

distributions of the main hydrochemical properties have been attributed to complicated lateral and vertical mixing processes which are intensified in some regions in winter when the surface layer is thoroughly mixed [13,14], as well as to the rate of organic matter input from the euphotic layer [2].

In the present paper we attempt to define the ranges and to discuss the possible reasons of the spatial and temporal variability in the density dependent vertical distribution of nutrients and oxygen in the layer of the main pycnocline of the Black Sea, based on the chemical data obtained through the 1991-1994 basin-wide surveys.

2. Materials and Methods

Data sets of IMS-METU, Erdemli-Içel, Turkey and MHI-NASU, Sevastopol, Ukraine have been used in this work. These data sets have been obtained as the national contribution of international programmes: CoMSBlack and TU-Black Sea. Net of oceanographic stations covers the main part of the Black Sea (look, for example, Fig. 3). Information on accuracy of data is available in reports prepared for every international multi-ship experiment. Part of this information is in Table 1.

TABLE 1. Information on the accuracy of hydrochemical data.

Parameter	Mean value	Standard deviation	Mean value	Standard deviation
Dissolved oxygen	324	1.4	4.1	1.1
Hydrogen sulfide	39	0.8	1.9	1.3
Phosphates	6.26	0.06	0.03	0.05
Silicic acid	107	1.1	6.9	0.04
Nitrates	5.21	0.13	0.19	0.02
pH	8.41	0.005	7.86	0.008

3. Results and Discussions

3.1. DISSOLVED OXYGEN

Basin-wide density dependent profiles of dissolved oxygen (DO) (Fig. 1) imply that the water mass above the isopycnal surface 14.5-14.6 is well oxygenated, and below that, an oxygen gradient zone (the so-called "oxycline"), coinciding with the upper part of the main pycnocline, is located [5-7]. The oxycline is apparently established between density surfaces of 14.5-14.6 and 15.6-15.9. The thickness of this layer shows marked regional variations. The DO values rapidly diminish to 10-30 μM at 15.6-15.9 density surfaces and gradually decrease to less than 5 μM within the sub-oxic zone [2,5-7,15]. The vertical gradient of oxygen concentration in the oxycline, depends on the

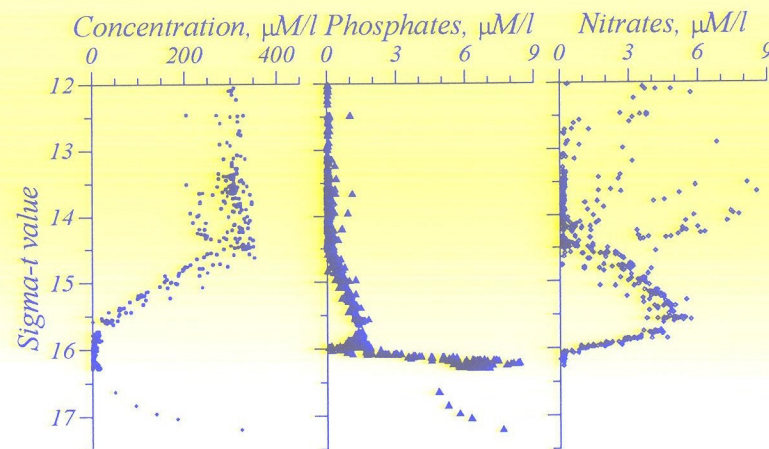


Figure 1. Distribution of dissolved oxygen, hydrogen sulfide, phosphates, and nitrates versus sigma-t in May 1994

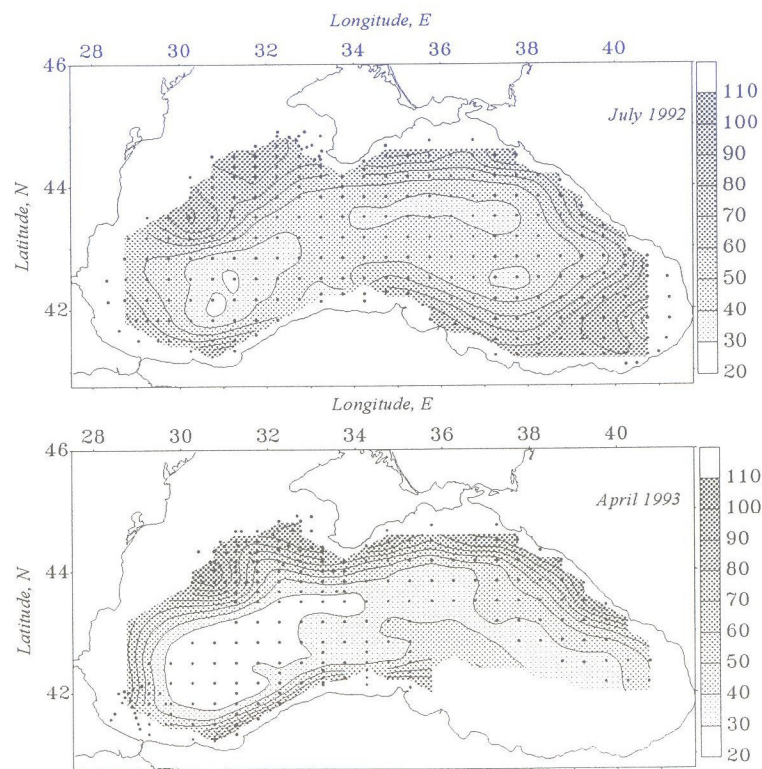


Figure 2. The depth (m) of the 14.6 isopycnal surface in July 1992 and April 1993.

hydrographic structure (Fig. 2). The DO depletion rate at a constant depth increases from coastal margins towards the cores of the cyclonic gyres [16].

