

Identification of the oxic/anoxic interface by isopycnal surfaces in the Black Sea

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Abstract—The analysis of hydrochemical data collected in the Black Sea since 1987 shows that the upper boundary of the oxic/anoxic interface zone coincides with the nitrate maximum at the depths of $\sigma_t \approx 15.40 \pm 0.10$ isopycnal surface. Its lower boundary corresponds to the phosphate maximum depth at $\sigma_t \approx 16.20 \pm 0.05$ isopycnal surface, independent of the geographical location and season. In the absence of the continuous pump cast measurement system, and when the oxygen and sulphide concentrations are too low to be measured with sufficient precision within the interface zone, such features of the oxygen–nitrate and H_2S –phosphate correlations at specific density levels provide a direct and practical way to identify the oxic/anoxic interface zone. This, in turn, allows for a more precise and systematic water sampling for studying the complex biogeochemistry of the layer.

INTRODUCTION

THE Black Sea, the largest anoxic basin in the world, possesses various oceanographic features that make it distinctively different from other marine environments. Among those features, formation of a transitional layer between oxic and anoxic layers and its associated biogeochemistry have been of great interest to marine scientists. In this characteristic layer, the redox potential of the water decreases sharply due to oxygen deficiency and the appearance of hydrogen sulphide at its lower boundary. Based on the measurements of trace level oxygen and hydrogen sulphide concentrations by the conventional titrimetric methods, the co-existence of oxic and sulphidic waters (the so-called C-layer) in this redox zone has been debated for many years (GRASSHOFF, 1975; SOROKIN, 1983; MURRAY *et al.*, 1989; CODISPOTI *et al.*, 1991). At micromolar levels, $O(10 \mu M)$, the measurements of H_2S and oxygen (hereafter referred to as DO) by conventional titrimetric methods suffer from analytical and sampling errors due to the atmospheric contamination, and therefore require very special sampling and analytical techniques (MURRAY *et al.*, 1989; CODISPOTI *et al.*, 1991). The technical difficulties in the standard titrimetric methods have mistakenly led to overestimation of the layer's thickness (CODISPOTI *et al.*, 1991; MILLERO, 1991).

Using the continuous pump cast measurements, which avoids the water samples from the atmospheric contamination, MURRAY *et al.* (1989) and CODISPOTI *et al.* (1991) have recently shown that the oxygenated and sulfidic waters do not overlap and are separated by

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the so-called the suboxic zone. In this zone, the oxygen and sulphide concentrations do not overlap and have concentrations too low ($\sim <1\text{--}5\ \mu\text{M}$) to be measured accurately by the conventional titrimetric methods. They also suggested the shoaling of the anoxic sulphidic boundary in recent years. However, KEMPE *et al.* (1990) and TUGRUL *et al.* (1992) have expressed a contrary view, noting that comparison of the existing data do not conclusively demonstrate such a trend in the vertical displacement of the sulphidic boundary.

In the absence of continuous profiling system, properly-collected and closely-spaced water sampling are needed to study the biogeochemistry of this transitional layer. The lack of *a priori* knowledge for the specification of the positions of the boundaries of the oxic/anoxic interface, however, leads to serious sampling problems since this interface zone is subject to considerable spatial variability associated with the mesoscale variability of the circulation and the thermohaline structure of the Black Sea (SOROKIN, 1983; BRYANTSEV *et al.*, 1988; OGUZ *et al.*, 1991, 1992, in press; MURRAY *et al.*, 1991; CODISPOTI *et al.*, 1991). In this paper we attempt to show that the boundaries of the transitional layer, where the nutrients (nitrate and phosphate) reveal some special characteristic features, can be defined with a relative confidence by means of the specific isopycnal surfaces (i.e. σ_t values), independent of geographical location and season. In particular, we show that the upper boundary of the suboxic zone is defined by a specific density level at which a significant correlation exists between the maximum nitrate concentrations and trace level DO concentrations. We also show a similar significant correlation between the large phosphate anomalies and trace level hydrogen sulphide concentrations that defines the lower boundary of the suboxic zone. The transitional (redox) zone, where the DO and H_2S concentrations are too low to be determined accurately by conventional methods, can then be identified easily by means of standard *in situ* CTD measurements.

