. The above calculations suggest that both the heat loss and salinity increase alternatives are plausible, and with the existing data we cannot distinguish between them. If these variations are of a cyclic nature due to natural climatic cycles there should be no cause for alarm. If, however, the changes are due to diversion of freshwater inflow we should expect a further unidirectional decrease in the vertical salinity gradient with consequences regarding the distribution of oxygen and sulfide that are difficult to predict. For this reason we feel that the θ–S relations in the Black Sea should be carefully monitored.

Deep-water features

The hydrography of the deep water of the Black Sea contains interesting features that must reflect variability in the deep ventilation. The salinity increases smoothly through most of the water column below 200 m (Fig. 4a). The potential temperature, however, has a maximum at about 475 m and decreases by about 0.005°C to a shallow minimum at 600 m (Fig. 4b). The origin of these features is not easy to determine based only on the hydrographic data. They could represent the relatively recent lateral injection of warmer water at 475 m or colder water at 600 m. In some cases there is considerable fine structure at the temperature maximum, suggesting an intrusive origin. It is clear, however, that cold water has to originate at the surface while warm water is associated with Bosporus inflow.

The stability ratio, R_ρ, is defined as the ratio of the stability due to the stabilizing component relative to the instability due to the destabilizing component (TURNER, 1973; IMBODEN and WÜEST, in press). Throughout most of the water column in the Black Sea salinity increases with depth and is the stabilizing component for the density structure. Thus, the stability ratio in the Black Sea is defined as the relative density gradient due to salt divided by that due to temperature.

$$R_\rho = \frac{\beta \, \mathrm{d}S/\mathrm{d}z}{\alpha \, \mathrm{d}\theta/\mathrm{d}z}, \tag{2}$$

where α is the thermal expansion coefficient ($=-\rho^{-1}\,\mathrm{d}\rho/\mathrm{d}T$) and β is the haline contraction coefficient ($=-\rho^{-1}\,\mathrm{d}\rho/\mathrm{d}S$) ($\rho$ being the density, T the temperature and S the salinity). If R_ρ becomes much greater than 1, the destabilizing component can be ignored.

The stability ratio approaches a maximum (actually $+\infty$) at 475 m (Fig. 10a) because the temperature gradient passes through an inflection. Large values of R_ρ indicate that changes in salinity are the largest influence on the density gradient, and this suggests that the temperature maximum at 475 m has a Bosporus origin. It is very unlikely that this temperature maximum is a steady-state feature.

The single most interesting feature of the deep Black Sea is the benthic bottom layer that extends from about 1750 m to the bottom (Table 1, Fig. 5a–c). This pool of water has very

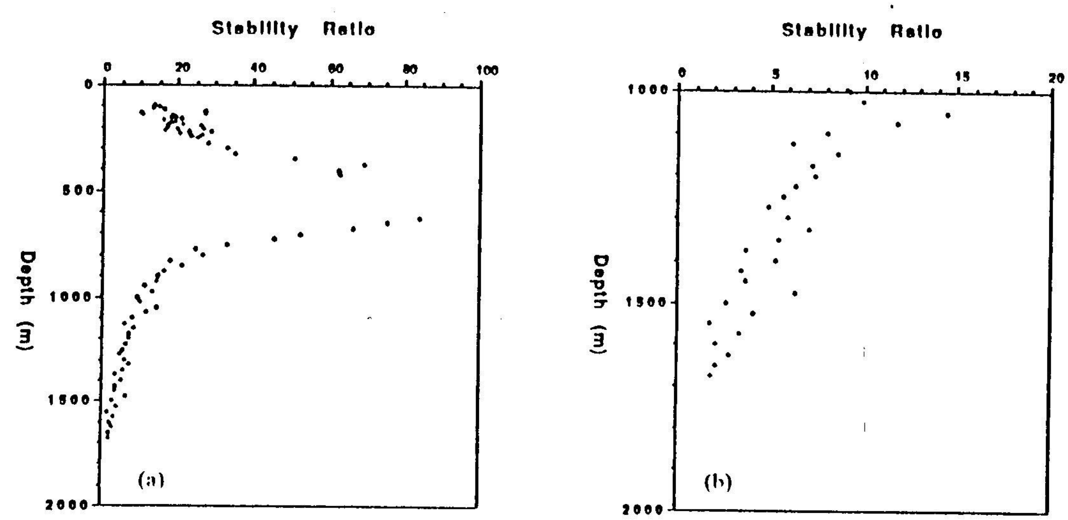


Fig. 10. Profiles of the stability ratio (R_ρ) defined as $\beta\mathrm{d}S/\mathrm{d}z/\alpha\mathrm{d}\theta/\mathrm{d}z$ for Sta. BS3-2 HC-20. (a) Full scale vertical profile. (b) 1000–2000 m profile.

uniform properties (Table 2), and there are no discernible regional gradients in either the properties or the depth of the upper boundary (Table 1). The existence of a basin-wide layer with uniform depth and properties suggests efficient homogenization by convectively driven motions. The lack of elevated concentrations of dissolved silica, ammonia and other constituents of known benthic origin, and the occasionally detectable tritium values (TOP and CLARKE, 1983), indicate that this is not a relic layer. The top of the layer can be identified by a sharp density step (Fig. 5c) that also shows up as a maximum in the Brunt–Väisälä frequency (N) (Fig. 3b). The value of N^2 increases from background values of less than $0.1\ h^{-2}$ to a maximum value of about $0.3\ h^{-2}$. The sharp step in hydrographic properties at the interface at the top of the benthic bottom layer should be smoothed out by diffusion. Its presence suggests that the uniform bottom layer is produced and maintained by convection, possibly driven by geothermal heat flow from the sediments. TURNER (1969) described similar interfaces at the top of the Red Sea brine layers.