The surface oxygen shows remarkable seasonal and year-to-year variations in the subsurface maximum, depending on the water temperature and the level of the primary productivity. The different realizations of the spatial distribution of DO are displayed in Fig. 3 on the 14.6 isopycnal surface, which approximately defines the oxycline onset (Fig. 1) and corresponds to the core of the Cold Intermediate Layer (CIL).

Briefly, the DO concentrations vary from 160 μM to 260 μM over the basin for July 1992 and from 280 μM to 340 μM for April 1993, and up to 310 μM for May 1994 (Fig. 3). The DO concentration in the core of the CIL is consistently higher in the cyclonic regions than in the anticyclonically dominated area near the shelf break. The core of the CIL appears to be more oxygenated, by about 20–40 μM , in April 1993 compared to May 1994 and by 40–80 μM compared to July 1992. The core waters of the CIL are up to 90–115% saturated with oxygen throughout the year.

The processes of winter convective mixing and phytoplankton activity could be responsible for increasing oxygen concentration in the CIL waters. Basinwide variations in the depth of the 14.6 density (σ_t) surface (Fig. 2) indicate that it may be as shallow as 25–30 m (April 1993), or up to a depth of 40–50 m within the cyclonic regions in late spring–summer months. Direct convective mixing in winter can reach depths of the 14.5–14.7 surface [14], but the influence of convective mixing can be detected down to the depths of 15.6–15.7 isopycnal surfaces, in distributions of temperature [11], and chemical properties [17]. Because the 25–30 m depth levels could be the base of euphotic zone in the central region of the Black Sea where the phytoplankton activity could lead to increases of oxygen, it is not yet clear whether the physical or the biological processes are more important in determining the oxygen variations in the CIL waters.

Examination of the DO content of waters at 15.6 the density surface, which roughly defines the lower boundary of the oxycline (Fig. 4), shows oxygen concentration variations in the range of 10–30 μM . Interestingly, in July 1992, hypoxia ($\text{DO} < 10 \mu\text{M}$) was recorded at some sections of the central part of the basin where the primary production was also unexpectedly very high, which was limiting the euphotic zone to the upper 10 meters in depth. DO concentrations as high as 80–140 μM (Fig. 4) were recorded in the north and north-eastern parts of the basin, surrounded by the water masses possessing very low DO levels. In April 1993, the lowest concentrations of dissolved oxygen occurred near the same place, but the position of the highest values was different (Fig. 4).

It is rather difficult to explain the elevated DO concentrations in a particular region due to the complexity of mixing processes within the main pycnocline. In general, only physical processes can provide cross-isopycnal fluxes leading to an increase of oxygen in this layer, while the chemical and biochemical Redox processes would be expected to lead to a decrease. The low DO content of waters on the 15.6 density surface indicates limited ventilation of the permanent pycnocline even within central regions during the winter mixing processes, and/or intensive utilisation of DO