MATERIALS AND METHODS

The hydrochemical data examined for this study were collected during the cruises of the R.V. *Knorr* in June–July 1988 and the R.V. *Bilim* in 1987–1991, covering mainly the Turkish Exclusive Economic Zone (approximately southern half of the sea), and the R.V. *Dm. Mendeleyev* in August 1989 covering the entire basin. During the R.V. *Bilim* and the R.V. *Knorr* cruises, the hydrographic data were collected by using the Sea-Bird Model SBE-9 CTD system. A Soviet made CTD system was used during the R.V. *Dm. Mendeleyev* cruise. Sea water samples were generally collected by Go-Flo Rosette bottles in the R.V. *Bilim* surveys, and by Niskin bottles in the R.V. *Dm. Mendeleyev* cruise. The continuous pumping system (CODISPOTI *et al.*, 1991) was used in the R.V. *Knorr* surveys we discuss here.

Nutrient analyses were carried out using multi-channel autoanalyser systems by all parties. For the determination of DO and H_2S concentrations, the samples collected by the R.V. *Bilim* and R.V. *Dm. Mendeleyev* cruises were analysed by the conventional Winkler and iodimetric titration methods. For the R.V. *Knorr* cruises, the DO and H_2S concentrations were measured by colorimetric techniques.

RESULTS AND DISCUSSION

We first examine the data obtained by the pump cast measurements in the R.V. *Knorr* 1988 cruises (FRIEDERICH *et al.*, 1990). These are the most reliable and precise DO and H_2S

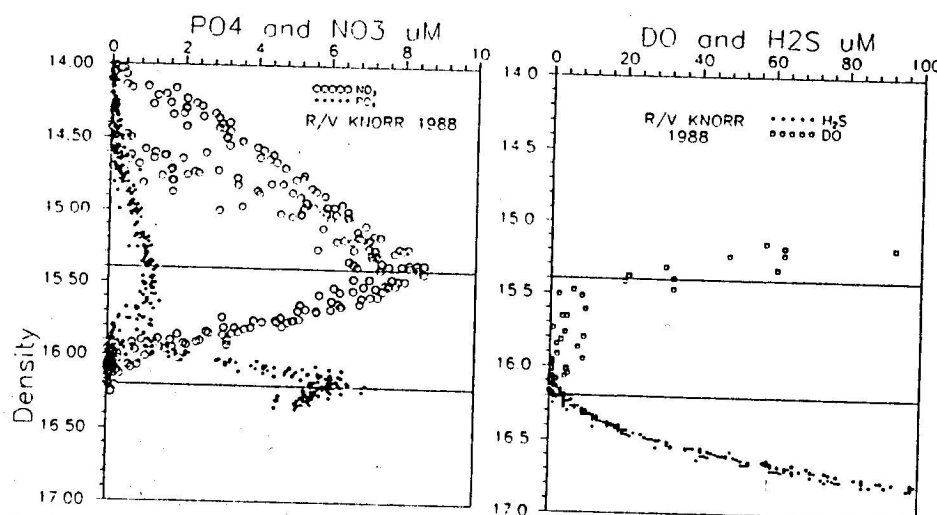


Fig. 1. Composite profiles of nitrate (NO_3), phosphate (PO_4), oxygen (DO) and hydrogen sulphide (H_2S) versus density (σ_t) for 12 pump cast stations of the R. V. *Knorr* 1988 cruises. Density is given in terms of kg m^{-3} , and others by μM .

data, measured accurately up to $\sim 1\text{--}5 \mu\text{M}$ concentrations in the Black Sea. Composite profiles of DO, H_2S , nitrate and phosphate concentrations relative to density (σ_t) at 12 pump cast stations (Fig. 1) reveal that (i) the upper and lower boundaries of the oxic/anoxic interface, defined as the $\text{DO} < 20 \mu\text{M}$ and H_2S concentrations less than $5 \mu\text{M}$, lie between the isopycnal surfaces of $\sigma_t \approx 15.40 \pm 0.10$ and $\sigma_t \approx 16.20 \pm 0.05$; and (ii) these density surfaces correspond to the nitrate and phosphate maxima formed at the upper and lower boundaries of this transitional layer, respectively. There is a pronounced increase in the nitrate concentrations starting at the depths corresponding to $\sigma_t \sim 14.0$, and reaching to a maximum of $8\text{--}9 \mu\text{M}$ at the depths of $\sigma_t \approx 15.40 \pm 0.10$. As stated by MURRAY *et al.* (1989) and MURRAY and IZDAR (1989), the level of this nitrate maximum coincides with the sharp drop in the oxygen concentrations below $20 \mu\text{M}$ as a result of the denitrification process in the oxygen deficient water (SOROKIN, 1983; SEITZINGER, 1988).

