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Vertical variations in the principle chemical properties of the Black Sea in the autumn of 1991

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Abstract

Basin-wide principal hydrochemical data for the upper 500 m of the Black Sea were obtained at a total of 197 stations during a multi-ship, multi-institutional, HYDROBLACK-91 cruise in September 1991. Only offshore stations, 38 from the 1991 joint cruise, 5 from R/V *Knorr* (1988), 16 from R/V *Atlantis-II* (1969), and 9 from R/V *Bilim* (1990) cruises, are considered in conjunction with the present and past data as a function of potential density rather than depth. The oxycline, coinciding with the upper boundary of the permanent pycnocline ($\sigma_\Theta = 14.2–14.3$), extended down to the $\sigma_\Theta = 15.3–15.4$ surfaces during warm periods (June–September) and to the $\sigma_\Theta = 15.75$ surface during spring periods. The lower boundary of the oxycline ($O_2 \leqslant 20\ \mu M$) has remained constant within the last two decades when past and present spring data are considered, but has risen by 0.30 density units when late summer–autumn data are considered. Independent of the geographical location, the base of the transition layer was established at the $\sigma_\Theta = 16.15–16.20$ surfaces where $H_2S \geqslant 5\ \mu M$. Nitrate and phosphate reached their maxima at $\sigma_\Theta = 15.3–15.4$ surfaces and then decreased steadily with different slopes until the $\sigma_\Theta = 15.85–15.95$ surfaces. At the anoxic interface, phosphate concentration increases about 10 fold from ~0.02–0.5 μM at the $\sigma_\Theta = 15.85–15.90$ surface to 4–6 μM at the $\sigma_\Theta = 16.15–16.20$ surface. Comparison with the data from the 1970's suggests that both the maximum values and the depth integrated mass of nitrate (g NO_3–N/m^2) between the $\sigma_\Theta = 14.2$ and 16.0 surfaces have increased 2–3 fold, and the density surface where the NO_3 maximum is established has shifted by 0.30 units in the late 1980's.

1. Introduction

In recent years there has been a growing scientific interest and curiosity about the biochemistry of the oxic–anoxic interface and the changes in the ecosystem of the Black Sea which have occured during the last 2–3 decades (Bologa, 1985; Murray et al., 1989; Shushkina et al., 1990; Smayda, 1990; Bodeanu, 1992; Gomoiu, 1992; Mee, 1992). As has been clearly and strongly emphasized by Mee (1992) and Bodeanu (1992), the natural ecosystem of the Black Sea has been changed drastically in recent decades. In particular, eutrophication is very intense in the northwestern and western shelves due to the large input of land-based nutrients by the major rivers, though the volume fluxes have been reduced by some 40–50% since the late 1970's (Bologa, 1985; Dorogan et al., 1985; Tolmazin, 1985; Fashchuk and Ayzatullin, 1986). Annual nitrate and phosphate discharges of the Danube river have increased from 143 × 10³ and 12.5 × 10³ tons in the 1950's to about 740 × 10³ and 30 × 10³ tons in the late 1980's, respectively; whereas the discharge of reactive silicate has decreased by 30–50% from 784 × 10³ tons in

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1950 to 330 × 10^3 tons in 1988 (Dorogan et al., 1985; Bodeanu, 1992). Correspondingly, the N/P ratio of the Danube River has increased, whereas Si/N and Si/P ratios have decreased during the same period (Smayda, 1990). The collapse of the ecosystem of the Black Sea has been followed by a decrease in the relative abundance of diatoms, but an increase in the low-food value planktons, such as *Noctilica miliaris* (Porumb, 1992) and other dinoflagellates during the 1983–1988 period (Bodeanu, 1989, 1992). Invasion by opportunistic organisms such as ctenophores (*Mnemiopsis leidyi*) (Vinogradov et al., 1989; Shushkina and Musaeva, 1990; Shushkina et al., 1990; Smayda, 1990) and the reduction of the light transparency in the surface layer of the Black Sea (Bologa, 1985; Mee, 1992) contributed further stress onto the ecosystem.

Prior to the expedition of University of Washington (USA) (R/V *Knorr*, 1988, WHOI) and the publications related to it (Murray et al., 1989; Friederich et al., 1990; Codispoti et al., 1991), temporal and spatial variations of the principal chemical parameters were basically discussed in terms of water depths and thus related to the hydrodynamics of the basin. Recently, it has been shown to be misleading to describe the spatial and temporal variations in the levels of the principal chemical parameters with depth (Murray et al., 1989; Bezborodov and Eremeeva, 1990; Codispoti et al., 1991; Oguz et al., 1993; Saydam et al., 1993). The apparent co-existence of oxic and sulphidic layers within the interface has been debated for years caused principally by the inadequacy of the sampling and measurement of trace quantities of oxygen (Fashchuk and Ayzatullin, 1986; Stoyanov, 1986; Leonov and Ayzatullin, 1987; Bryantsev et al., 1988; Ayzatullin and Fashcuk, 1989; Lukashov and Stoyanov, 1991).

According to Murray et al. (1989) and Codispoti et al. (1991), both the upper and lower boundaries of the oxic–anoxic transition layer have risen as compared to their depths in 1969, resulting in the formation of a suboxic zone of 20–30 m thick where $O_2 \leqslant 5$ μM and H_2S is not detectable. However, comparison of historical depth profiles from similar locations have led researchers to derive conflicting conclusions on the long-term changes in the depths of the chemical boundaries defining the oxic–anoxic interface (Fashchuk and Ayzatullin, 1986; Leonov and Ayzatullin, 1987; Bryantsev et al., 1988; Murray et al., 1989; Codispoti et al., 1991) because of the temporal and spatial variations in the position of the permanent pycnocline (Sorokin, 1983; Murray et al., 1989, 1993; Codispoti et al., 1991; Oguz et al., 1991; Saydam et al., 1993). The chemistry of the entire basin as a function of water density rather than that of depth has been examined by numerous investigators recently (Murray et al., 1993; Tugrul et al., 1992; Saydam et al., 1993) in order to define the chemical boundaries of the transition zone; however, research goes back to the 1970's when Spencer and Brewer (1971) discussed the depth/oxygen zero-relation. All these investigators have shown that the vertical distributions of chemical elements are consistently corresponding to certain density surfaces independent of geographical locations.

Based on the permanence of the pynocline in the basin, Tugrul et al. (1992) compared historical hydrochemical data with respect to density and suggested that the upper boundary of the transition layer ($O_2 \leqslant 10$ μM) has risen, confirming the suggestion of Murray et al. (1989), whereas the upper boundary of the sulfidic layer has not changed during recent decades. On the other hand, nitrate concentration within the lower oxycline has increased 2–3 fold since 1970 whereas any change in phosphate concentration has remained insignificant (Codispoti et al., 1991; Tugrul et al., 1992), and reactive silicate concentration has decreased with 50% during the same period (Smayda, 1990; Trotsenko, 1989; Bodeanu, 1992).

Insufficiency of the available previous data on examinations and comparisons of the spatial variations in the principle chemical boundaries forced the various oceanographic institutes of riparian countries to conduct a basin-wide, multi-ship investigation by collecting data of the required resolution around the transition zone. To achieve this, several institutions of the Black Sea riparian countries and Woods Hole Oceanographic Institution (USA) contributed hydrographic (T, S, σ) as well as chemical data related to the concentrations of dissolved oxygen, hydrogen sulfide and nutrient elements (PO_4, NO_3, NO_2) under the auspices of the Hydroblack-91 joint cruise (September 2–29, 1991). R/V *Akademik* of the Institute of Oceanology (Bulgaria), R/V *Bilim* of the METU-Institute of Marine Sciences (Turkey), and R/V *Professor Kolesnikov* and R/V *Parshin* of the Marine Hydrophysical Institute (Ukraine) participated in the cruise. The entire Black Sea was covered with sections, each group working within their own exclusive economic zone.