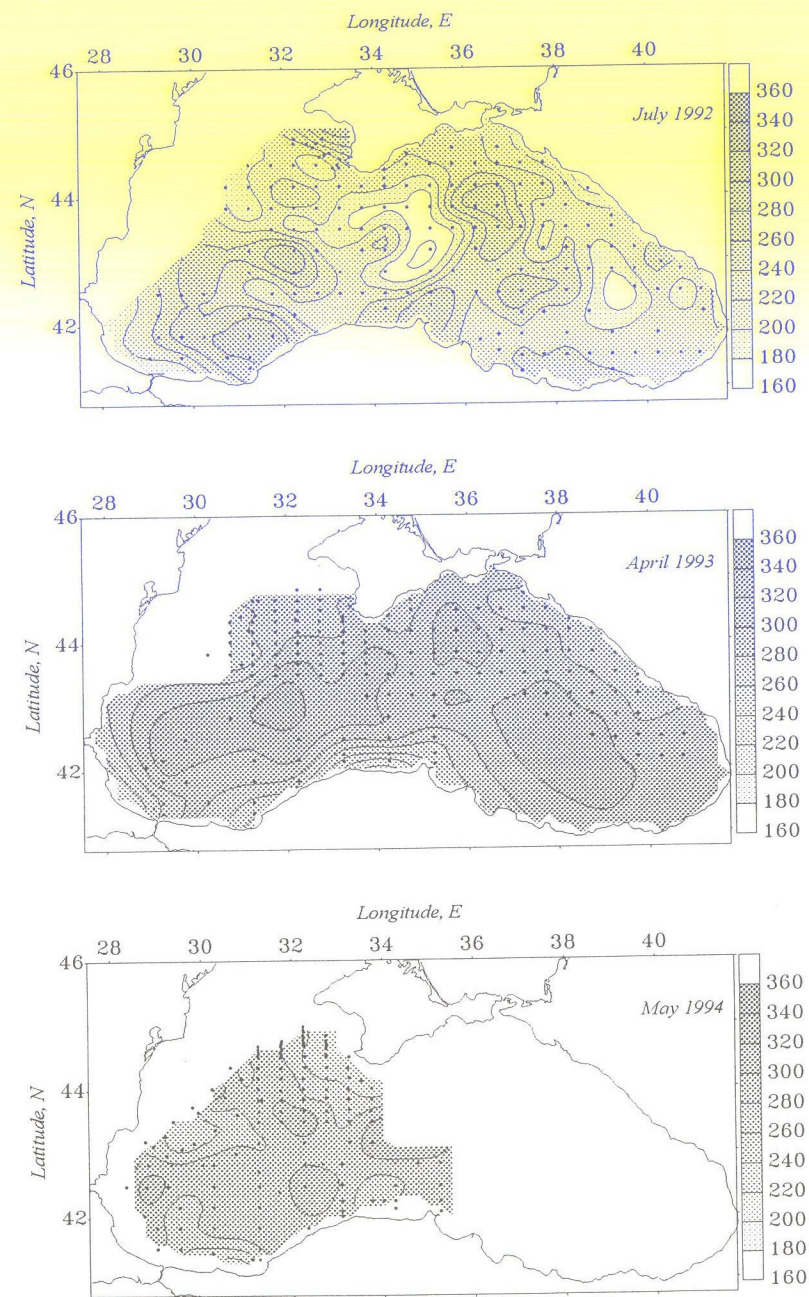


Figure 3. Dissolved oxygen (μM) at the 14.6 sigma-t surface.

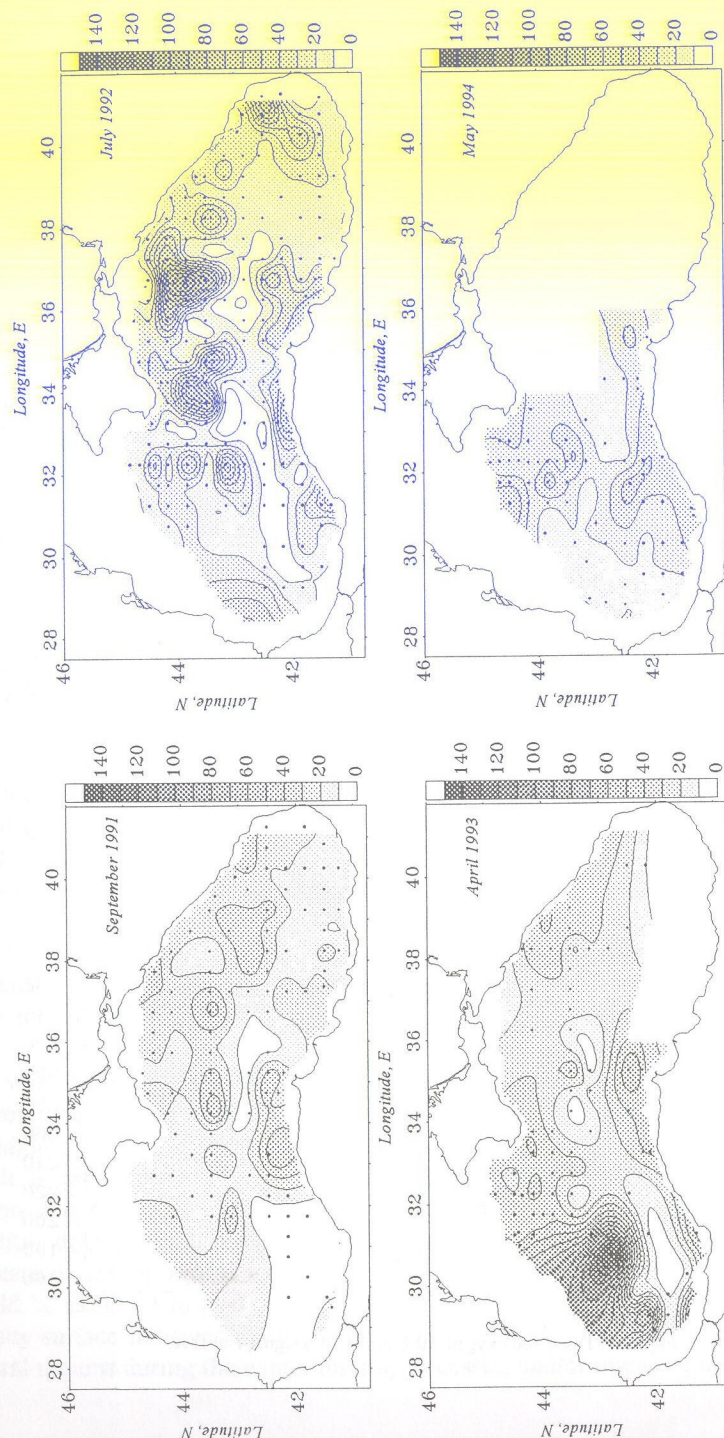


Figure 4. Dissolved oxygen (μM) at 15.6 sigma-t surface.

