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Analysis of Observations and Methods of Calculating Oceanic Hydrophysical Fields

Investigation of the formation of vertical structure of biogenic elements fields in the Black Sea, using the method of spatial isopycnic analysis*

V. N. EREMEEV, S. K. KONOVALOV and A. S. ROMANOV

Abstract — The method of two-dimensional isopycnic analysis is applied to study the distribution of inorganic phosphates and nitrates in the Black Sea. The effect of winter-time ventilation in the central sea on the formation of chemical fields is examined, as well as the outcropping of biogenic elements from the layer of high concentrations ($\sigma_t \sim 14.5$–16.0). It is demonstrated that the amount of nitrates entering the upper active layer of the sea as a result of winter-time convective ventilation may attain values comparable with their overall annual input by river discharge, and that they control the intensity of winter–spring phytoplankton blooming in the central sea. The spatial variability of the vertical phosphate distribution is analysed. For the annual cycles with fairly cool winter conditions, an occurrence of three peaks on the phosphates vertical profile in spring has been documented over a vast sea area where the rim current represents an external dynamic boundary.

INTRODUCTION

Analysis of the spatial distribution and vertical fluxes of phosphates and nitrates is of primary importance for understanding the regularities of the geobiochemical processes taking place in the sea, for evaluating the reserves and dynamics of biogenic elements, as well as for the analysis of possible changes in the productivity of waters.

Furthermore, the peculiar vertical distribution of chemical parameters in the Black Sea waters continues to command considerable attention of the researchers in connection with the notorious phenomenon of this basin — the presence of a powerful anoxic layer beneath the constant halocline and oxic waters above it, which provides specific physico- and biochemical conditions near the O_2/H_2S interface, affecting the dynamics of the biogenic elements.

Formation of the vertical structure of the phosphates and nitrates fields was studied in refs 1–6. In addressing this problem, certain progress was made when a conventional density scale was applied (since the late 1980s) to handle the data alongside the traditional scale of depths. That had allowed the authors of refs 7–11 to demonstrate the relative universality of the vertical distribution of some chemical parameters in the Black Sea waters.

The utilization of the conventional density scale enables one to neglect the influence of hydrodynamic processes upon the spatial variability of the density stratification

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and to concentrate on the analysis of the processes of different origin, which contribute to the generation of the chemical fields' vertical structure. Specifically, the following peculiarities of the biogenic elements has been noted: in the abyssal Black Sea, maximal nitrates content is normally observed when conventional density equals 15.4–15.6 [9, 12]; nitrite maxima border nitrate maxima from both sides [13]; an upper phosphate maximum occurs at $\sigma_t \sim 15.6$, an intermediate maximum takes place at $\sigma_t \sim 18.85$ [14] and $\sigma_t \sim 15.95$ [15], with a lower maximum at $\sigma_t \sim 16.2$ [14, 16].

An idealization of that approach had led to the conviction [7] that vertical distribution of the chemical parameters *versus* conventional density in the Black Sea waters is identical for the entire deep-water part of the basin. As a result, the scatter of the element concentrations on the isopycnic surface was explained by the methodical errors of determination, and the possible influence of diapycnic fluxes, or chemical and biological processes, either was not considered at all, or was taken to be the same throughout the abyssal part of the sea.

The peculiarities described for the vertical distribution of phosphates and nitrates are typical in the sense that the characteristic inhomogeneities of the vertical structure for each element, according to refs 7 and 14, are observed within a narrow range of conventional density values. However, it is known that sometimes such extrema are not recorded or may have an essentially different magnitude [12].

We had to cope with this problem in the course of interpreting the oceanographic data collected in the Black Sea on the CoMSBlack program. The investigations encompassed the whole of the sea area. A scatter of phosphates and nitrates concentrations in the domain of their largest values essentially exceeded the methodical errors of determination. That made one doubtful as to the authenticity of some data and led to their different interpretation.