The gradients of heat and salt in the deep Black Sea are both negative upward, and thus it is possible that vertical transport is controlled by double diffusion. Double diffusion occurs when the gradients of temperature and salinity have the same sign and thus have opposite effects on the density. The case such as in the Black Sea, where salinity is the stabilizing component, is called the diffusive regime. A master variable for double diffusion is the stability ratio, R_ρ (TURNER, 1965, 1973). Double diffusion comes into play when $1 < R_\rho < D_T/D_S \sim 70$ and is expected to become stronger as R_ρ approaches 1 (TURNER, 1965). The value of R_ρ, in the deep Black Sea, progressively decreases with depth as the influence of temperature becomes greater and reaches a value of 2 just above the benthic bottom layer (Fig. 10b). A source of heat is necessary to drive this double diffusion, and it could be heat associated with either Bosporus inflow or geothermal heat flow. The inflow of heat associated with Bosporus inflow is the most important source for the Black Sea as a whole. It is not possible to construct a heat budget for the benthic bottom layer alone; however, we expect that the relative importance of geothermal heat flow should be larger.

There have been a number of theoretical and experimental studies describing the processes that occur when a linearly stratified salt solution is heated from below (TURNER and STOMMEL, 1964; TURNER, 1965, 1968, 1973; HUPPERT and LINDEN, 1979). Convective stirring first produces a layer at the bottom that is well mixed. This layer does not continue to grow indefinitely. Because heat diffuses faster than salt, a second layer eventually forms above the first followed by a third layer and so on. In time, many such layers should form with sharp interfaces separating turbulent convecting regions. Eventually the bottom layers coalesce to form a thicker bottom layer (HUPPERT and LINDEN, 1979). Natural environments where this type of double diffusion are thought to occur include the Red Sea brines (TURNER, 1969), the Canada Basin in the Arctic Ocean (PADMAN and DILLON, 1987, 1988, 1989) and Antarctic lakes (HOARE, 1966). The distributions in the Red Sea brines are similar to those in the Black Sea in that the 100 m thick well-mixed bottom convective layers have single sharp interfaces at their top. The Red Sea differs from the Black Sea in that it has two such convective layers.

Existing theories of mixed-layer development in a double diffusively stratified fluid have been derived from laboratory experiments combined with basic energy balances. We can attempt to compare the characteristics of the Black Sea benthic layer with the available models to see if they support the double-diffusion hypothesis. TURNER (1968) and HUPPERT and LINDEN (1979) estimated the time required for the formation of a layer with thickness

h (time required for the propagation of the convective front from the bottom to its present position) from

$$t = (h/a)^2 H_*^{-1} S_*, \tag{3}$$

where $H_* = -(g\alpha H/\rho C_p)$ and $S_* = -\frac{1}{2}g\beta(dS/dz)$ are the normalized forms of the bottom heat flux (H) and initial salinity gradient (dS/dz), respectively. Taking $a = 1$ (TURNER, 1968) or $a = 1.7$ (HUPPERT and LINDEN, 1979), $H = 0.9 \times 10^{-6}$ cal cm^{-2} s^{-1} (ERICKSON and SIMMONS, 1974), $h = 400$ m, $\alpha = 0.13 \times 10^{-3}$, $\beta = 0.78 \times 10^{-3}$ and $dS/dz = 0.024‰/1000$ m, we estimate the time of growth as $t = 12$ or 34 y, depending on the choice of a. This estimate appears to be too short for the benthic bottom layer of the Black Sea, which is thought to have a residence time on the scale of hundreds of years.

According to TURNER (1968), there is a maximum thickness h, reached by the convective layer when the diffusive boundary layer above it breaks down and a secondary convective layer is formed:

$$h_1 = \left(\frac{\nu R_c}{64\varkappa^2}\right)^{1/4} H_*^{3/4} S_*^{-1}, \tag{4}$$

where $\varkappa$ and ν are the thermal diffusivity and molecular viscosity, g is the acceleration of gravity and R_c is a critical Rayleigh number given by HUPPERT and LINDEN (1979) as $R_c \cong 10^4$. Taking $\varkappa = 1.5 \times 10^{-7}$ and $\nu = 1.5 \times 10^{-6}$ m^2 s^{-1} we find $h_1 = 43$ m which would have been reached in less than a year after the initiation of the heat flux.

The failure of the above models to yield reasonable predictions suggests a basic difference between the theory and the observations. Indeed, recent experiments by FERNANDO (1987) have indicated the possibility of different regimes in the development of the convective layer. Initially, the layer thickness increases as $h \sim t^{1/2}$ as given above, until it reaches a critical thickness of

$$h_c = C(H/N^3)^{1/2} = cH_*^{1/2} S_*^{-3/4} \tag{5}$$

which occurs at about $t \cong 860\, N^{-1} = 610\, S_*^{-1/2}$ ($h_c = 20$ m and $t_c \cong 1$ month for the Black Sea), where $N^2 = 2S_*$ in the notation of FERNANDO (1987), with the constants evaluated experimentally as $C \cong 41.5$ and $c \cong 34.6$, respectively. After that time, the growth is slowed down considerably, because the interfacial entrainment by eddies becomes inefficient and the only remaining component of transport is the molecular diffusion. In fact, although reliable predictions of the growth rate cannot be made in this regime, the development of the mixing layer almost comes to a stop.