3.2. THE SUBOXIC ZONE

The "suboxic zone", first introduced by Murray et al. [3], was defined as a zone located "between the layer of oxygen decrease to suboxic levels (less than $5 \mu\text{M}$) and that of the first appearance of hydrogen sulfide". Later, Tugrul et al. [5] and Saydam et al. [6] suggested to use the position of subsurface nitrate maximum and the 16.2 density surface as the boundaries of the SO zone. In this study, the DO values of the $20 \mu\text{M}$ and 16.2 density surfaces define the upper and lower boundaries of the SO zone (Fig. 5). The oxycline extends to the depths of 10-30 μM of oxygen [18]. In this way, we avoid any uncertainties related to the determination of low concentrations of oxygen and hydrogen sulfide, and overcome the questions on variations in the position of the nitrate maximum. Based on these definitions, the basin-wide variations in the thickness of the SO layer in terms of depth (m) and sigma-t (σ_t) units are plotted respectively in Figs. 6 and 7. The thickness of the suboxic layer varies in space and time from 20 to 70 meters and from 0.3 to 0.8 density (σ_t) units (Figs. 6 and 7). These estimates are in good agreement with the values announced by Murray et al [3] and later by Tugrul et al. [5] for the summer period of 1988.

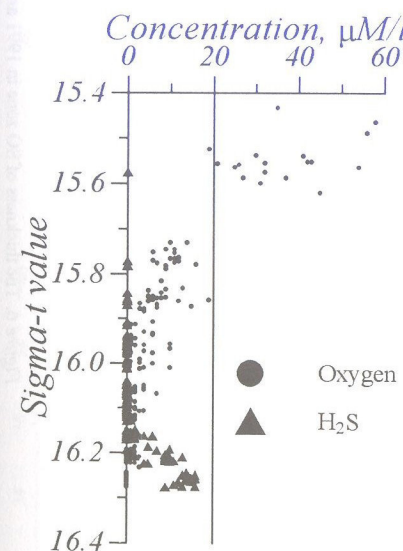


Figure 5. Oxygen and hydrogen sulfide in oxic/anoxic transition zone.

Noticeable spatial and temporal variations of the thickness of SO zone are recognised in the Black Sea waters (Figs. 6 and 7). It is yet unclear what processes are more important for spatial and temporal variations of the thickness of the SO zone, although various physical, chemical, and biochemical processes are expected to be important for different periods of the year. Good correlation between the phosphate concentration in the layer of local minimum ($\sigma_t \sim 15.95$) and the thickness of SO zone in spring (Fig. 8) implies considerable role of Redox processes. On the other hand, seasonal weather conditions for similar periods were different from 1991 to 1994, resulting in variable intensity and spatial features of the ventilation of the main pycnocline [19]. This would in turn imply

variations in the cross-isopycnal flux of all the other properties, resulting in variable intensity of the Redox processes. Biochemical processes should be more important during the blooms of phytoplankton, when great amounts of particulate organic matter sink from the euphotic zone. For example, the upper boundary of the SO zone rises upward by the 15.1-15.2 density surface in a limited area of the central Black Sea in July 1992, probably due to the excess organic matter input into the permanent pycno-