The circumstances indicated above had dictated the necessity of conducting the present work, whose purpose was to study the vertical structure of the biogenic elements field in the Black Sea, using a unique methodical approach implying the application of a spatial isopycnic analysis of the hydrological/chemical data. Moreover, our goal was to identify and study the processes that control deviations from the isopycnic distribution of biogenic elements, the peculiarities of the vertical structure of the phosphates and nitrates fields during the winter–spring period, as well as the diapycnic fluxes and influx of these elements to the photic layer of the sea.

EXPERIMENTS

As original data, we have used the information collected during Cruise 30 of the R/V *Professor Kolesnikov* from 2 to 30 April 1993. Figure 1 schematically shows the test area and the arrangement of stations.

Water samples were taken by means of a CTD-probe ISTOK-7, featuring a rosette of sixteen 1-litre bathometers. Sampling depth levels were prescribed in conformity with the following isopycnic surfaces: 14.60, 14.80, 15.00, 15.20, 15.40, 15.60, 15.80, 15.90, 16.00, 16.05, 16.10, 16.15, 16.20, 16.30, and 16.40 units of conventional density. This choice of the depth levels has allowed us to study the peculiarities of vertical distribution of the basic chemical parameters (oxygen, phosphates, nitrates, nitrites, silicates, pH, alkalinity, hydrogen sulphide) in the transition area between the oxic and the anoxic layers. At a number of stations, we also conducted repeated probings and samplings at depths larger than the 14.6 isopycnic surface and below 16.4.

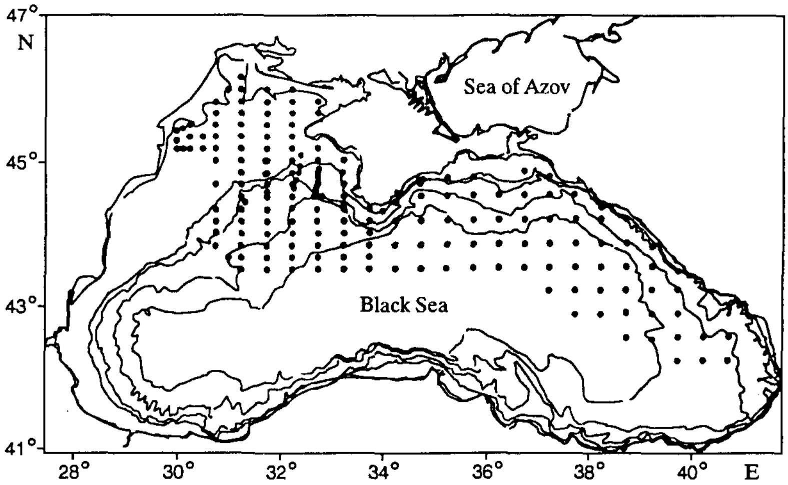

Figure 1. The arrangement of drift oceanographic stations occupied during Cruise 30 of the R/V *Professor Kolesnikov.*

The samples were not stored. Oxygen, hydrogen, sulphide, inorganic phosphates, nitrites, nitrates, and dissolved silicates concentration, pH values and alkalinity were determined immediately following the retrieval of a sample.

Dissolved inorganic phosphates content was analysed using Murphy and Raighley's modified method [17], with ascorbic acid being used as a reducer.

Nitrates concentration was determined by reducing them to nitrites using Cd pipes (1.2 m-long, 1-mm internal diameter). The inner surface of the pipes was copper-plated by treating them with a 2% solution of copper sulphate. Nitrites content in the sample after the nitrates reduction was determined by the method suggested in ref. 18, using sulphanilamide and N-(1-naphthyl) dihydrochloride ethylenediamine. In calculating nitrates concentration, we considered the nitrites content in the original sample. The total error of the method was assessed to be equivalent to 10–20%.