TURNER (1973) has shown that for the diffusive regime the fluxes of salt, heat and bouyancy depend on R_ρ and the temperature step between the layers (ΔT) according to the 4/3 flux law. Thus

$$\alpha g F_T = (0.32/R_\rho^2)(g/\varkappa\nu)^{1/3}(\varkappa g)((\alpha\Delta T)^{4/3}), \tag{6}$$

where R_ρ and ΔT, the temperature step at the interface, are the main variables. Oceanographic measurements suggest that this laboratory-based 4/3 flux law is valid to within a factor of 2 uncertainty, and it has been applied to diffusive regime staircases in the ocean (KELLEY, 1989). The calculation of F_T, according to the Turner equation, converted to a thermal flux for the conditions at the top of the benthic bottom layer, is shown in Table 3. The predicted double-diffusion thermal flux (F_{Th}) is 0.074 W m^{-2}, which is within a

Table 3. Calculation of the double-diffusive vertical thermal energy (F_{Th}) flux for the conditions just above the benthic bottom layer in the Black Sea using the TURNER *(1973) and* KELLEY *(1990) equations*

Turner 4/3 flux law

For the diffusive regime (TURNER, 1973) the following 4/3 flux law equation can be used to calculate the vertical temperature flux.

$$F_T = 1/\alpha 0.32/R_\rho^2 (g/\varkappa\nu)^{1/3} \varkappa (\alpha \Delta T)^{4/3},$$

where

$$\begin{aligned}
\alpha &= 13.1 \times 10^{-5}\ \mathrm{K^{-1}} && = \text{coefficient of thermal expansion} \\
\varkappa &= 1.3 \times 10^{-7}\ \mathrm{m^2\,s^{-1}} && = \text{diffusion coefficient of heat} \\
\nu &= 1.3 \times 10^{-6}\ \mathrm{m^2\,s^{-1}} && = \text{viscosity} \\
g &= 9.81\ \mathrm{m\,s^{-2}} && = \text{gravity acceleration.}
\end{aligned}$$

Assume

$$R_p = 2.0 \qquad = \text{observed value at 1700 m (Fig. 10).}$$

Assume that ΔT corresponds to the temperature step at the top of the benthic bottom layer (Fig. 5b).

$$\Delta T = 0.005°\mathrm{K}.$$

Thus

$$F_T = 1.76 \times 10^{-8}\ \mathrm{m\,s^{-1}\,°K}.$$

Convert F_T to a thermal flux:

$$F_{Th} = C_p F_T,$$

where

$$C_p = 4.2 \times 10^6\ \mathrm{J\,m^{-3}\,°K^{-1}} = \text{heat capacity of water.}$$

Thus

$$\begin{aligned}
F_{Th} &= 7.4 \times 10^{-2}\ \mathrm{J\,m^{-2}\,s^{-1}} = \text{thermal energy flux} \\
&= 0.074\ \mathrm{W\,m^{-2}}.
\end{aligned}$$

KELLEY (1990) equation

$$F_T = 1/\alpha C (g/\varkappa\nu)^{1/3} \varkappa (\alpha \Delta T)^{4/3},$$

where

$$\begin{aligned}
C &= 0.0032 \exp(4.8/R_\rho^{0.72}) \\
&= 0.059 \\
F_T &= 1.28 \times 10^{-8}\ \mathrm{m\,s^{-1}}\,\varkappa \\
F_{Th} &= 0.054\ \mathrm{W\,m^{-2}}.
\end{aligned}$$

factor of 5 of the measured geothermal heat flow (1×10^{-6} cal cm^{-2} s^{-1} or 0.40 W m^{-2}) (ERICKSON and SIMMONS, 1974). KELLEY (1990) recently has shown that the flux values at low R_ρ are overestimated by equation (6). Using his modified equation, we calculate a thermal flux of 0.052 W m^{-2} (Table 3). Both of these approaches have an uncertainty of at least a factor of 2. Within these uncertainties, the thermal flux across the top of the benthic bottom layer agrees well with the geothermal heat flow. This agreement supports, but does not prove, the argument that vertical transport across the sharp boundary at the top of the benthic bottom layer is controlled by double diffusion, driven by geothermal heat flow.

The density flux ratio for the diffusive regime is equal to

$$R_f = \frac{\beta F_s}{\alpha F_T}. \tag{7}$$

Turner (1965, Fig. 7) showed that for values of R_ρ greater than 2 the density flux ratio has a constant value of 0.15. Using this value we calculate that the value of F_S equals 4.22×10^{-10} m s^{-1}, and thus the predicted double-diffusion salt flux across the diffusive interface at the top of the benthic bottom layer (ρF_S) equals 4.29×10^{-7} g m^{-2} s^{-1}. The predicted ratio of the temperature to salinity flux equals:

$$\frac{F_T}{F_S} = 41.7\ \text{K‰}^{-1}. \tag{8}$$

The region in the deep-water column above the benthic bottom layer is more problematical. At first glance the physical properties appear to increase smoothly with depth (Fig. 5). If double diffusion is occurring we would expect a series of steps of predictable thickness to exist above the bottom convective layer (Turner, 1968; Huppert and Linden, 1979). For the Black Sea conditions the predicted step thickness is about 1 m. Slightly smaller-scale lengths (0.2 m) are calculated from R_ρ and N using an equation presented by Kelley (1989) for the dimensionless layer thickness. It would not be possible for us to resolve steps with this dimension in our data. We have looked at the original data of all the deep CTD casts in detail and tried to find evidence for staircase structure above the benthic bottom layer. Two examples are shown in Fig. 11. In some cases, like BS4-11 (Fig. 11a), the potential temperature decreases smoothly with decreasing depth. In others, like BS4-7 (Fig. 11b), temperature maxima occur with a vertical dimension of about 20 m. Maxima of this type are not uncommon for double diffusion (e.g. Padman and Dillon, 1988) and suggest diffusive instabilities. However, they could equally well reflect ventilation layers of Bosporus origin. Our present data set is not sufficient to enable us to reach a conclusion about the role of double diffusion in this region.

Bosporus inflow, entrainment and deep-water ventilation

The trend of increasing potential temperature and salinity with depth (Fig. 1) is due to input of relatively warm and salty water from the Mediterranean and Sea of Marmara through the Bosporus. A profile in the Bosporus (Fig. 7) shows that the inflowing bottom water in late July 1988 had a potential temperature of about 14.0°C and a salinity of 36.0‰. The long-term average salinity of the Bosporus inflow has been estimated to range from about 38.0‰ (Gunnerson and Ozturgut, 1974) to 35‰ (Sorokin, 1983; Unluata *et al.*, 1989). The value of 35‰ appears to be the best estimate for the long-term average. Water with this salinity is not observed in the deep Black Sea; thus entrainment of the Bosporus inflow must occur with water of lower salinity to produce deep water with a salinity of about 22.33‰. The fact that the Bosporus is the only source of salt is an important constraint.