This paper aims to discuss the vertical distributions of chemical parameters within the offshore regions of the Black Sea and describes observed changes in the chemical properties within the oxic layer of the Black Sea with respect to density surfaces by utilizing the data collected during both the joint 1991 cruise and other cruises, such as R/V *Atlantis-II* (April 1969; see Brewer, 1971), R/V *Knorr* (June–August 1988; see Friederich et al., 1990), R/V *Trepang* (March 1992; Konovalov, pers. commun., 1993), and R/V *Bilim* (February/April 1990; IMS, unpubl. data). Locations of offshore stations used are shown in Fig. 1.

2. Materials and methods

Water samples were collected either by a rosette or discrete bottle casts at standard depths or at pre-determined density surfaces with a minimum resolution of 5 m between the 15.0 and 16.2 isopycnal surfaces. Neither nitrate and dissolved oxygen below the 16.20 surface nor H_2S concentrations above the 15.4 surface were analyzed during the cruise. Nutrient elements were measured on board the vessels using either a single-channel auto-analyzer or a colorimeter, and dissolved oxygen by standard or modified semi-automatic Winkler methods. Before each sampling, reagents and sampling bottles were flushed with oxygen-free argon gas for 3–5 min and then immediately filled with the sample and reactives were added. Samples for hydrogen sulfide were transfered into 250 ml

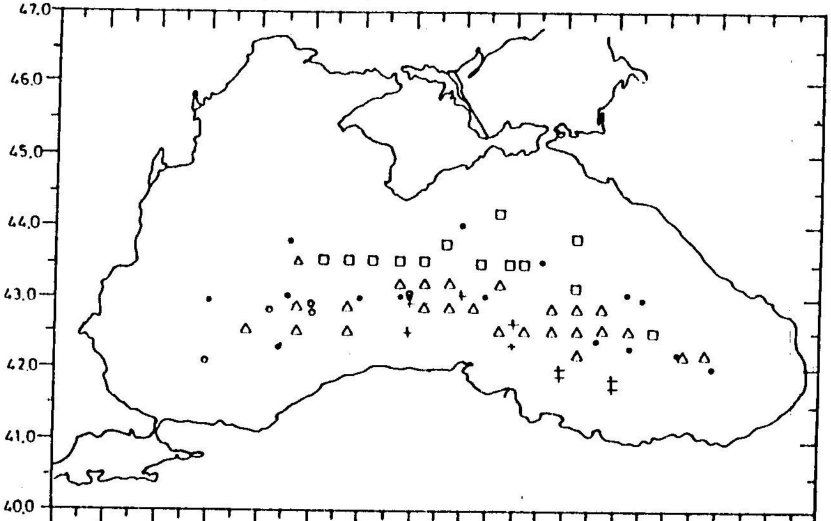

Fig. 1. Black Sea: positions of offshore stations for R/V *Atlantis-II* (April 1969) (●); R/V *Knorr* (May–June 1988) (○); R/V *Bilim* (February–April 1990)(+); R/V *Bilim* (September–October 1991) (△) and R/V *Kolesnikov* (September–October 1991) (□).

volumetric flasks which were flushed with argon gas and containing standardized iodine solution, and then titrated against standard thiosulfate as given in APHA-AWWA-WPCF standard methods (Greenberg et al., 1985).

3. Results and discussion

The depth (e.g. pressure) dependent composite plots of O_2 and NO_3-N data obtained by the R/V *Bilim* 1991 joint cruise at offshore stations of the Black Sea (Fig. 1) are displayed in Fig. 2a,b to show the advantages of using σ_θ as the principle variable. Vertical and horizontal scattering in the data (Fig. 2a,b) due to the differences in the locations and hence in the associated hydrodynamics such as heating–cooling, advection–diffusion and biochemical processes disappears when they are plotted in terms of σ_θ surfaces (Figs. 6 and 8), and the data become easier to interpret and to compare with other data sets. Therefore, throughout the scope of this work, vertical variations of chemical parameters will be discussed in terms of σ_θ surfaces.

The composite plots of potential temperature and salinity with respect to σ_θ and that of σ_θ with respect to depth for a randomly chosen set of offshore stations are shown in Figs. 3a–c, 4a–c and 5a–c, respectively, for locating the selected density surfaces used in discussions. The upper sections of the oxic layer were uniform down to 30–50 m (σ_θ = 13.8–14.2) during late winter–early spring (Fig. 5a,b) and down to 10–20 m (σ_θ = 12.0–14.2) during the summer periods (Fig. 5c,d). The thermocline is located just below this layer; there the temperature reaches its minimum of 6.5–7.0°C (σ_θ = 14.20–14.30) (Fig. 3a–d) which characterizes the core of the Cold Intermediate Layer (CIL). Since the salinity (Fig. 4a–d) does not show a detectable gradient down to 14.2–14.3 surfaces, the pycnocline is mainly controlled by the changes in temperature above this density surface (Fig. 5). The CIL always occupies a position at the upper edge of the halocline below which the increase in the density is primarly controlled by the increase in salinity.

Formation and renewal of the CIL by cold surface water at the centers of cyclonic gyres during the winter period (Ovchinnikov and

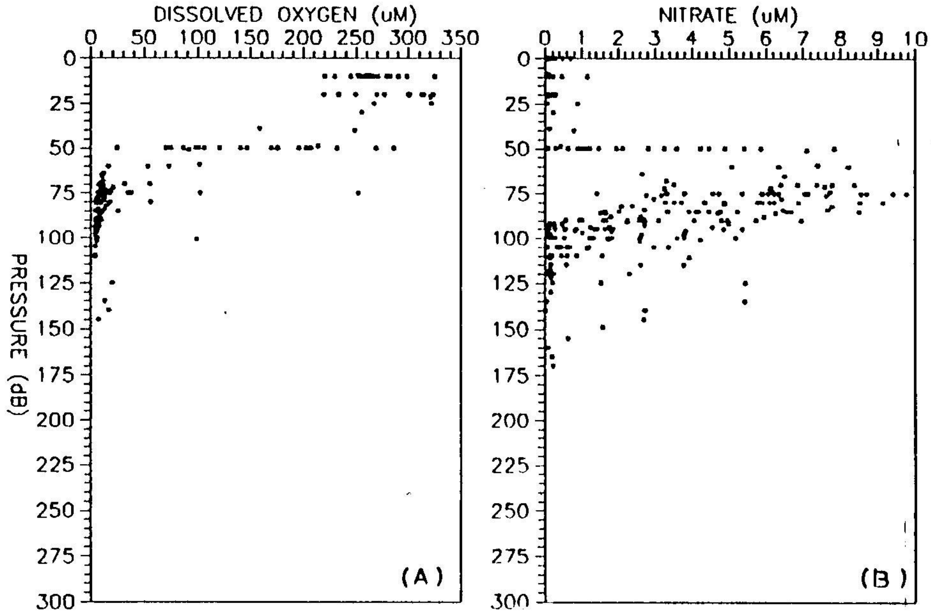

Fig. 2. Composite depth profiles of dissolved oxygen (A) and nitrate (B) for offshore stations of the R/V *Bilim* September–October 1991 cruise in the Black Sea.