The composite profiles for phosphate exhibits two maxima (SHAFFER, 1986; MURRAY *et al.*, 1989; CODISPOTI *et al.*, 1991). The relatively broad upper maximum, established at the lower boundary of the oxygenated layer, has resulted from the aerobic oxidation of biodegradable organic matter of algal origin and coincides with the nitrate maximum. The deeper maximum has been formed at the upper boundary of the anoxic sulphidic layer. In the relatively narrow density surfaces $\sigma_t = 15.9$ and 16.2 , phosphate concentration increases sharply from the minimum levels to the large values to form the deeper characteristic maximum at $\sigma_t = 16.2 \pm 0.05$, significantly correlating with the first appearance of the anoxic sulphidic water, independent of geographical location (see also TUGRUL *et al.*, 1992). SHAFFER (1986) first suggested that the phosphate anomaly (a sharp increase in concentration) is mainly the result of the redox processes involving iron and manganese responsible for the vertical transport of phosphate ions across the suboxic/anoxic interface. Thus the deeper phosphate maximum has shown a significant correlation

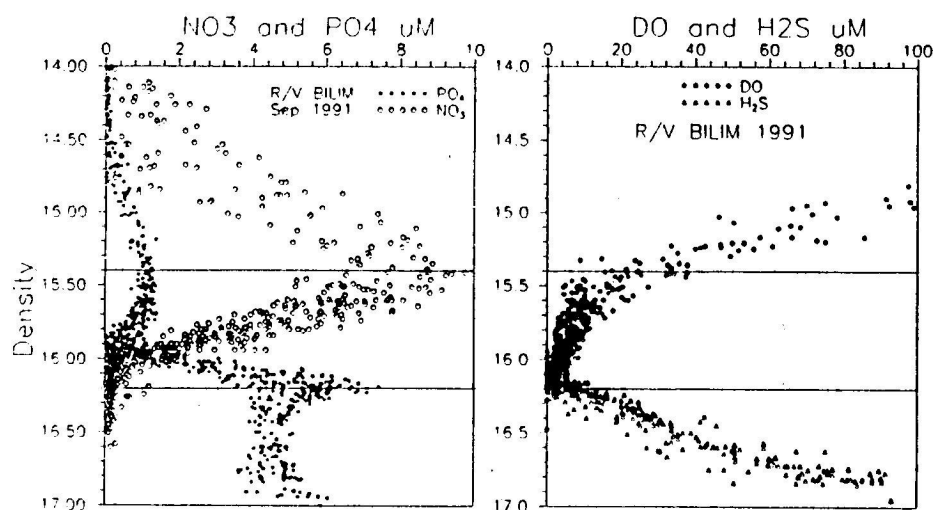


Fig. 2. Composite profiles of nitrate (NO_3), phosphate (PO_4), oxygen (DO) and hydrogen sulphide (H_2S) versus density (σ_t) for 51 stations of the R.V. *Bilim* 1991 cruise. Density is given in terms of kg m^{-3} , and others by μM .