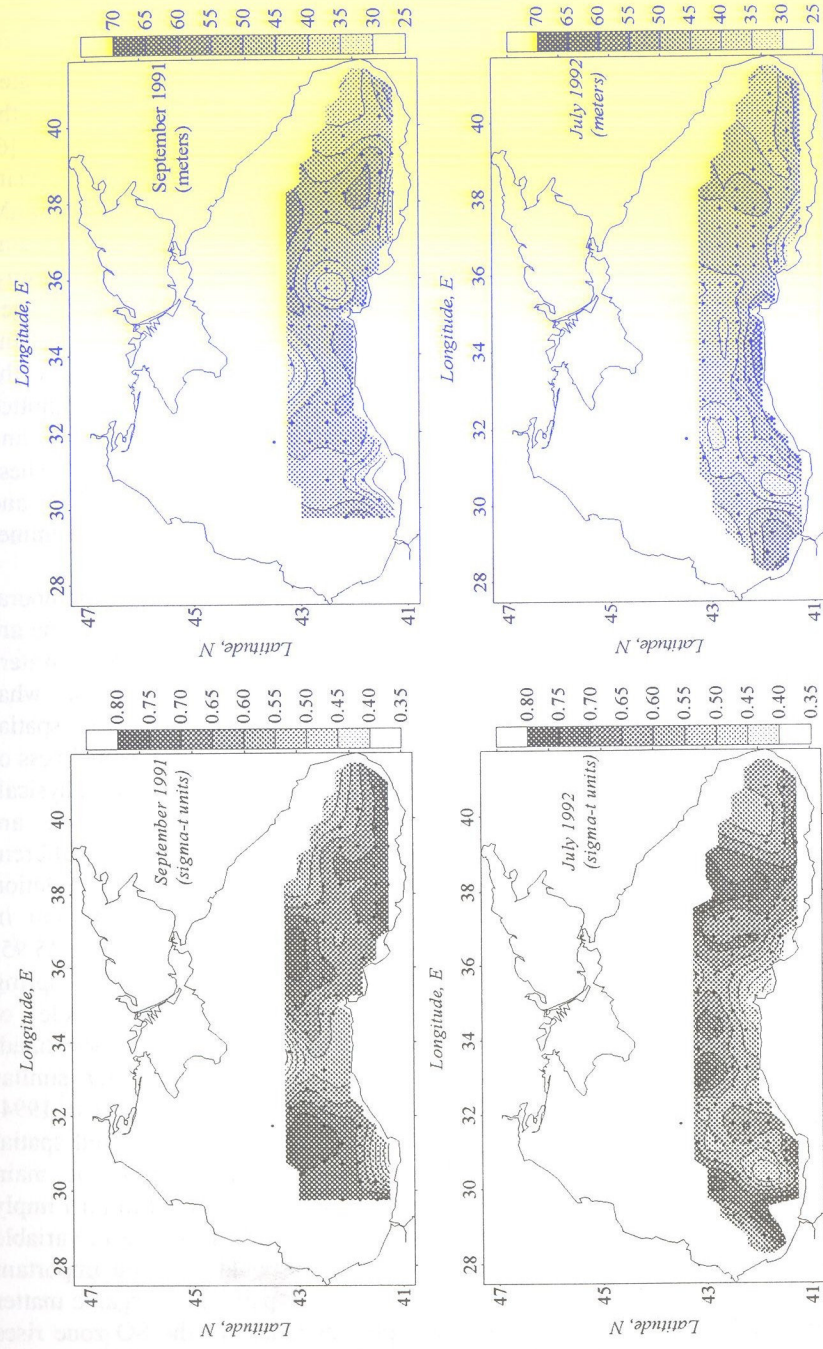


Figure 6. The thickness of SO zone in 1991 and 1992.