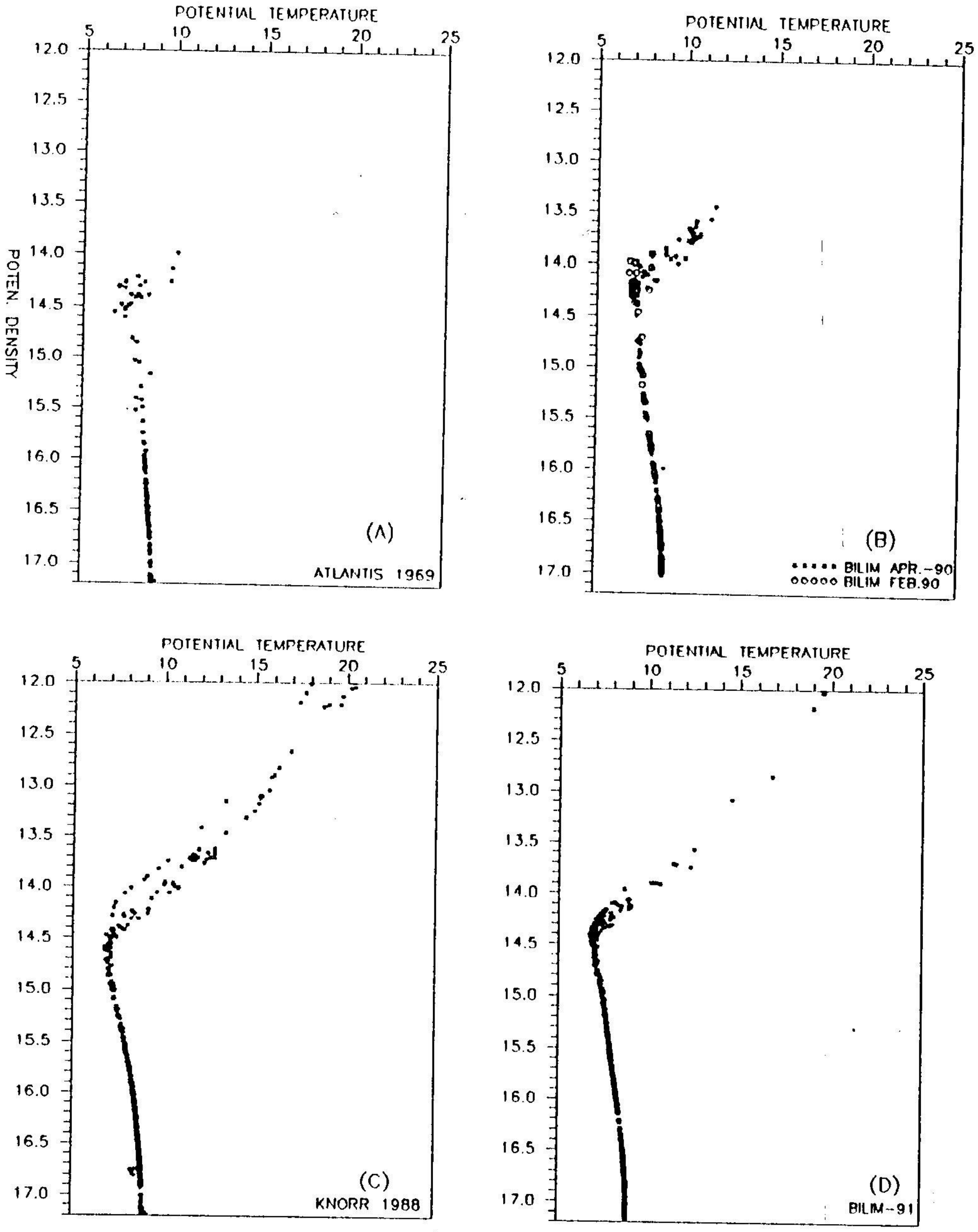

Fig. 3. Potential density-dependent variations of potential temperature for offshore regions of the Black Sea. (A) R/V *Atlantis-II* (April 1969). (B) R/V *Bilim* (February–April 1990). (C) R/V *Knorr* (May–June 1988). (D) R/V *Bilim* (September–October, 1991).

Popov, 1986; Oguz et al., 1991) leads to intensive downward and lateral transport of oxygen-saturated surface water and seems to be the most important path of oxygen supply to the intermediate waters. Oguz et al. (1991) showed that the convectively mixed layer extends down to 60 m with uniform values of temperature (6.8°C), salinity (18.5) and σ_Θ (14.5) in January 1989, as shown in an offshore station (42°35′N–36°00′E). Once formed, this layer persists throughout the year although its thickness shows spatial inhomogeneity. Therefore, the vertical distributions of many chemical properties above this surface ($\sigma_\Theta = 14.5$) are determined by the formation

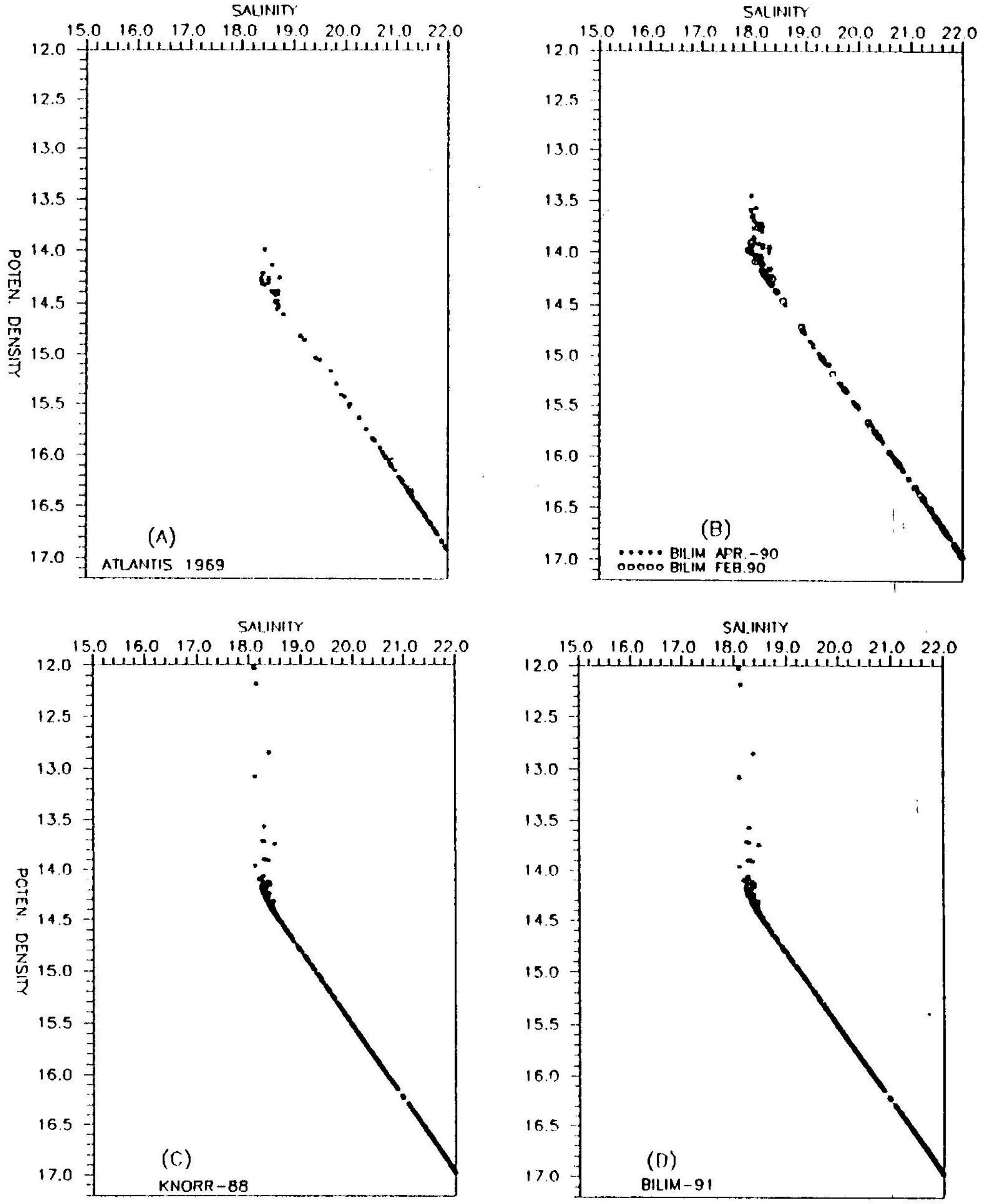

Fig. 4. Potential density-dependent variations of salinity for offshore regions of the Black Sea. (A) R/V *Atlantis-II* (April 1969). (B) R/V *Bilim* (February–April 1990). (C) R/V *Knorr* (May–June 1988). (D) R/V *Bilim* (September–October 1991).

and renewal of the CIL during the winter season which forms an additional barrier for vertical mixing in the oxic layer during warm seasons. Below this surface, the potential density starts to increase (Fig. 5), O_2 to decrease (Fig. 6), and NO_3 (Fig. 8) and PO_4 (Fig. 9) start to increase to attain their corresponding maxima in the upper mixed layer.