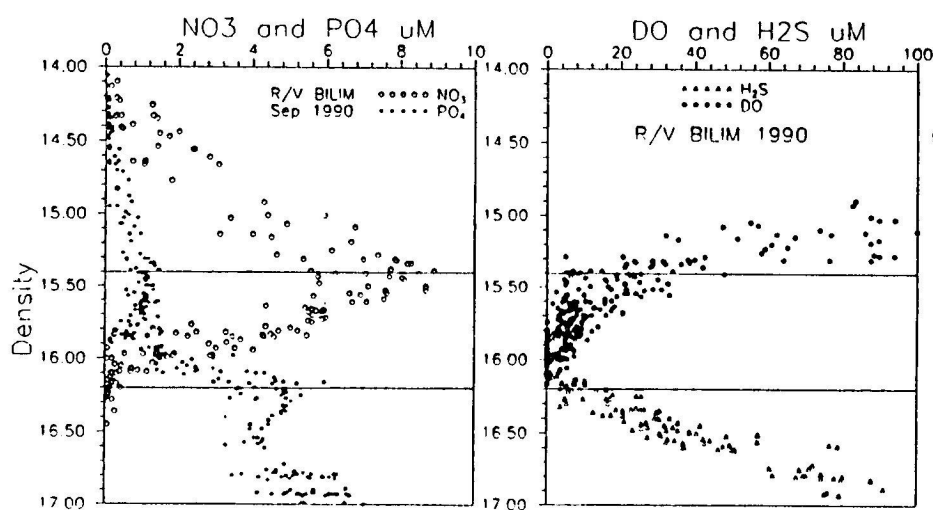


Fig. 3. Composite profiles of nitrate (NO_3), phosphate (PO_4), oxygen (DO) and hydrogen sulphide (H_2S) versus density (σ_t) for 26 stations of the R.V. *Bilim* 1990 cruise. Density is given in terms of kg m^{-3} , and others by μM .

with that of the sulphidic boundary across the basin although its depth varies markedly in space and time associated with the circulation and hydrography.

Similar composite profiles of the DO , H_2S , nitrate and phosphate concentrations for the September 1991 and September 1990 R.V. *Bilim* surveys (Figs 2 and 3) provide a confirmation for the presence of the oxic/anoxic interface zone between similar density

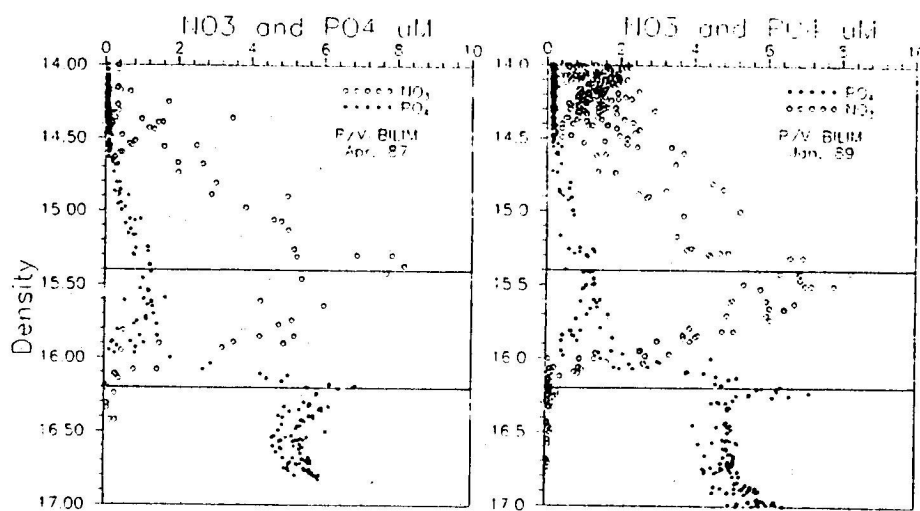


Fig. 4. Composite profiles of nitrate (NO_3), phosphate (PO_4) versus density (σ_t) for the R.V. *Bilim* April 1987 at 17 stations (left) and R.V. *Bilim* January 1989 at 24 stations (right) surveys. Density is given in terms of kg m^{-3} , and NO_3 and PO_4 by μM .

surfaces found earlier by means of the R.V. *Knorr* data. As in the previous case, the nitrate concentrations reach the maximum at $\sigma_t \sim 15.40 \pm 0.10$ at which the DO concentrations drop to the values $\sim <20 \mu\text{M}$ from about $100 \mu\text{M}$ at $\sigma_t = 15.0$. As compared with the *Knorr* 1988 data, relatively higher DO concentrations measured in the suboxic zone seem to suggest overestimation of the DO values by at least $5 \mu\text{M}$ due to air contamination during sampling from Rosette bottles.

Figures 2 and 3 also show that the phosphate anomaly is formed at a narrow range of density surfaces, similar to that in Fig. 1. Once again, the deeper phosphate maximum appears at $\sigma_t = 16.20 \pm 0.05$ throughout the Black Sea, and coincides with the beginning of the anoxic sulphidic layer identified here by the H_2S concentrations of about $5 \mu\text{M}$.