ANALYSIS OF THE ACQUIRED DATA

The vertical distribution of inorganic phosphates and nitrates with respect to the conventional density for the entire set of observations is shown in Fig. 2. High phosphates concentrations, with respect to surface waters (Fig. 2a), were revealed at $\sigma_t > 13.9$–14.0; however, at $\sigma_t > 14.5$, they tended to dramatically increase. The upper maximum of phosphates concentration was documented at $\sigma_t \sim 15.6$–15.7 (Fig. 5b). An intermediate minimum, in the case of its occurrence, corresponded, on average, to $\sigma_t \sim 15.98$ (Figs 2a and 5b), with phosphates concentration within that layer, as observed at a number of individual oceanographic stations, being at the level of the method's sensitivity. The lower phosphates maximum, in the majority of the cases, occurred at the upper boundary of the anoxic layer, conventional density being 16.20. The largest phosphates concentration within that layer attained $8.40\,\mu\text{mol}\cdot\text{l}^{-1}$.

The concentration of nitrates was largest (Fig. 2b) within the stratum bounded by the 14.0 and 16.05 isopycnic surfaces. For the majority of the stations, nitrates concentration started to grow when conventional density was > 14.5. The largest content of nitrates ($\sim 6.4\,\mu\text{mol}\cdot\text{l}^{-1}$) was observed at $\sigma_t = 15.4$–15.6.

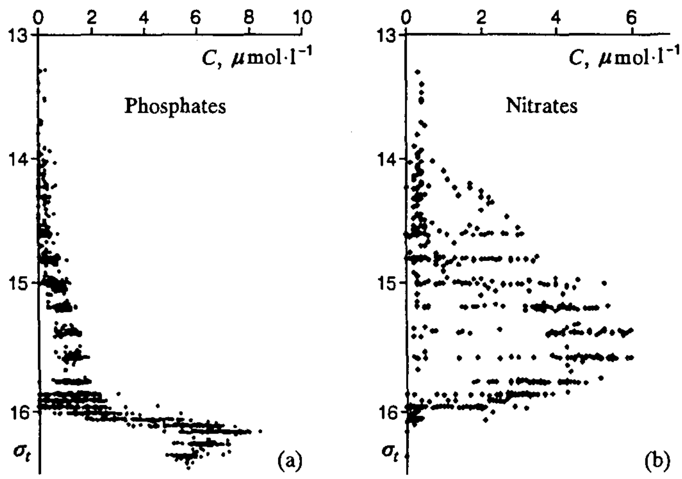

Figure 2. Vertical distributions of (a) phosphates and (b) nitrates relative to conventional density (cruise dataset).

It should be emphasized that the largest concentrations of biogenic elements varied within a wide range. In the case of nitrates, the range of variability was particularly large. So, nitrates content in the layer of maximum concentrations (σ_t = 15.4–15.6) in various parts of the sea changed within 0.4–6.4 μmol·l^{-1} (Fig. 2b). Nitrates concentrations are distributed rather uniformly over the entire range of quantities characteristic of each isopycnic surface under study (Fid. 2b), which had not been previously observed [7, 12]. Phosphates concentration within the layer of the intermediate minimum, when the latter was observed, varied from 0 to 2.6 μmol·l^{-1} (Fig. 2a), and within the layer of the upper maximum ($\sigma_t \sim$ 15.6), from 0.6 to 2.2 μmol·l^{-1} (Fig. 2b).

Following the joint analysis of the results of the expeditions conducted by the R/Vs *Atlantis-II* and *Knorr* in 1969 and 1988, respectively, the concept was generated that the biogenic elements' vertical distribution, relative to the conventional density, for the greater part of the Black Sea must be universal, similar to O_2 and H_2S [7]. According to ref. 12, only at a few stations occupied in the margins of the abyssal zone does the phosphates vertical distribution not exhibit an intermediate minimum. The authors explained this as the result of the specific state of the environment in these local areas, i.e. by the reducing properties of the bottom sediments and by the intense turbulent diffusion resultant from the interaction of the current (obviously, the Black Sea rim current) with the surface of the continental slope. Thus, the lack of an intermediate phosphates minimum was regarded as a fairly rare phenomenon, which can be observed solely within spatially restricted zones of the O_2/H_2S interface's contact with the continental slope. However, the data from the expedition of the R/V *Knorr* in 1988 were compiled at a small number of oceanic stations, which does not provide a sufficient basis for broad generalizations.