One of the early concepts related to the transition zone is the "layer of co-existence" (*C*-layer), which is confined between 0 μM O_2 as the lower and 0 μM H_2S as the upper boundaries within which they exist together (Sorokin, 1971; Grasshoff, 1975; Fashchuk and Ayzatullin, 1986; Stoyanov, 1986, 1991; Vinogradov et al.,

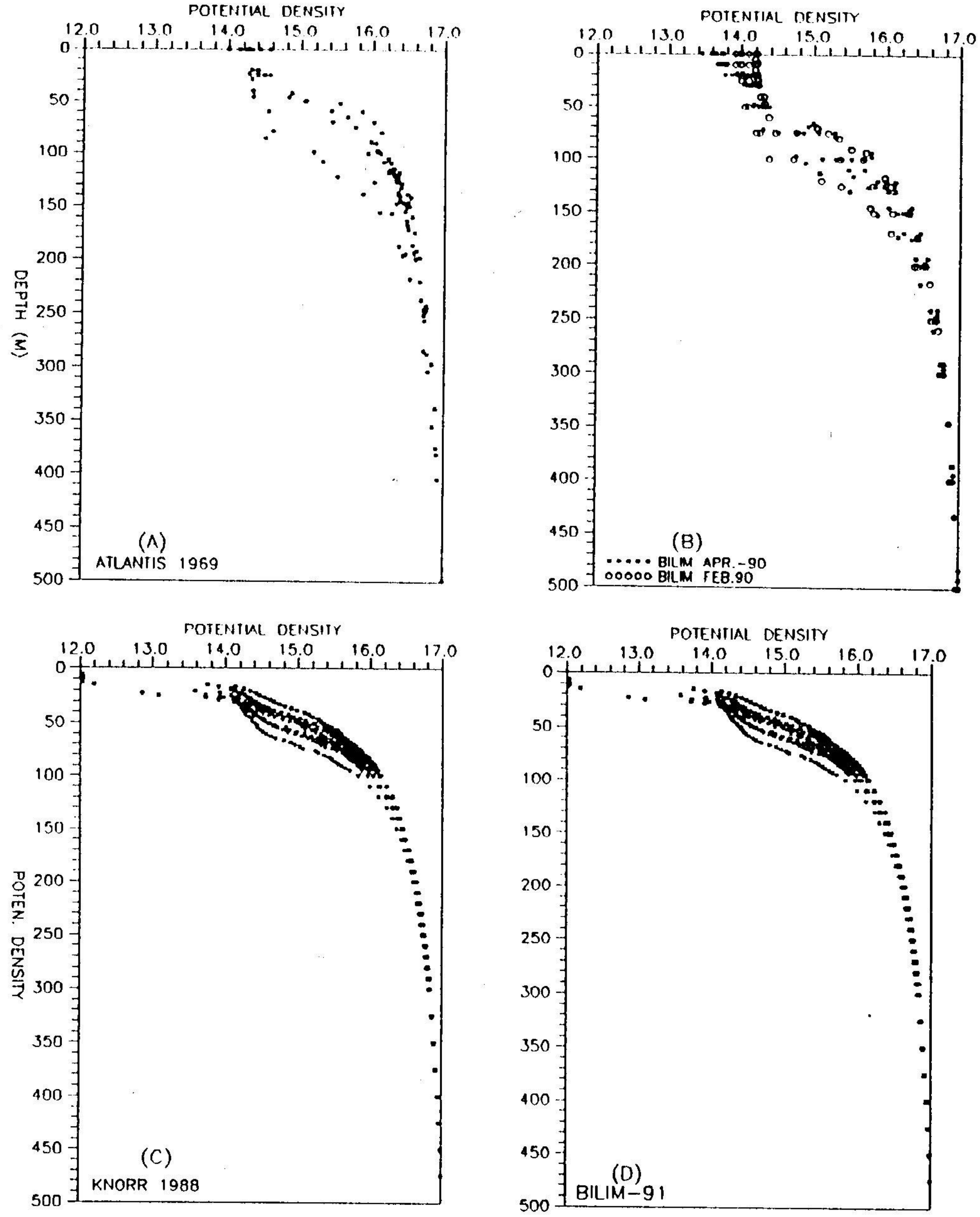

Fig. 5. Depth-dependent variations of potential density for offshore regions of the Black Sea. (A) R/V *Atlantis-II* (April 1969). (B) R/V *Bilim* (February–April 1990). (C) R/V *Knorr* (May–June 1988). (D) R/V *Bilim* (September–October 1991).

1986; Leonov and Ayzatullin, 1987; Bryantsev et al., 1988; Ayzatullin and Fashcuk, 1989; Fashcuk et al., 1990). Another concept, the so called "sub-oxic zone", in which $O_2 \leqslant 5$ μM and H_2S is undetectable, was suggested by Murray et al. (1989) and Codispoti et al. (1991) after the Black Sea expedition of University of Washington (USA) on R/V *Knorr* (WHOI) in June–August 1988. The thickness of this layer varies from 5–15 m (Codispoti et al., 1991; Bezborodov, 1992; Novoselov, 1992) to as much as 45–120 m (Fashcuk and Ayzatullin, 1986). Here, we will define the oxic/anoxic transition zone as a layer in which $O_2 \leqslant 20$ μM and $H_2S \geqslant 5$ μM for