As a first approximation the main basin of the Black Sea can be viewed as a low-salinity surface layer overlying a high-salinity deep layer. A simple box model with surface, entrainment and deep-water reservoirs can be used to learn more about the entrainment process and the residence time of deep water in the Black Sea (Table 4). This model is similar to that used by Boudreau and LeBlond (1989) to model the increase in salinity in the deep Black Sea during the Holocene. A box of unknown volume is used to simulate the

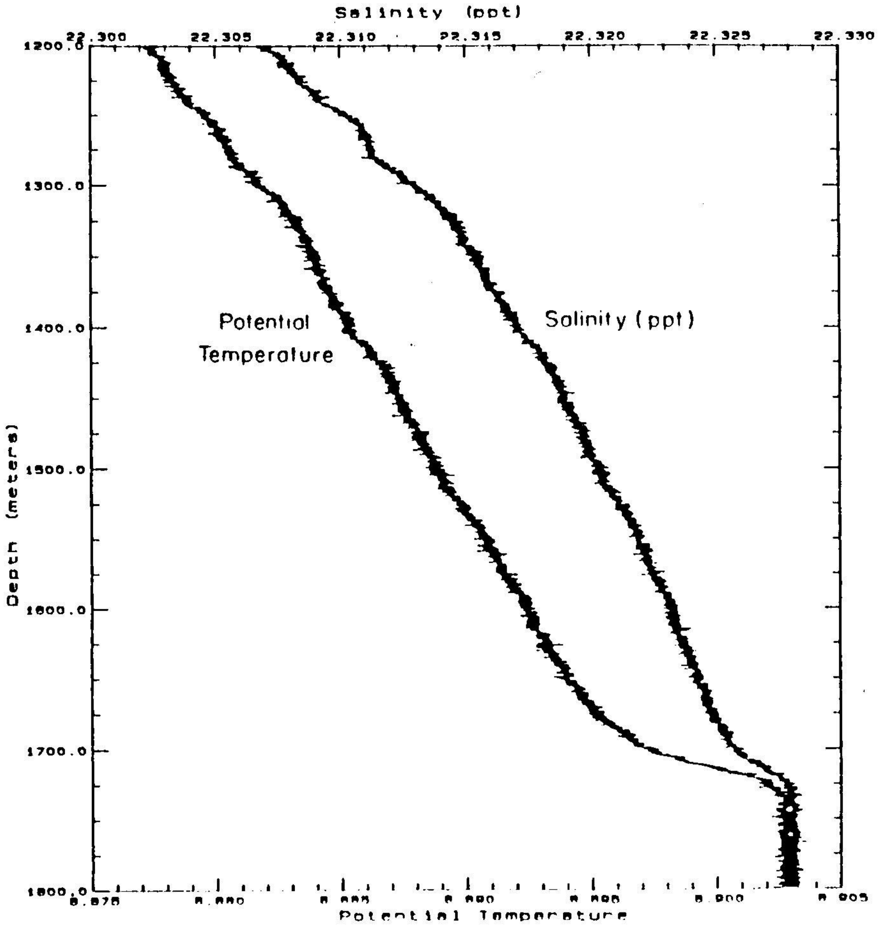


Fig. 11. Enlargements of the potential temperature and salinity profiles in the region from 1200 m to the top of the benthic bottom layer: (a) Sta. BS4-11 HC-1, (b) Sta. BS4-7 HC-1.

entrainment process. Steady-state equations are written for the deep-water balances of water, salt and heat (Table 4). There are three equations and four unknowns. We assume that the salinity of the entrained water (S_E) is 18.5‰, i.e. representing the salinity of the surface water down to the CIL (about 50 m). The results that follow are not very sensitive to this assumption. A variation of 0.5‰ in the salinity of the entrained water (S_E) changes the residence time by only 10%. We use the deep box salt balance to solve for the rate of formation of deep box water (Q_D) and the entrainment volume (Q_E). We assume an average Bosporus inflow of $3.12 \times 10^2\ km^3\ y^{-1}$ as determined by UNLUATA et al. (1989). The resulting ratio of entrainment to Bosporus inflow is Q_E/Q_B 3.30. Assuming an area of the Black Sea below 50 m of $3.7 \times 10^{11}\ m^2$ the resulting average upwelling velocity is $3.6\ m\ y^{-1}$. This compares with a value of $0.8\ m\ y^{-1}$ calculated using Bosporus inflow (Q_B) alone.

We have ignored geothermal heat flow in the deep-water heat balance equation. We can justify this for the deep Black Sea as a whole because the heat input associated with the