Further confirmation of the correlations between the nitrate, phosphate maxima and the boundaries of oxic/anoxic interface comes from the R.V. *Bilim* data obtained in April 1987 and January 1989 (no DO and H_2S data available) and from the Soviet R.V. *Dm. Mendeleyev* survey in August 1989 (Figs 4 and 5). Although there are relatively few data for nitrate and phosphate profiles, it is still possible to observe the nitrate maximum and the phosphate anomaly at nearly identical range of density surfaces. In the R.V. *Dm. Mendeleyev* data the DO and H_2S concentrations (Fig. 5), confined within these density surfaces, are considerably higher compared with other data sets presented in Figs 1–3. We note that DO concentrations in this transitional layer may be as high as approximately $20 \mu\text{M}$. This may suggest a higher degree of atmospheric contamination and the subsequently apparent observation of the C-layer, i.e. DO and H_2S are overlapped in the oxic/anoxic interface zone. Air contamination is clearly shown in Fig. 5 by the presence of DO concentration of about $10 \mu\text{M}$ within the anoxic layer.

Other scientific evidence for the possible use of the certain density levels for delineating the boundaries of the oxic/anoxic interface zone is provided by the light transmission measurements of the R.V. *Knorr* 1988 cruises (WHITE *et al.*, 1989). These measurements reveal the existence of a minimum formed consistently at $\sigma_t \sim 16.1$ – 16.2 and subsequent

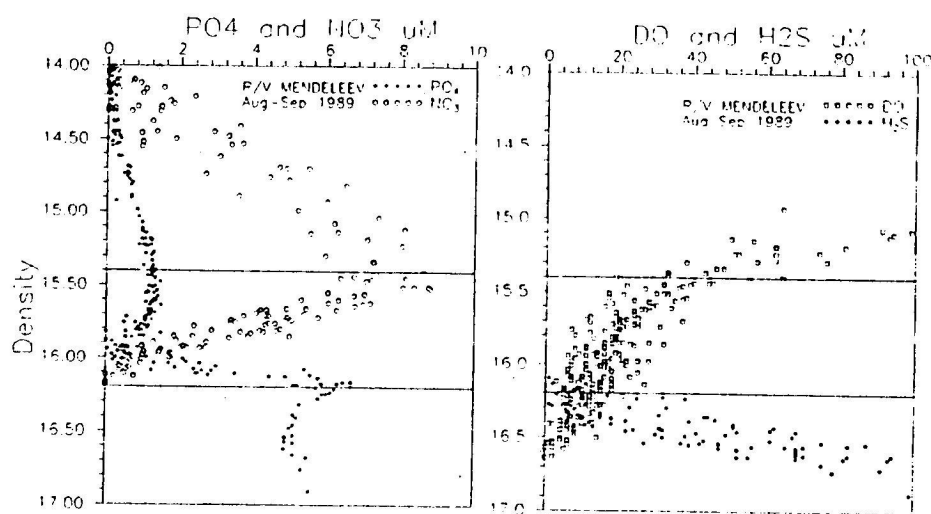


Fig. 5. Composite profiles of nitrate (NO_3), phosphate (PO_4), oxygen (DO) and hydrogen sulphide (H_2S) versus density (σ_t) for 15 stations of the R.V. *Dm. Mendeleev* 1989 cruise. Density is given in terms of kg m^{-3} , and others by μM .

increase to the background levels at $\sigma_t \sim 16.20 \pm 0.05$. The decrease in the intensity of light transmission is associated with the Fine Particle Layer (FPL) observed by KEMPE *et al.* (in press) at the same range of the density surfaces. The FPL most probably originates from the remobilized Mn and Fe particles (KEMPE *et al.*, in press) as well as the particulate organic matter chemosynthetically produced immediately above the anoxic sulphidic layer (SAPOZHNIKOV *et al.*, 1985). The base of the peaks in the light transmission, therefore, corresponds to the sulphide bearing lower boundary of the suboxic zone below which the Mn and Fe oxyhydroxides will dissolve (SHAFFER, 1986) due to the decreases in the redox potential. We note that the formations of both the FPL and phosphate minimum and their interactions are not yet fully understood because of the complicated biogeochemical processes taking place in the transitional zone.