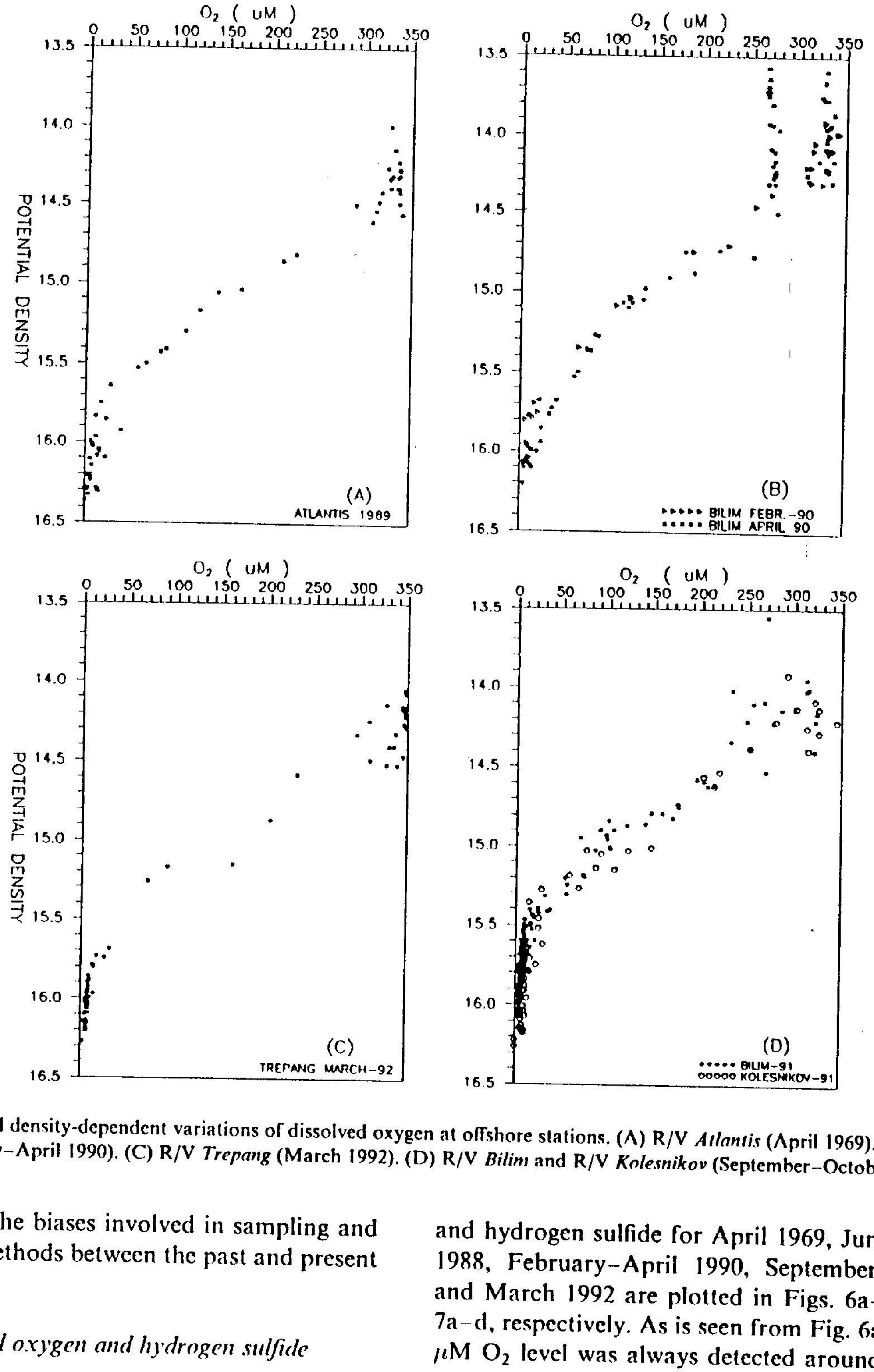

Fig. 6. Potential density-dependent variations of dissolved oxygen at offshore stations. (A) R/V *Atlantis* (April 1969). (B) R/V *Bilim* (February–April 1990). (C) R/V *Trepang* (March 1992). (D) R/V *Bilim* and R/V *Kolesnikov* (September–October 1991).

minimizing the biases involved in sampling and analytical methods between the past and present data.

3.1 Dissolved oxygen and hydrogen sulfide

Composite profiles of the dissolved oxygen and hydrogen sulfide for April 1969, June–July 1988, February–April 1990, September 1991, and March 1992 are plotted in Figs. 6a–d and 7a–d, respectively. As is seen from Fig. 6a–c, 20 μM O_2 level was always detected around 15.75 surface during the 1969, 1990 and 1992 spring periods irrespective of the geographical location. This implies that vertical mixing processes are responsible for the renewal of water masses down to 14.5 surface and lateral transport processes for the water masses between 14.5–15.80 surfaces other wise a broadening in the nitrate curve should be expected. The 0.30 density unit shift in the position of 20 μM O_2 ($\sigma = 15.40$–15.45) during the summer–autumn periods of 1988 and 1991 is mainly caused by the suppression of the vertical mixing and hence oxygen supply by the CIL during warm periods and to the increased consumption of oxygen by increased sinking detritus, and probably not by the unidirectional increase in the thickness of the transition layer (as was stated by e.g. Murray et al., 1989, and Tugrul et al., 1992).

Although there was no apparent unidirectional shift in the position of the 20 μM O_2 (except seasonal changes), the curve of the oxycline shifted from nearly linear in the 1970's (Fig. 6a) to dome-shaped in the late 1980's (Fig. 6b,c). Assuming there is no change in the oxygen supply rates within the last 2–3 decades, the slope of the O_2 vs. σ_Θ curve between the $\sigma_\Theta = 14.30$ and $\sigma_\Theta = 15.0$ surfaces, and between the $\sigma_\Theta = 15.0$ surface and 20 μM O_2 level was calculated as 245–260 and 160–170 μM per unit density, respectively. Although the upper slope of the oxycline ($\sigma_\Theta = 14.3$–15.0) has not shown a detectable difference since 1969 (245 μM/σ_Θ in April 1969, and 260 μM/σ_Θ in February–April 1990), the slope of O_2 curve has increased to 315 μM/σ_Θ in September 1991. However, the slope of the lower part of the oxycline ($\sigma_\Theta > 15.4$) has become more pronounced (~ 250 μM $O_2/\sigma\Theta$ in 1969 and 160–170 μM $O_2/\sigma\Theta$ in 1990 and 1991). This steepening in the gradient or increase in the consumption rate of O_2 may partially be caused by the increased downflux of organic detritus which, in turn, is affected by the long term changes in the hydrographic properties through the revisions on major fresh water inputs or those in climatic conditions which affect vertical and horizontal transport of materials. The evidence for the latter is not clear yet, and it is necessary to examine the decadal climatic changes for the region. The former possibility seems to be more realistic because there is an increased influx of organic matter and nutrient elements through coastal discharges (Bologa, 1985; Dorogan et al., 1985; Fashchuk and Ayzatullin, 1986; Smayda, 1990; Bodeanu, 1992) during the last 2–3 decades.

The thickness of the transition zone where $O_2 \leqslant 20$ μM and the $H_2S \geqslant 5$ μM has varied from 0.55 ($\sigma_\Theta = 15.75$–16.30) density units in April 1969 to 0.45 ($\sigma_\Theta = 15.75$–16.20) units in February–April 1990 and to 0.85 ($\sigma_\Theta = 15.45$–16.20) units in September 1991. These differences are considered to be seasonal rather than unidirectional long-term changes. This point needs further elucidation with more spring and summer data in the future. A remarkable point is the steady decrease of the O_2 concentration at the $\sigma_\Theta = 15.40$ surface where the nitrate maximum is established. Its concentration has decreased from 90–100 μM in April 1969 to 60–70 μM in February–April 1990 and, still lower, to 20–25 μM in September 1991. This continuous decrease in O_2 is considered to be the result of the increased downflux of organic detritus of both autochthonous and allochthonous origin into this layer. Water masses above the $\sigma_\Theta = 14.50$ surface are frequently ventilated directly by vertical mixing (Oguz et al., 1991), and water masses below this surface where the largest density gradient was observed (Fig. 5) are ventilated intermittently by lateral transport of water masses of different origin (Buesseller et al., 1991; Oguz et al., 1991).

The intermittent ventilation of water masses down to the $\sigma_\Theta = 16.50$ isopycnal surface can be deduced from the distribution of H_2S (Fig. 7a–d). H_2S distribution does not show a sharp increase at the $\sigma_\Theta = 16.20$ surface. It increases down to the $\sigma_\Theta = 16.50$ surface and then remains nearly constant below the base of permanent the pycnocline ($\sigma_\Theta = 16.50$ surface, i.e at 250–300 m). It is clear that the upper sections ($\sigma_\Theta = 16.20$–16.50) of the sulfidic zone are more influenced by biochemical redox processes and by lateral transport of water masses.