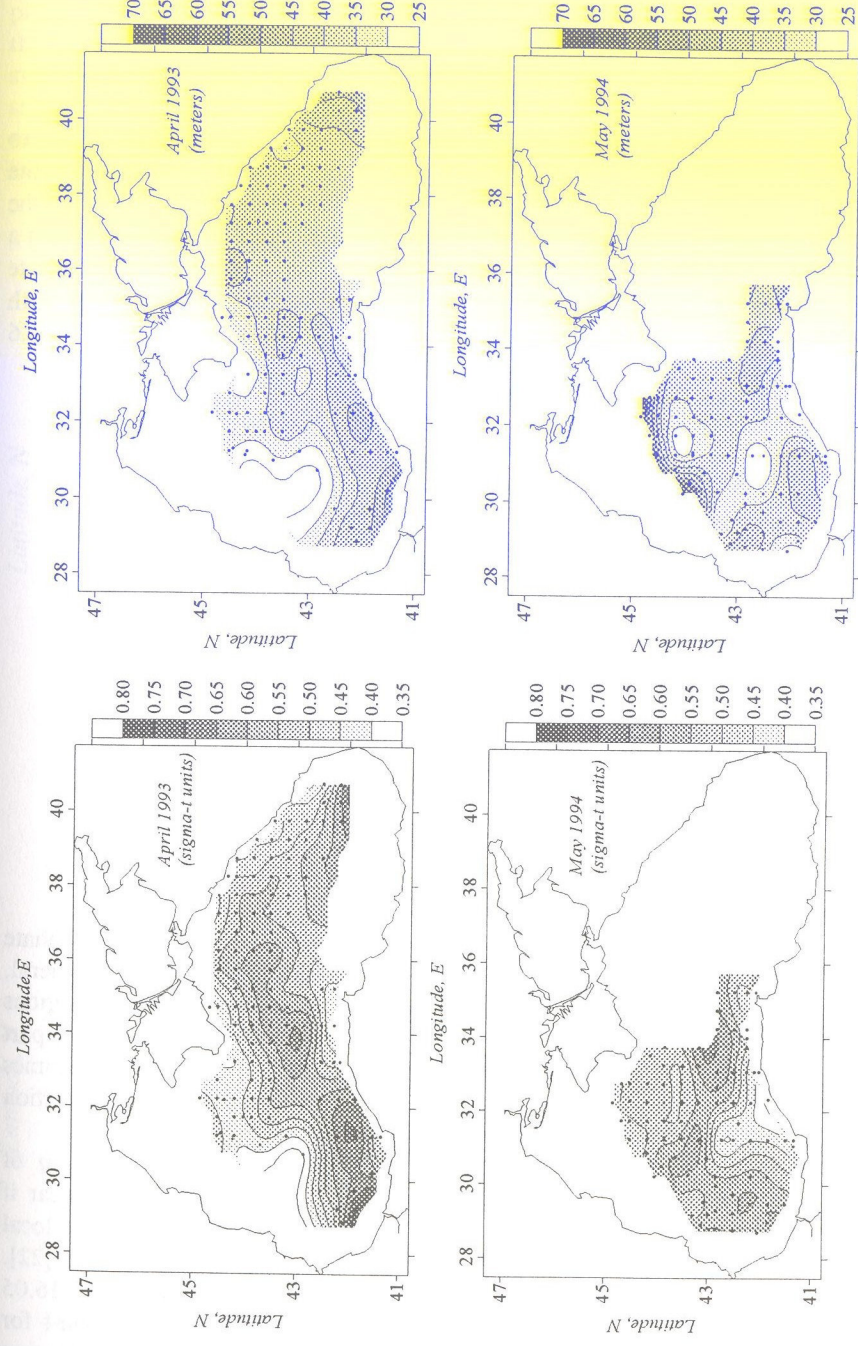


Figure 7. The thickness of SO zone in 1993 and 1994.

cline waters and the weak cross-isopycnal fluxes in the same region.

3.3. PHOSPHATES

The vertical distribution of reactive *ortho*-phosphate indicates the existence of two distinguished features (minimum at $\sigma_t \sim 15.95$ and maximum at $\sigma_t \sim 16.20$) within the oxic/anoxic transition layer, as it was recently emphasized [4,5,20-22]. Although the depths of these characteristic features are variable over the basin, they are located in a narrow range of density (Fig. 1). On the other hand, the onset of the phosphate gradient consistently appears at different σ_t values across the region. This depth corresponds to about 14.2-14.3 density in the anticyclonic regions and 14.5-14.6

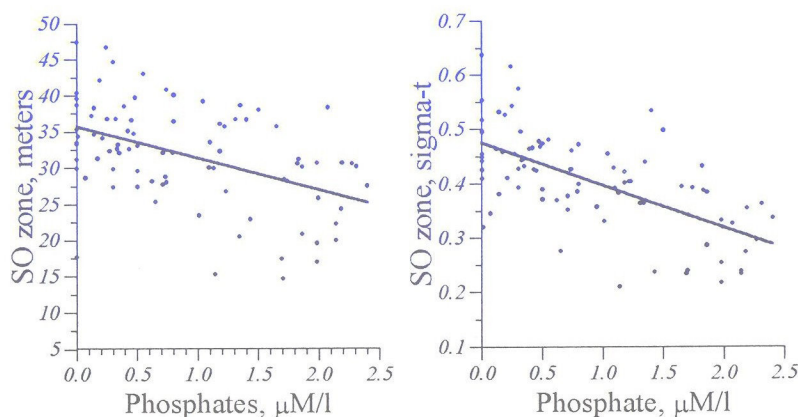


Figure 8. Concentration of phosphates in the local minimum ($\sigma_t \sim 15.95$) and the thickness of SO zone.

density in the cyclonic regions in September 1991 [16].

The local phosphate minimum is formed between the primary and deep phosphate maxima within the SO zone. The position of phosphate minimum varies, in general, from 15.85 to 16.05. It was observed to be a permanent feature of the cyclonic regions and tends to weaken or disappear completely towards the periphery of the deeper part of the Black Sea [12,16]. Accordingly, the upper phosphate maximum becomes apparent when a local minimum is formed, otherwise phosphate concentration increases monotonously with σ_t density from ~ 14.0 to ~ 16.2 [12].

The upper broad phosphate maximum is formed by the aerobic oxidation of biogenic organic matter within the oxygenated, upper pycnocline. It is yet unclear if biologically mediated chemical processes could be responsible for creating the local phosphate minimum at σ_t of ~ 15.95 , as suggested by Sapognokov et al. [22]. Phosphate concentrations measured at the depth of P-minimum, between 15.85-16.05 σ_t and at the depth of P-maximum corresponding to 16.15-16.30 σ_t for April 1993, depicted in Fig. 9, indicate significant spatial changes, with concentration increasing from the coastal margins towards the interior of the basin. The highest

phosphate concentration corresponding to the deep maximum always occurred within the cyclonic regions, where the subsurface minimum is also a prominent feature of the system. The suggestion of Shaffer [20] linking the local minimum (at around 15.95 σ_t) and the maximum (at around 16.2) to the transport of the phosphate-associated metal oxides, from suboxic to the anoxic zone seems to be the most reliable hypothesis so far.