The confinement of the suboxic zone between fixed density levels, of course, does not mean that this layer remains constant at the same depths throughout the entire basin. Figure 6a,b shows the distribution of $\sigma_t = 15.40$ and $\sigma_t = 16.20$ surfaces, respectively, for the September 1990 survey to the east of 32°E longitude. It is evident that the location of the $\sigma_t = 15.40$ surface varies from 70 to 125 m within the basin in accordance with the general circulation in the region (OGUZ *et al.*, in press). It is shallower in the cyclonic regions and deeper in the anticyclonic regions, with most pronounced variations taking place along the rim current encircling the periphery of the basin. The $\sigma_t = 16.20$ surface also has similar characteristics, varying between 120 and 165 m at the centers of the cyclonic and anticyclonic eddies, respectively. Contrary to the pronounced horizontal variability of the boundaries of the transitional layer, Fig. 6a,b suggests that this layer has a constant thickness of about 50 m. In fact, the average thickness for the entire data set amounts to 52 ± 7 m. A relatively deeper suboxic layer is situated in the regions of anticyclonic eddies (generally along the coast) as compared to the shallower layer in the cyclonically-dominated regions (usually within the interior of the basin). These are further

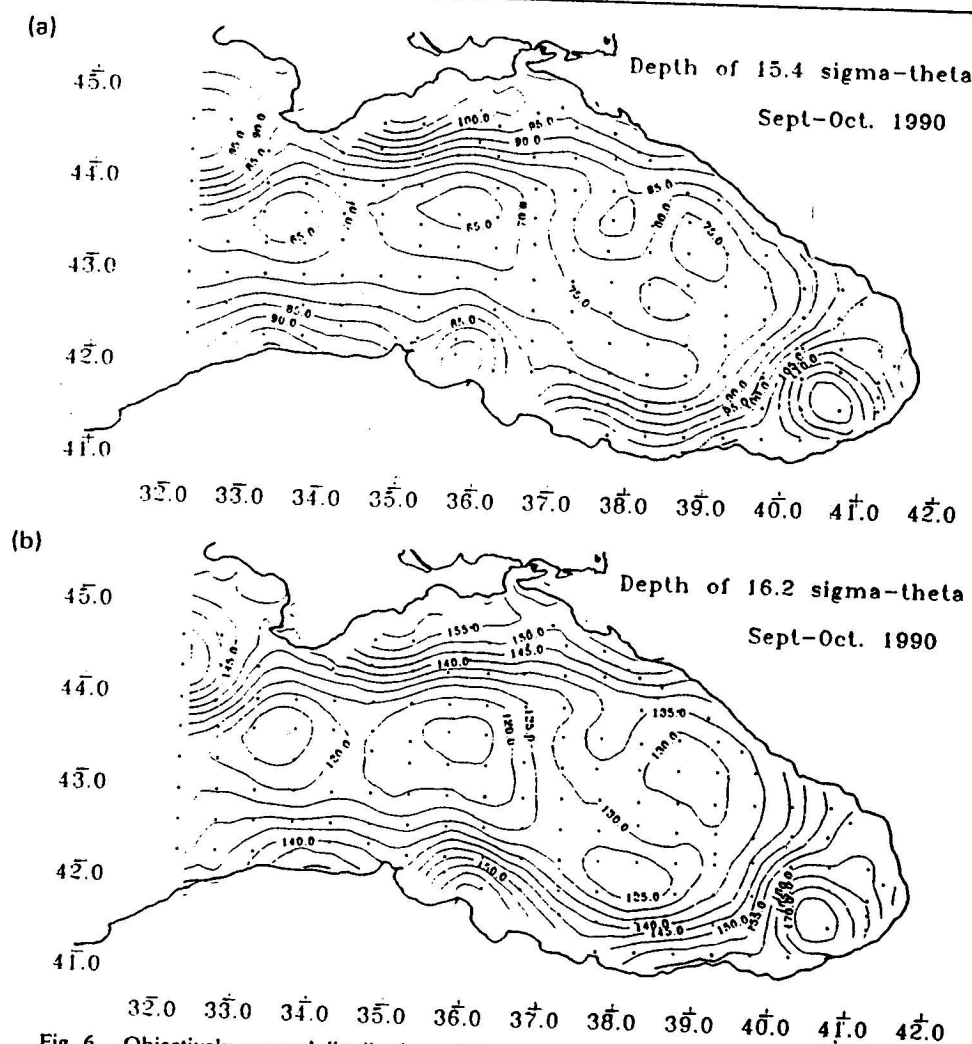


Fig. 6. Objectively mapped distributions of the depths of $\sigma_t = 15.4$ density surface for the joint cruise of the R.V. *Bilim* and R.V. *Lomonosov* in September–October 1990. Contour interval is 5 m. The station locations are shown by dots. (b), Same as (a) for the depths of $\sigma_t = 16.2$ density surface.

supported by other R.V. *Bilim* cruises conducted during 1987–1991, although they all have different numbers of sampling stations and locations.

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