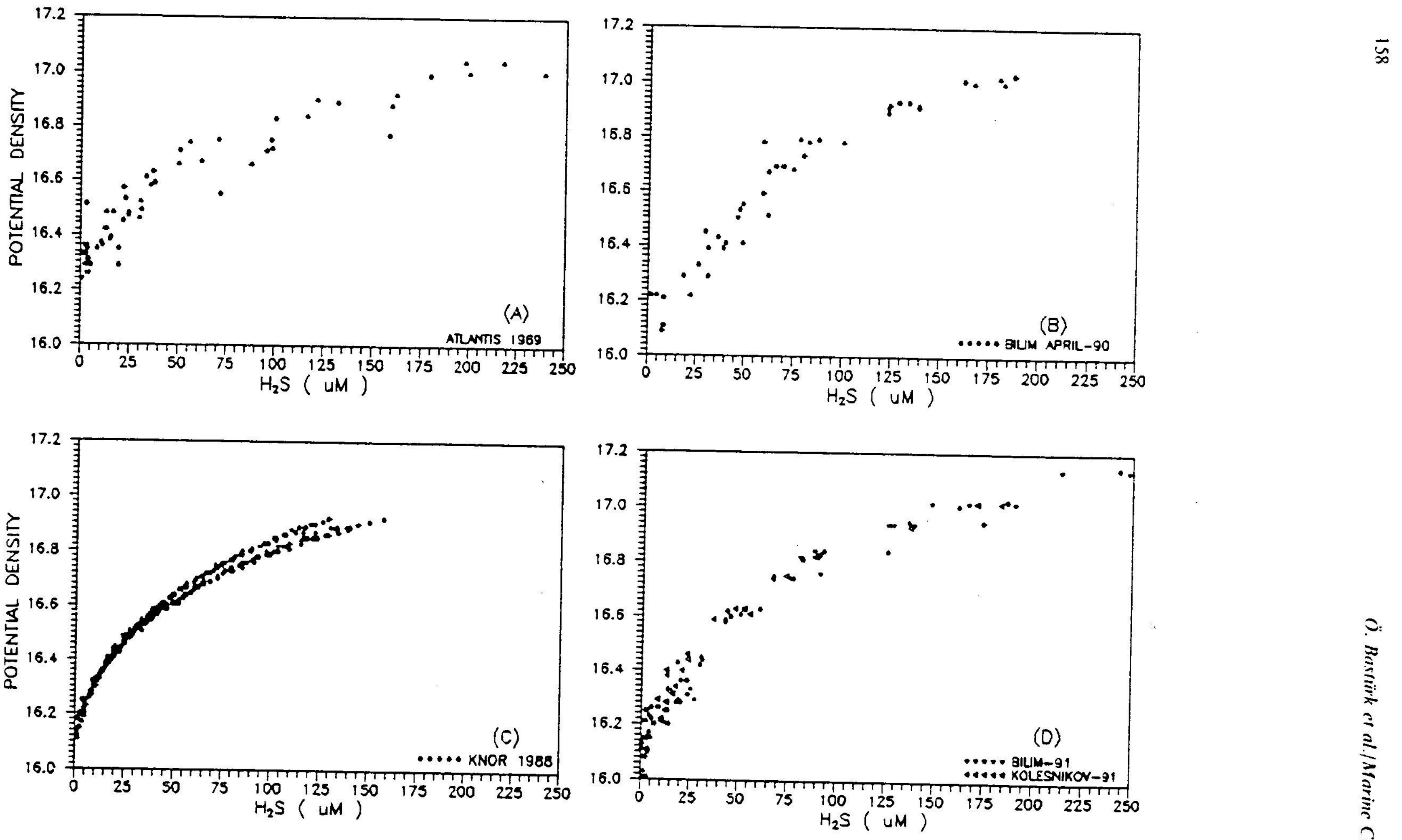

Fig. 7. Potential density-dependent variations of hydrogen sulfide at offshore stations. (A) R/V *Atlantis* (April 1969). (B) R/V *Bilim* (February–April 1990). (C) R/V *Knorr* (May–June 1988). (D) R/V *Bilim* and R/V *Kolesnikov* (September–October, 1991).

3.2 Nitrate and phosphate

Figures 8a–d and 9a–d show that NO_3 and PO_4 concentrations are nearly zero due to consumption by plankton above the seasonal pycnocline ($\sigma_\Theta = 14.20–14.30$). Below this surface their concentrations increase to a maximum at around the $\sigma_\Theta = 15.40–15.45$ surface due to the microbial oxidation of sinking organic matter and then decrease steadily towards the oxic/anoxic interface ($\sigma_\Theta = 15.85–15.95$). Nitrate concentration diminishes completely just before the onset of H_2S caused by heterotrophic denitrification but not by ammonification reactions

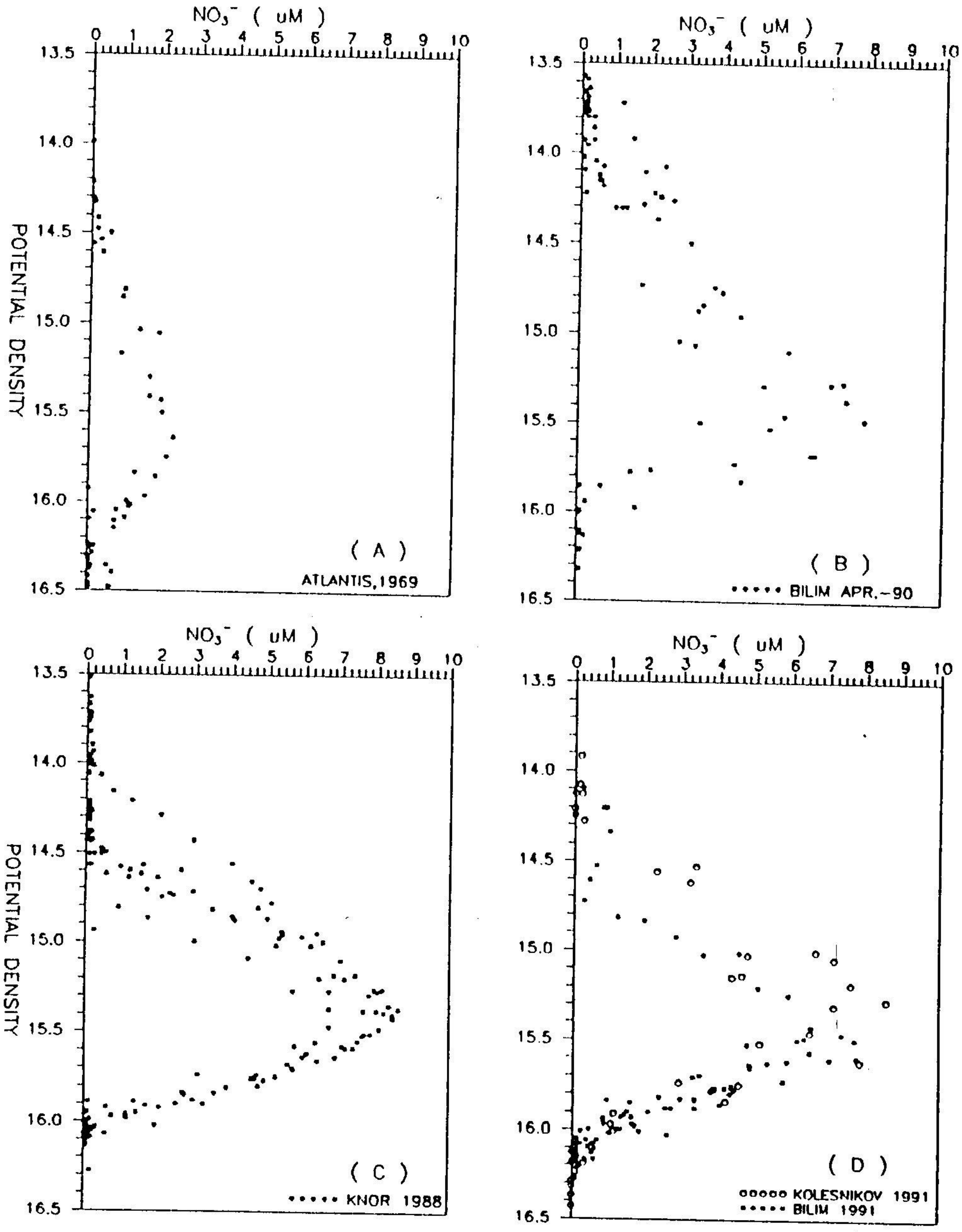

Fig. 8. Composite plots of nitrate vs. potential density at offshore stations of the Black Sea. (A) R/V *Atlantis* (April 1969). (B) R/V *Bilim* (April 1990). (C) R/V *Knorr* (May–June 1988). (D) R/V *Bilim* and R/V *Kolesnikov* (September–October 1991).