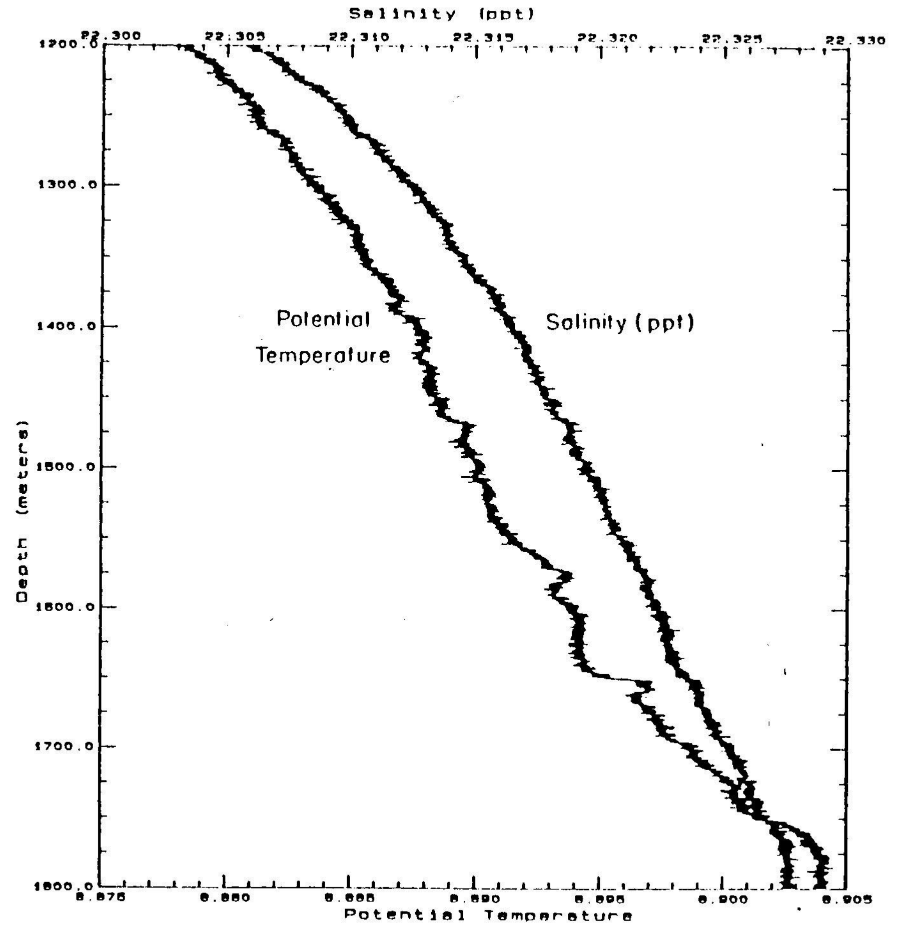


Fig. 11. *Continued.*

Bosporus inflow is the dominating factor. Assuming the value of Q_D calculated above, the heat input is given by

$$\text{deep water heat input} = V_D \times T_D \times C_p \times \rho$$

$$= \frac{13.4 \times 10^2\ \text{km}^3\ \text{y}^{-1} \times 8.906°\text{C} \times 0.97\ \text{cal g}^{-1}°\text{C}^{-1} \times 1.017 \times 10^{15}}{3.1 \times 10^7\ \text{s y}^{-1}}\ \text{g km}^{-3}$$

$$= 379 \times 10^9\ \text{cal s}^{-1}. \tag{9}$$

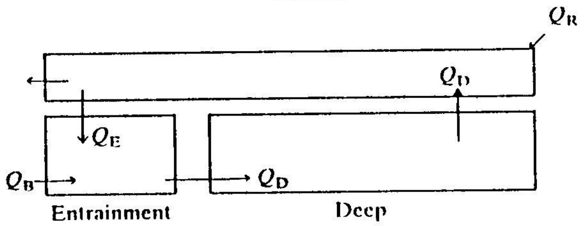
The corresponding input from the sediments is

$$\begin{aligned} \text{sediment input} &= \text{geothermal heat flow} \times \text{sediment area} \\ &= 1 \times 10^{-6}\ \text{cal cm}^{-2}\ \text{s}^{-1} \times 2.0 \times 10^{15}\ \text{cm}^2 \\ &= 2 \times 10^9\ \text{cal s}^{-1}. \end{aligned} \tag{10}$$

For the deep box of the Black sea, heat input associated with the inflow from the Bosporus is almost 200 times greater than sedimentary heat flow. It is not possible to determine how much of this Bosporus inflow goes into the benthic bottom layer, thus, this argument does not invalidate our earlier suggestion that convection in the benthic bottom layer is driven by heat flow.

The deep-water heat balance can be solved for the average temperature of the entrained water (T_E), and the resulting value is 7.36°C. Examination of the temperature–salinity diagram indicates that the entrained water must be either winter surface water or CIL water (Fig. 2). Deep-water input is thought to occur year round (UNLUATA, 1989), thus we argue that the CIL is the main source of the entrained water. BUESSELER *et al.* (1991) have

Table 4. A simple three box model for the Black Sea to determine the amount of entrainment (Q_E), the temperature of the entrained water (T_E) and the residence time of the deep water (τ_{DW}). The transport terms (Q) have units of $km^3\,y^{-1}$



where

Q_R = river input
Q_B = Bosporus input
Q_E = entrainment
$Q_D = Q_E + Q_B$ = rate of formation of deep water.

Deep box balances (3)

Water $Q_B + Q_E = Q_D$
Salt $Q_B \cdot S_B + Q_E \cdot S_E = Q_D \cdot S_D$
Heat $Q_B T_B + Q_E \cdot T_E = Q_D \cdot T_D$.

Known variables (5)

Q_B, S_B, T_B, S_D, T_D.

Unknown variables (4)

Q_E, S_E, T_E, Q_D.

Values assumed

$Q_B = 3.12 \times 10^2\ km^3\,y^{-1}$	Q_E = ?	Q_D = ?
S_B = 35.0‰	S_E = 18.5‰	S_D = 22.33
T_B = 14.0°C	T_E = ?	T_D = 8.906.

Thus

$Q_D = 13.44 \times 10^2\ km^3\,y^{-1}$
$Q_E = 10.32 \times 10^2\ km^3\,y^{-1}$
$Q_E/Q_B = 3.30$
T_E = 7.36°C
τ_{DW} = 387 y (using volume below 50 m of 5.20×10^{17} l).