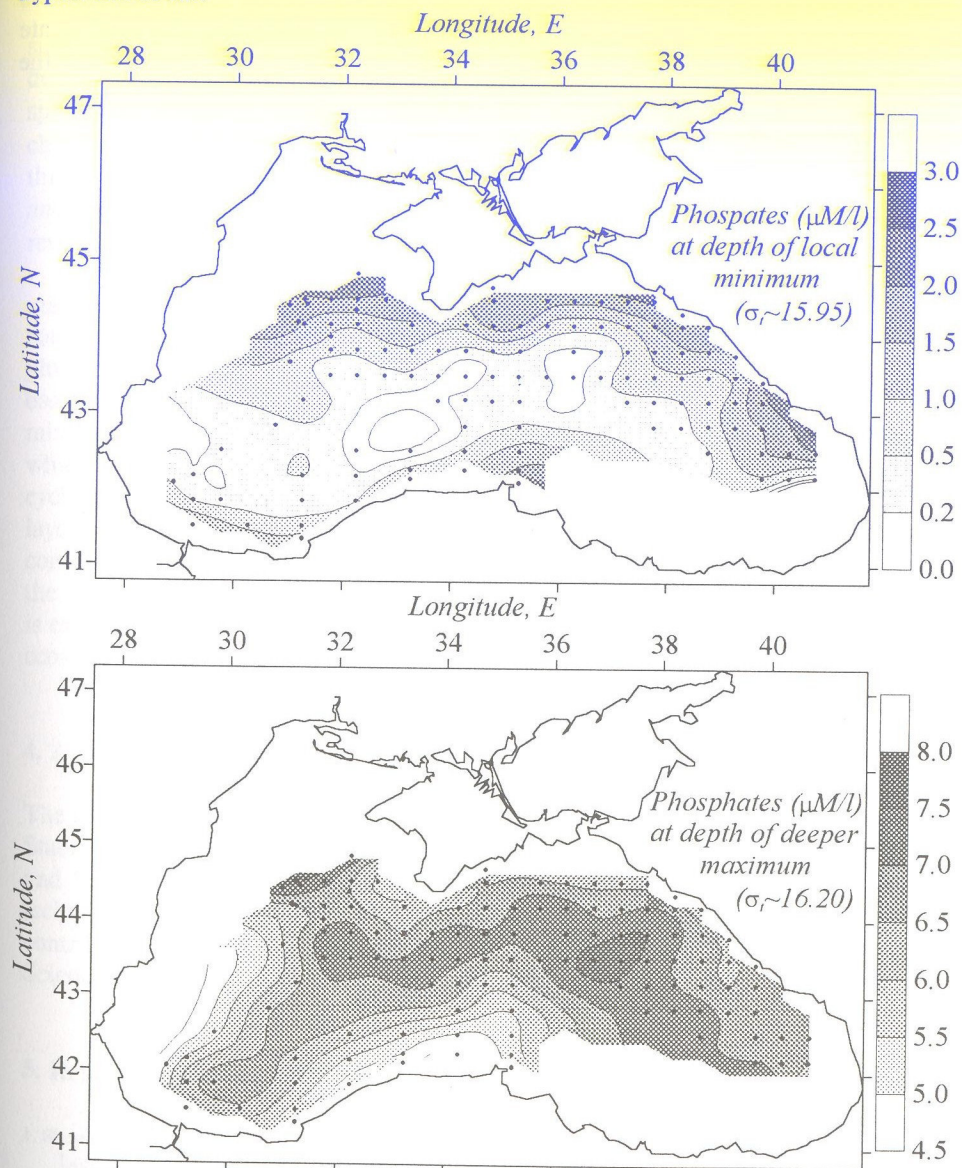


Figure 9. Concentration of phosphates in the layer of local minimum ($\sigma_t \sim 15.95$) and deeper maximum ($\sigma_t \sim 16.20$) in April 1993.

3.4. NITRATES

As shown in Fig. 1, the nitrate concentrations start to increase below 14.2-14.5 σ_t and attain peak values of 4-6 μM at intermediate depths of the main pycnocline, where the DO concentrations decrease to 10-40 μM . Markedly higher surface values were also recorded at the north-western shelf where polluted Danube and Dnieper Rivers discharge fresh waters to the surface. In the suboxic zone waters of the system, nitrate values decrease sharply with depth and decrease to undetectable levels within the