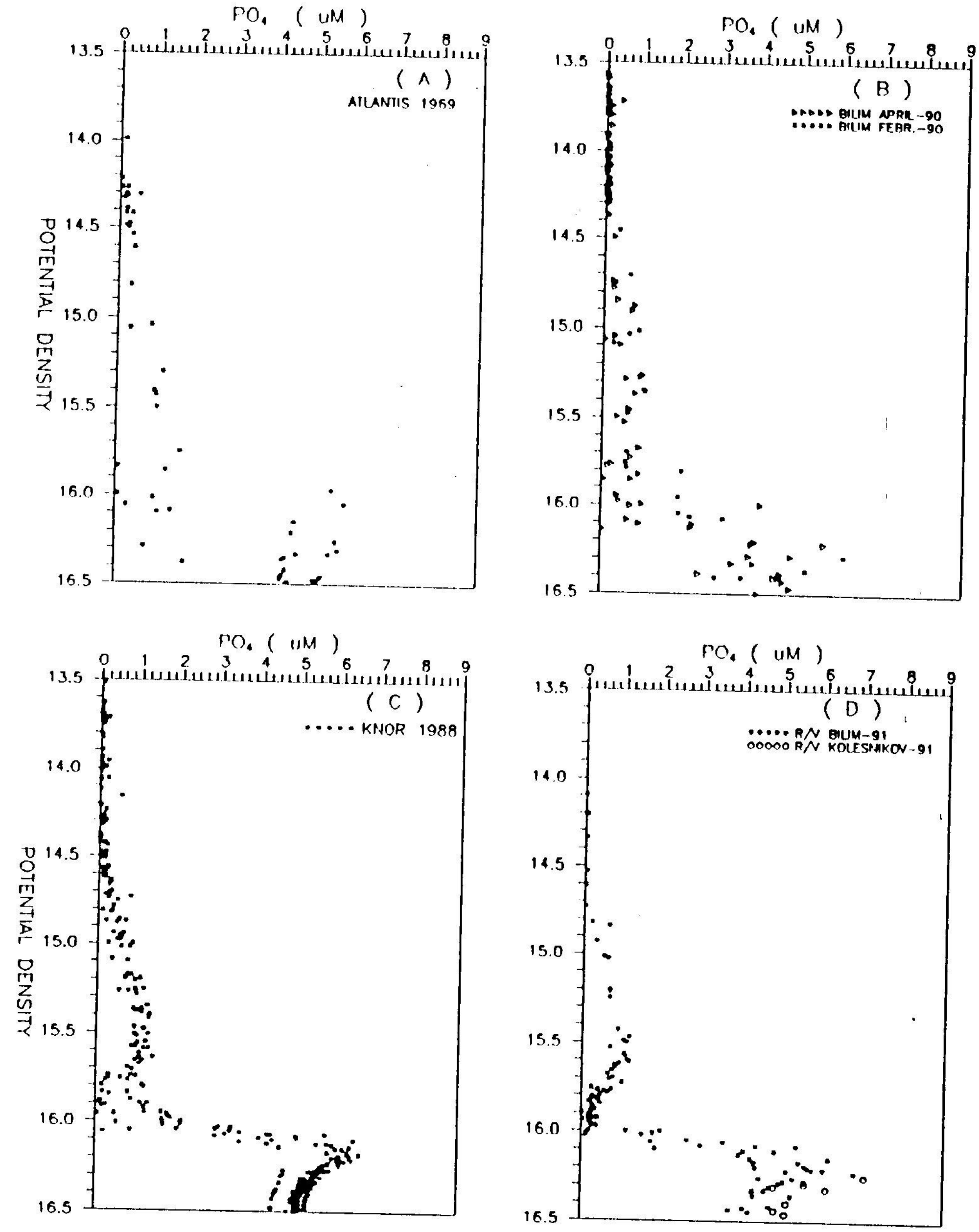

Fig. 9. Composite plots of phosphate vs. potential density at offshore stations of the Black Sea. (A) R/V *Atlantis* (April 1969). (B) R/V *Bilim* (February–April 1990). (C) R/V *Knorr* (May–June 1992). (D) R/V *Bilim* and R/V *Kolesnikov* (September–October 1991).

since there is no overlap of ammonia and nitrate within the transition layer (Murray et al., 1993). Ward and Kilpatrick (1991) found detectable nitrate reduction rates coinciding with the nitrite maximum and concluded that the nitrite maximum is caused by the decreased rates of nitrite removal by oxidation and increased nitrite production via nitrate reduction, the contribution of NH_4 oxidation being small. Other mechanisms responsible for the decrease in NO_3-N concentration are the oxidations of diffused NH_4^+, Mn(II) and Fe(II) compounds by nitrate (Murray et al., 1993), indicating that new production in the Black Sea is extremely small. If this is the case, the only remaining source of nitrogen for the photic zone is the autotrophic nitrogen fixation which was shown to be very little (Karl and Knauer, 1991) and anthropogenic inputs.

Although there has been practically no shift in the position of the density surface where nitrate starts to increase (σ_Θ = 14.20–14.30), there have been detectable changes both in the magnitude and position of the nitrate maximum (Fig. 8a,b) and in the shape of the NO_3 vs. σ_Θ curve. The concentration of nitrate at its maximum has approximately been tripled, from 2.0–2.3 μM in 1969 (Fig. 8a) to 6–9 μM in 1988–1991 (Fig. 8b–d). Whilst the depth at which the nitrate concentration started to increase varied seasonally, the position of the nitrate maximum, which was located at around the σ_Θ = 15.75 surface in 1969, has shifted upward to the σ_Θ = 15.40 surface and remained there, i.e. an upward shift of 0.30–0.35 density units since the 1970's. Secchi disk depths at offshore regions of the Black Sea have decreased from about 50–60 m in the early 1960's (Finenko, 1991, cited in Mee, 1992) to 25–35 m in the 1980's (Bologa, 1985) and to 10–15 m at present. The shoaling of the photic zone due partly to the anthropogenic inputs of light absorbing dissolved organic matter and partly to the increased biological production within the photic zone (Bodeanu, 1992; Gomoiu, 1992) is clearly evident. This shoaling has resulted in the shoaling nutrient regeneration depth in the oxic layer.

It is interesting to note that the relative positions of the NO_3 maximum and the 20–30 μM O_2 concentrations coincide well for the April 1969 and September–October 1991 periods (Figs. 8 and 6) but not for the spring period of 1990 where they are established at σ_Θ = 15.40–15.45 and σ_Θ = 15.75 surfaces, respectively. This deviation from the expected pattern can only be explained by the differences in the magnitudes of horizontal ventilation rates of the water masses below the σ_Θ = 15.5 surfaces with waters of low nitrate content; otherwise, a detectable decrease in the maximum concentration of nitrate due to dilution should be observed in the February–April 1990 period. All these variations indicate that the water masses down to the σ_Θ = 14.5–14.6 surfaces and those below the σ_Θ = 15.5–15.6 surfaces are ventilated by different mechanisms.