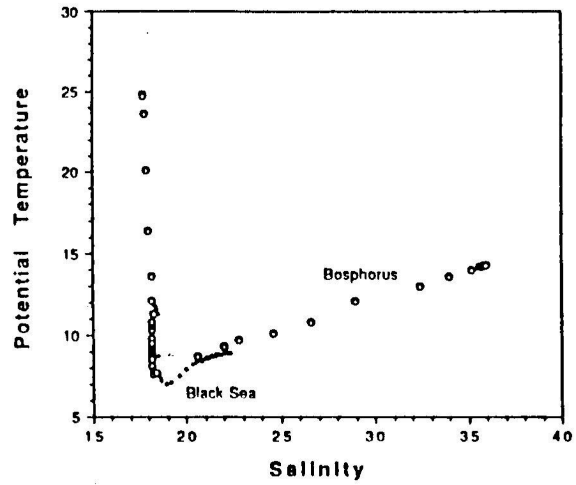


Fig. 12. Potential temperature–salinity diagram that includes data from the Black Sea (solid dots) and Bosporus (open circles) on the same plot.

reached a similar conclusion for water from 50 to 150 m on the basis of cesium isotopes. For this depth range the extent of entrainment is larger and the fraction of CIL entrained is about 90%. When observed on a large scale the temperature and salinity of the Black Sea deep water fall approximately on a straight line joining CIL water and Bosporus bottom water (Fig. 12). Assuming a volume of the deep Black Sea below 50 m of 5.20×10^5 km^3, the residence time of deep water with respect to V_B and V_E is 387 y. For comparison, a Bosporus inflow of 1.80×10^2 km^3 y^{-1} (SPENCER and BREWER, 1971) results in a deep-water residence time of 670 y. The only way that the residence time of the deep Black Sea could approach 2000 y would be if the input to the deep water was the same as the Bosporus inflow with no entrainment. BOUDREAU and LEBLOND (1989) concluded that it took about 6000 y to establish a steady-state salinity distribution; however, their model incorporates much less entrainment than is required here.

Hydrographic observations by LATIF *et al.* (1991) support our argument that the entrained water is from the CIL. As part of a hydrographic survey conducted during the 1988 expedition, they traced the inflowing Bosporus water across the shelf of the southwestern Black Sea. Using a detailed CTD survey they determined near-bottom salinity along the inflowing channel. It is clear from their data that most of the entrainment occurs in the 50–100 m depth range. By the time the inflow reaches the 100 m contour it has a salinity between 22 and 23‰. The core of the CIL is also in this depth range, suggesting that horizontal mixing produces the entrainment flow.

The deep-water residence time of the order of 500 y is much less than the reported ^{14}C ages of 2000 y (OSTLUND and DYRSSEN, 1986). To address this problem we need to first use this box model approach to calculate the flux of carbon into the deep box and then to construct a ^{14}C balance.

The total CO_2 balance for the deep water of the Black Sea can be written as

$$Q_B C_B + Q_E C_E + J_{CO_2} = Q_D C_D, \tag{11}$$

where Q is transport as defined before and C is the concentration of total CO_2. Based on the analyses of GOYET *et al.* (1991) we assume $C_B = 2000\ \mu$mol kg^{-1}, $C_E = 3100\ \mu$mol kg^{-1}

and $C_D = 4100\,\mu$mol kg^{-1}. The resulting value of J_{CO_2} is $16.9 \times 10^{17}\,\mu$mol y^{-1}, which on an area basis is equal to $F_c = 4.56$ mol C m^{-2} y^{-1}. It is not necessary to divide this flux of total CO_2 into its organic carbon and calcium carbonate fractions for this purpose. The $\Delta^{14}C$ values of the organic carbon and calcium carbonate fractions of the sediments are the same (CALVERT et al., 1987).

The ^{14}C balance for the deep water of the Black Sea can be written as

$$Q_B C_B R_B + Q_E C_E R_E + J R_E = Q_D C_D R_D + V_D C_D R_D \lambda, \tag{12}$$

where Q and C are the mass transports and total CO_2 values, respectively, R is the $^{14}C/^{12}C$ ratio, J is the input of total CO_2 and λ is the decay constant for ^{14}C. Assuming that the pre-nuclear $\Delta^{14}C$ values of the Bosporus inflow and deep Black Sea are -50‰ ($R_B = 0.950$) and -220‰ ($R_D = 0.780$), respectively (OSTLUND and DYRSSEN, 1986), we calculate that the $\Delta^{14}C$ of the entrained water from the CIL is -200‰ ($R_E = 0.800$). Since it is assumed that the CIL is replaced annually with surface water (TOLMAZIN, 1985a) this implies that the same value would apply to the surface water as well. In other words, the pre-nuclear 'apparent' ^{14}C age of the surface water of the Black Sea would have been about 1430 y. The implications for Black Sea ventilation is that deep water upwells to the surface and is then cooled and removed from the atmospheric contact to form the CIL on a time scale that is rapid compared to atmospheric ^{14}C equilibration, which is of the order of 10 y (BROECKER and PENG, 1974). The CIL is then entrained with the Bosporus inflow to become the inflow into the deep Black Sea. The ^{14}C age of the deep Black Sea should thus be calculated relative to an input value much more depleted that the value of $\Delta^{14}C = -50$‰ normally assumed.

If the ^{14}C in the surface Black Sea was depleted to the extent calculated here this may help resolve some of the controversy about the sedimentary chronology. A major feature in the Black Sea stratigraphy is the boundary between the organic-rich sapropel called Unit II and the overlying black and white laminae called Unit I (ROSS and DEGENS, 1974). Ross and Degens reported ^{14}C dates that placed the Unit I/II boundary at 3090 y. CALVERT et al. (1987) used AMS ^{14}C analyses to date this boundary in two cores as 3600 and 4000 y, respectively. Counts of the laminae, assuming they are annual varves, leads to an age of 900–1000 y (DEGENS et al., 1980; NEFF et al., in preparation). HAY et al. (1991) argue that the aluminium accumulation rates support the younger dates. DEGENS et al. (1980) and CALVERT et al. (1987) argued that the ^{14}C dates were about 2000 y too old because of the input of old terrestrial organic carbon. Recent organic geochemical analyses, however, suggest that these sediments contain only trace amounts of terrigenous material (HEDGES, personal communication). In addition, the ^{14}C dates on $CaCO_3$ and organic carbon are the same. We propose that the ^{14}C dates are old because the $\Delta^{14}C$ of the surface water of the Black Sea was highly depleted and thus the carbon fixed by plankton and the resulting carbon flux to the sediments had an apparent age of approximately 1400 y.