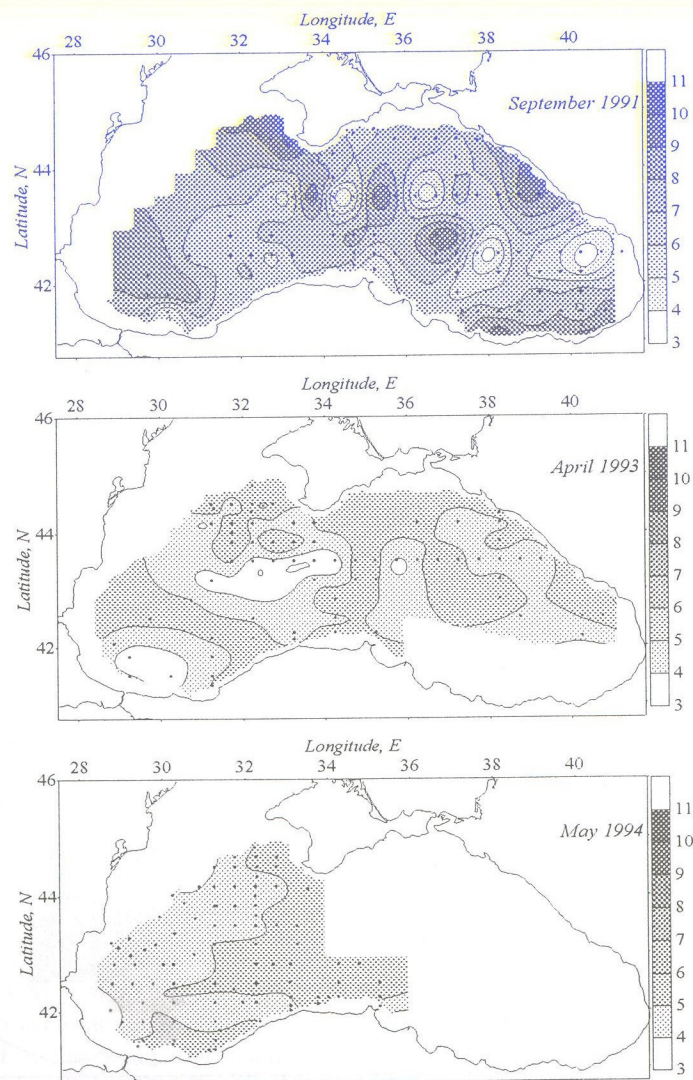


Figure 10. The highest values of nitrate concentration in the layer of the main pycnocline.

anoxic interface. As first noticed by Codispoti et al. [4], individual nitrate-density profiles from different locations are very similar, in particular the nitracline commences at similar density surfaces (Fig. 1). However, it always commences at greater density, but at shallower depths in the cyclonic regions, probably due to the shoaling of the permanent pycnocline near the base of the euphotic zone [16] or as a result of winter convective mixing [11].

The composite profile possesses a maximum established between the density surfaces of 15.4 and 15.6 over the basin (Fig. 1), but in some regions it is located deeper, till the 15.8 isopycnal surface [11]. The nitrate maximum and its depth exhibit spatial and temporal variability (Fig. 10). Interestingly, the peak values of nitrate changed from 4-9 μM in September 1991 to 3-6 μM in April 1993 and May 1994 throughout the entire basin, except in the north-western shelf areas where the Danube and Dnieper discharges are effective. The comparison of long-term data on nitrate reveals that the maximum nitrate concentration varies from 3 to 9 μM [5].

The maximum nitrate increases as a result of oxidation of particulate organic matter sinking from the euphotic zone. Processes that could decrease the nitrate concentration in the layer of the main pycnocline are: denitrification, utilisation by phytoplankton (in cases where the onset of the nitrate gradient is shallower than the base of euphotic zone), and winter convective mixing (if the intensity and depth of this mixing is sufficient to reach the upper part of the main pycnocline). It is unclear yet which of these processes are more important, but they all are relevant for the nitrogen cycle in the Black Sea waters. The seasonal variation in the total mass of nitrate in the layer of the main pycnocline is estimated to be up to $2 \cdot 10^5$ tons [11]. This amount is comparable in magnitude with the total annual input of nitrate by river discharges into the Black Sea. That is why the investigation of nitrate balance at the main pycnocline is extremely important for better understanding of the processes driving the Black Sea ecosystem.

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SUSPENDED MATTER AS AN INDEX OF PRODUCTIVITY IN THE WESTERN BLACK SEA (APPLICATION FOR PRODUCTIVITY AND EUTROPHICATION CONTROL)

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Abstract. Suspended matter distribution and composition in relationship with different productivity parameters were investigated in the western part of the Black Sea (BS) for better understanding the scales of river influence and eutrophication in the area. Good correspondence between the total amount of suspended matter (SM), particulate organic matter (POM), total plankton biomass (Bo), algae biomass (Bp) and primary production (Pp) spatial variability is pointed out. The SM concentrations in the western BS change in the range of 0.3-7.0 mg/l, dependent on the level of productivity and river influence. The organic matter contribution to total SM shows general tendency of its insignificant growth from the open sea to the coastal regions. In surface waters the POM/SM ratio rises from 40% in the open sea, to 70% in shallow, more productive regions and from 33% to 55% in the euphotic zone respectively. Below the layer of photosynthesis, the OM portion in suspended material varies in the range of 18-28 without essential difference between shelf and open waters. The role of living biomass in the SM is found to elevate from 11% in the open and outer shelf regions, to 22-26% in shelf zone, on the average. The suspended matter composition analysis shows biogenic indigenous origin of the SM in the most part of the western Black Sea shelf. Results suggest the conclusion that the total suspended and particulate organic matter spatial variability reflects the production processes development in the western BS, induced by the river nutrient inflow and local eutrophication. The possibility of monitoring Black Sea productivity, by in-situ and satellite measurements of suspended matter and its components is discussed.

1. Introduction

The suspended matter (SM) studies in the Black Sea touches upon the interests of different marine disciplines: biology, geology, geochemistry, optics and etc. It is also important for monitoring aquatic environments and remote sensing programs focused on the river influence and eutrophication control.