The observed decrease in O_2 concentration at the σ_Θ = 15.40 surface, from 90–100 μM in April 1969 to 60–70 μM in April 1990 accounts for about 1.2–1.6 μM NO_3–N/l increase. If one accepts 2 μM N/l at the σ_Θ = 15.4–15.5 surface in 1969 as the preformed nitrate concentration then the expected NO_3–N concentration at the same density surface in April 1990 should be around 3.2–3.6 μM. When the 20 μM DO in 1991 (σ_Θ = 15.45) is considered, a further introduction of about 3.2–3.6 μM/l NO_3–N will lead to about 5.0–5.5 μM/l NO_3–N level in September 1991.

The upper slope of the nitrate curve (Fig. 8) has increased 2–4 fold, from 1.84 in 1969 to 4.4 μM NO_3–N/σ_Θ in April 1990, and to 8.6 μM NO3/σ_Θ in the summer–autumn periods of 1988 and 1991. On the other hand, the slope of the lower part of the curve has decreased 4–6 fold from −2.8 in April 1969 to −11.2 in April 1990, and to −16 and −14 μM NO_3/σ_Θ in the summer–autumn periods of 1988 and 1991, respectively.

Increase in the magnitude of the NO_3 maximum and the difference between the relative changes in the upper and lower slopes of the nitrate distribution curves lead us to conclude that the observed changes are the outcome of anthropogenic impacts and presumably due to the marked reduction in the fresh water inputs to the Black Sea (Zhorov et al, 1984; Dorogan et al., 1985; Zhorov and Boguslavsky, 1985; Faschuk and Ayzatullin, 1986; Murray et al, 1989) and the increase in the influx of all forms of combined nitrogen through rivers (Tolmazin, 1985; Mee, 1992). Anthropogenic enrichment of the oxic layer of the Black Sea by nitrogen and phosphorus has led to long-term decline in the Si:N and Si:P ratios (Trotsenko, 1989; Smayda, 1990) which favoured non-diatom blooms in response to eutrofication. All these changes forced the Black Sea ecosystem to shift from a productive to a consumptive system which increased the consumption of dissolved oxygen within the oxic layer. Another factor may be the rising of the depth of the CIL during recent decades (Kaminskij et al., 1989). The overall effect of these changes is the confinement of primary production and of the oxidative regeneration of nutrients into a narrower depth range.

The depth-integrated total mass of NO_3–N between the surface and the 16.00 density surface was calculated as 1.64 for April 1969; 4.40 for February 1990; 4.10 for April 1990; 3.68 for May–June 1988 and 3.7 g N/m^2 for September–October 1991. 2.0–2.6 fold increase in the total NO_3–N content of the mixed layer during recent decades implies that the increase in NO_3 concentration is not due to the rising of the oxycline and hence confinement of the same quantity of nutrients into a narrower water mass, but rather to the increased anthropogenic fluxes of all kinds of wastes during recent decades.

Brewer and Murray (1973), using a one-dimensional diffusion–advection model, calculated the ratio of the net consumption rates for $CO_2 : NH_3 : PO_4$ around oxic/anoxic interface as 116:11:1 where the C/N ratio is 10.5. Their C/N ratio is very close to that of Cowie and Hedges (1991) (C/N = 10.3) for the surface sediments. Therefore, organic matter produced within the water column will be considered to have a composition of O:C:N:P = 283:116:11:1 rather than Redfield ratios. Assuming this ratio holds for the Black Sea, the decrease in oxygen concentration from 270–320 μM ($\sigma_\Theta = 14.30$) to 50 μM ($\sigma_\Theta = 15.40$) during April 1990 will yield nitrate and phosphate concentrations of oxidative origin as 8.5–10.5 μM-N and 0.8–0.95 μM-P, and for the summer–autumn period (DO = 20 μM at 15.40) as 9.7–11.7 μM-N and 0.9–1.1 μM-P, in respective orders. As can be seen from Figs. 8b–d and 9c–d, the maximum in-situ nitrate concentration (6–8 μM NO_3-N) are always below and those of phosphate (0.6–1.2 μM PO4–P) are in reasonably good agreement with these stoichiometrically calculated levels. This discrepancy between the calculated and measured concentrations of nitrate is considered to be due to the removal of NO_3 by bacterial reduction and denitrification (Ward and Kilpatrick, 1991; Murray et al., 1992) as well as reduction by the reduced compounds diffusing upward (Murray et al., 1993) between $\sigma_\Theta = 15.40$ and 15.90 surfaces.

Ward and Kilpatrick (1991) found the maximum NO_2 oxidation rates at around the $\sigma_\Theta = 15.5$ density surface. They also found that maximum nitrate reduction rates coincide with the sharp nitrite maximum. All these findings imply that the nitrate maximum is constantly formed by microbiologically mediated oxidative processes and removed by nitrate reduction and denitrification processes with little or no overlap with ammonium (Codispoti et al., 1991; Murray et al., 1993) in the sub-oxic zone.

This zone of low oxygen (20–40 μM) concentration also coincides with the layer of maximum mesoplankton, *Noctilica miliaris* (Vinogradov et al., 1986, 1990) having a biomass of up to 2–3 g/m^2 and sometimes of up to 30 g/m^2. Schiff et al. (1991) detected a primary maximum for the concentration of particulate manganese species residing within the $\sigma_\Theta = 15.40$–15.70 surfaces (Lewis and Landing, 1991) and also a Fe interface at the $\sigma_\Theta = 16.10$ density surface.

It may be supposed that the real position of the sub-oxic zone and its properties are determined mainly by the features of the O_2–H_2S interaction and by the vertical speciation of the interacting substances. Consequently, if the upper boundary ($\sigma_\Theta = 14.20$–14.30) of significant changes in the vertical distribution of the fundamental chemical properties is generally determined by such physical processes as renewal and transformation of the cold intermediate layer, then the position and thickness of the suboxic zone is determined by biochemical processes.

4. Conclusion

The total amount of nitrate which was integrated with respect to the depth down to the 16.00 isopycnal surface indicated that there is a 2–3 fold increase in the total nitrate content of the upper layer during last two decades due to the increased anthropogenic inputs of all dissolved nitrogen compounds and to the confinement of productive photic layer into a narrower water mass. Its depth of occurrence has also shifted upward by about 0.30 density units during the same period.

Examination of the past data also indicates that the thickness of the transition zone shows seasonal as well as inter-annual variations when the upper boundary of this layer is defined as the surface where $O_2 \leqslant 20$ μM. Comparison of the density surfaces for 1969 and 1990 where $O_2 = 20$ μM is measured does not imply the expansion of the sub-oxic zone since this oxygen concentration was detected at around the $\sigma_\theta = 15.75$ surface both in April 1969 (R/V *Atlantis-II*) and in February and April 1990 (R/V *Bilim*). However, the gradient of the oxycline between $\sigma_\theta = 15.00$ and $DO \leqslant 20$ μM surfaces decreased due to the oxidation of increased sinking particulate organic matter.

The thickness of the transition layer (defined as $DO \leqslant 20$ μM and $H_2S \geqslant 5$ μM) was found to be 0.55 and 0.45 density units in the spring periods of 1969 and 1990, and 0.85 units in the autumn of 1991. The observed interannual variations in the thickness of the transition layer imply that there is no long-term increase in the thickness of this layer, but rather seasonal changes. On the other hand, the observed shift in the position of the $H_2S \geqslant 5$ μM by 0.10 density units within the last 2–3 decades may not be a significant feature when the poor resolution of sampling in the past is considered. However, the magnitude of the affects of such a small shift in the position of the anoxic layer should also be considered in future.

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