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REFERENCES

BOGUSLAVSKIY S. G., A. S. SARKISYAN, T. Z. DZHIOYEV and L. A. KOVESHNIKOV (1976) Analyses of Black Sea current calculations. *Atmospheric and Oceanic Physics*, **12**, 205–207.

BOUDREAU B. P. and P. H. LEBLOND (1989) A simple evolutionary model for water and salt in the Black Sea. *Paleoceanography*, 4, 157–166.

BREWER P. (1971) Hydrographic and chemical data from the Black Sea. Reference No. 71-65, Woods Hole Oceanographic Institution, Woods Hole.

BROECKER W. S. and T.-H. PENG (1974) Gas exchange rates between air and sea. *Tellus*, XXVI, 21–35.

BUDYKO M. I. (1963) *Atlas of the heat balance of the earth sphere*. Joint Geophysical Committee, Presidium of the Academy of Sciences, Moscow, pp. 1–5, plates 1–69.

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** (Suppl.), S725–S745.

CALVERT S. E., J. S. VOGEL and J. R. SOUTHON (1987) Carbon accumulation rates and the origin of the Holocene sapropel in the Black Sea. *Geology*, **15**, 918–921.

CASPERS H. (1957) Black Sea and Sea of Azov. In: *Treatise on marine ecology and paleocology*, J. W. HEDGPETH, editor, *Geological Society of America Memoire 67*, **1**, 801–890.

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** (Suppl.), S691–S710.

DEGENS E. T., W. MICHAELIS, C. GARRASI, K. MOPPER, S. KEMPE and V. A. ITTEKKOT (1980) Warven-Chronologie und frühdiagenetische Umsetzungen Organischer Substanzen holozaner Sedimente des Swarzen Meeres. *Neues Jahrbuch Geologisch-Palaeontologischer Monatschefte*, **5**, 65–86.

ERICKSON A. and G. SIMMONS (1974) Environmental and geophysical interpretation of heat flow measurements in Black Sea. In: *The Black Sea-geology, chemistry and biology*, E. T. DEGENS and D. A. ROSS, editors, American Association of Petroleum Geologists, Memoir 20, pp. 50–62.

FASCHUK D. YA. and T. A. AYZATULLIN (1986) A possible transformation of the anaerobic zone of the Black Sea. *Oceanology*, 26, 171–178.

FERNANDO H. J. S. (1987) The formation of a layered structure when a stable salinity gradient is heated from below. *Journal of Fluid Mechanics*, **182**, 525–541.

FILIPPOV D. M. (1965) The cold intermediate layer in the Black Sea. *Oceanology*, **5**, 47–52.

FILIPPOV D. M. (1968) *Circulation and structure of the waters in the Black Sea*. Nauka, Moscow (260 pp.) (in Russian).

FRIEDRICH H. J. and E. V. STANEV (1989) Parameterization of vertical diffusion in a numerical model of the Black Sea. In: *Small-scale turbulence and mixing in the ocean*, J. C. J. NIHOUL and B. M. JAMART, editors, Elsevier, Amsterdam, pp. 151–167.

GEORGIEV YU. S. (1967) On dynamics of the cold intermediate layer in the Black Sea. In: *Okeanograficheskiye issledovaniya Chernogo Morya* (*Oceanographic investigations of the Black Sea*), Naukova Dumka, Kiev, pp. 105–113 (in Russian).

GOYET C., A. L. BRADSHAW and P. G. BREWER (1991) Carbonate system in the Black Sea. *Deep-Sea Research*, **38** (Suppl.), S1049–S1068.

GUNNERSON C. G. and E. OZTURGUT (1974) The Bosphorus. In: *The Black Sea—geology, chemistry and biology*, E. T. DEGENS and D. A. ROSS, editors, American Association of Petroleum Geologists, Memoir 20, pp. 99–114.

HAY B. J., S. HONJO, S. KEMPE, V. A. ITTEKKOT, E. T. DEGENS, T. KONUK and E. IZDAR (1990) Interannual variability in particle flux in the southwestern Black Sea. *Deep-Sea Research*, **37**, 911–928.

HAY B. J., M. A. ARTHUR, W. E. DEAN and E. D. NEFF (1991) Sediment deposition in the late Holocene abyssal Black Sea: terrigenous and biogenic matter. *Deep-Sea Research*, **38** (Suppl.), S711–S723.

HOARE R. A. (1966) Problems of heat transfer in Lake Vanda, a density stratified Antarctic lake. *Nature*, **210**, 787.

HUPPERT H. E. and P. F. LINDEN (1979) On heating a stable salinity gradient from below. *Journal of Fluid Mechanics*, **95**, 431–464.

IMBODEN D. M. and A. WÜEST (in press) Mixing mechanisms in lakes. In: *Lakes*, A. LERMAN, editor, Springer, New York.

JORGENSEN B. B., H. FOSSING, C. W. WIRSEN and H. W. JANNASCH (1991) Sulfide oxidation in the anoxic Black Sea chemocline. *Deep-Sea Research*, **38** (Suppl.), S1083–S1103.

KELLEY D. E. (1989) Explaining effective diffusivities within diffusive oceanic staircases. In: *Small-scale turbulence and mixing in the ocean*, J. C. J. NIHOUL and B. M. JAMART, editors, Elsevier, Amsterdam, pp. 481–502.

KELLEY D. E. (1990) Fluxes through diffusive staircases: a new formulation. *Journal of Geophysical Research*, 95, 3365–3371.

KEMPE S., G. LIEBEZEIT, A.-R. DIERCKS and V. ASPER (1990) Water balance in the Black Sea. *Nature*, 346, 419.

LATIF M. A., E. OZSOY, T. OGUZ and U. UNLUATA (1991) Observations of the Mediterranean inflow in the Black Sea. *Deep-Sea Research*, 38 (Suppl.), S711–S723.

MURRAY J. W. (in press) Hydrographic variability in the Black Sea. In: *Black Sea oceanography*, E. IZDAR and J. W. MURRAY, editors, Kluwer, Deventer, The Netherlands.

MURRAY J. W. and E. IZDAR (1989) The 1988 Black Sea Oceanographic Expedition: overview and new discoveries. *Oceanography*, 2, 15–16.

MURRAY J. W. *et al.* (1989) Unexpected changes in the oxic/anoxic interface in the Black Sea. *Nature*, 337, 411–413.

NEUMANN G. (1944) Das Schwarze Meer. *Zeitschrift Gesellschaft fur Erdkunde zu Berlin*, 3, 92–114.

OGUZ T., M. A. LATIF, E. ÖZSOY, H. I. SUR and U. UNLUATA (in press) On the dynamics of the Southern Black Sea. In: *Black Sea oceanography*, E. IZDAR and J. W. MURRAY, editors, Kluwer, Deventer, The Netherlands.

OSTLUND H. G. (1974) Expedition "Odysseus 65". Radiocarbon age of Black Sea Water. In: *The Black Sea—geology, chemistry and biology*, E. T. DEGENS and D. A. ROSS, editors, American Association of Petroleum Geologists, Memoir 20, pp. 127–132.

OSTLUND H. G. (1990) Black Sea 1988 tritium and radiocarbon results. University of Miami, Tritium Laboratory, Data Release #89-37.

OSTLUND H. G. and D. DYRSSEN (1986) Renewal rates of the Black Sea deep water. In: *The chemical and physical oceanography of the Black Sea*. Reports of the Chemistry of the Sea XXXIII, University of Göteborg, Göteborg, Sweden.

OVCHINNIKOV I. M. and YU. I. POPOV (1987) Evolution of the cold intermediate layer in the Black Sea. *Oceanology*, 27, 555–560.

ÖZSOY E., Z. TOP, G. WHITE and J. W. MURRAY (in press) A report on double diffusive intrusions and convective layering observed in the Black Sea during leg 4 of the 1988 Oceanographic Expedition. In: *Black Sea oceanography*, E. IZDAR and J. W. MURRAY, editors, Kluwer, Deventer, The Netherlands.

PADMAN L. and T. M. DILLON (1987) Vertical heat fluxes through the Beaufort Sea thermohaline steps. *Journal of Geophysical Research*, 92, 10799–10806.

PADMAN L. and T. M. DILLON (1988) On the horizontal extent of the Canada Basin thermohaline steps. *Journal of Physical Oceanography*, 18, 1458–1462.

PADMAN L. and T. M. DILLON (1989) Thermal microstructure and internal waves in the Canada Basin diffusive staircase. *Deep-Sea Research*, 36, 531–542.

ROOTH C. G. H. (1986) Comments on circulation diagnostics and implications for chemical studies of the Black Sea. In: *The chemical and physical oceanography of the Black Sea*, Reports of the Chemistry of the Sea XXXIII, University of Göteborg, Göteborg, Sweden.

ROSS D. A. and E. T. DEGENS (1974) Recent sediments of the Black Sea. In: *The Black Sea—geology, chemistry and biology*, E. T. DEGENS and D. A. ROSS, editors, American Association of Petroleum Geologists, Memoir 20, pp. 183–199.

SOROKIN YU. I. (1983) The Black Sea. In: *Ecosystems of the World 26: estuaries and enclosed seas*, B. H. KETCHUM, editor, Elsevier, Amsterdam, pp. 253–292.

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, 5877–5892.

SVERDRUP H. U., M. W. JOHNSON and R. H. FLEMING (1942) *The oceans*, Prentice-Hall, Englewood Cliffs, NJ.

TOLMAZIN D. (1985a) Changing coastal oceanography of the Black Sea. I: northwestern shelf. *Progress in Oceanography*, 15, 217–276.

TOLMAZIN D. (1985b) Changing coastal oceanography of the Black Sea. II: Mediterranean effluent. *Progress in Oceanography*, 15, 277–316.

TOP Z. and W. B. CLARKE (1983) Helium, neon and tritium in the Black Sea. *Journal of Marine Research*, 41, 1–17.

Top Z., E. Izdar, M. Ergun and T. Konuk (1990) Evidence of Tectonism from ^{3}He and residence time of helium in the Black Sea. *EOS*, **71**, 1020–1021.

Turner J. S. (1965) The coupled turbulent transports of salt and heat across a sharp density interface. *International Journal of Heat and Mass Transfer*, **8**, 759–767.

Turner J. S. (1968) The behavior of a stable salinity gradient heated from below. *Journal of Fluid Mechanics*, **33**, 183–200.

Turner J. S. (1969) A physical interpretation of the observations of hot brine layers in the Red Sea. In: *Hot brines and recent heavy metal deposits in the Red Sea*, E. T. Degens and D. A. Ross, editors, Springer, New York, pp. 164–172.

Turner J. W. (1973) *Buoyancy effects in fluids*. Cambridge University Press, New York.

Turner J. S. and H. Stommel (1964) A new case of convection in the presence of combined vertical salinity and temperature gradients. *Proceedings of the National Academy of Sciences*, **52**, 49–53.

UNESCO (1983) Algorithms for computation of fundamental properties of seawater. UNESCO technical papers in Marine Science No. 44, 77 pp.

UNESCO (1988) The acquisition, calibration and analysis of CTD data. UNESCO technical papers in Marine Science No. 54, 92 pp.

Unluata U., T. Oguz, M. A. Latif and E. Ozsoy (1989) On the physical oceanography of the Turkish Straits. In: *The physical oceanography of sea straits*, L. J. Pratt, editor, NATO/ASI Series, Kluwer, Deventer, The Netherlands.

White G., M. Relander, J. Postel and J. W. Murray (1989) Hydrographic data from the 1988 Black Sea Oceanographic Expedition. Special Report 109, School of Oceanography, University of Washington.

Worthington L. V. (1972) Negative oceanic heat flux as a cause of water-mass formation. *Journal of Physical Oceanography*, **2**, 205–211.