Analysis of the data collected by the R/V *Atlantis-II* in 1969 [5, 6] has shown that the evidence about the presence of a distinctly pronounced minimum in the phosphates' vertical distribution in the central Black Sea, which was hardly traceable or vanished altogether in the coastal areas, was available even at that time. However, this peculiarity of phosphates vertical distribution and the respective mechanism behind it had not been properly studied.

The data compiled by the R/V *Professor Kolesnikov* in April 1993, as well as the pattern of the depth levels that we had chosen to sample seawater have allowed us to apply the isopycnic method to the study of the spatial distribution of biogenic elements. That enabled us to gain insight not only into the variations of biogenic elements content *versus* conventional density at the vertical transects, but also their quasi-synchronous distribution on the isopycnic surfaces over vast sea areas.

PHOSPHATES

Figure 3 shows the distribution of inorganic phosphates on the 15.95 and 16.20 isopycnic surfaces. We have chosen these surfaces because the first surface (σ_t = 15.95), in most of the cases, corresponds to the location of an intermediate minimum of phosphates concentration in the phosphate vertical distribution profile relative to the conventional density; and the second surface (σ_t = 16.20) corresponds to the location of the second minimum (Fig. 2a). Advantages of this approach are manifest, as it allows one to determine why phosphate concentrations are scattered in the layers of maximal values.

The most significant inference that follows from the data depicted in Fig. 3 is that the variability of phosphate concentration at the individual vertical profiles depends upon the test area and is controlled by the specific natural processes characteristic of the Black Sea. The smallest phosphates concentrations in the intermediate minimum layer ($\sigma_t \sim$ 15.95) occur in the central areas of the sea, impacted by the major cyclonic gyres (Fig. 3a). Their concentration there may drop down to the analytical zero. As the shore is approached, phosphates concentration at the given isopycnic surface eventually increases up to values larger than 2.0 μmol$\cdot$l^{-1} (Fig. 3a). The areas of maximal phosphate concentration for σ_t = 15.95 coincide then with the areas accommodating anticyclonic eddies observed during the experiment.

For the isopycnic surface σ_t = 16.20 (Fig. 3b), an opposite situation is observed. The areas housing the western and eastern cyclonic gyres exhibit maximal phosphate concentrations, which at some stations are higher than 8 μmol$\cdot$l^{-1}. As one moves shoreward, their concentration in the maximum decreases by 1 to 2 μmol$\cdot$l^{-1}.

No less demonstrative is the distribution of the phosphates concentration *versus* conventional density at the oceanographic transects. For another comparison and analysis, we have chosen a transect along 32.25° E allowing us to estimate the variability of the vertical distribution of chemical parameters over a vast area, where diverse hydrodynamic processes occur. The starting point of that section was in the western cyclonic gyre area; then it crossed the Black Sea rim current and passed practically through the centre of the quasi-stationary anticyclonic gyre near the edge of the continental slope and through the eastern part of the shallow north-western shelf area of the Black Sea (Fig. 4).

It is readily visualized from Fig. 4a that phosphates concentration in the north-western shelf waters was minimal, tending to grow toward the deep part of the sea; however, even in the vicinity of the continental slope break, it was 0.2 μmol$\cdot$l^{-1}, at most. Minimal phosphate concentrations throughout the water column were observed in the northern section of the north-western shelf. Thus, the eastern shelf waters are hardly likely to be the source of phosphate for the photic layer of the sea.

Analysis of the phosphate distribution at the transect made along 32.25° E allows us to see more vividly the peculiarities of the phosphates distribution over the water

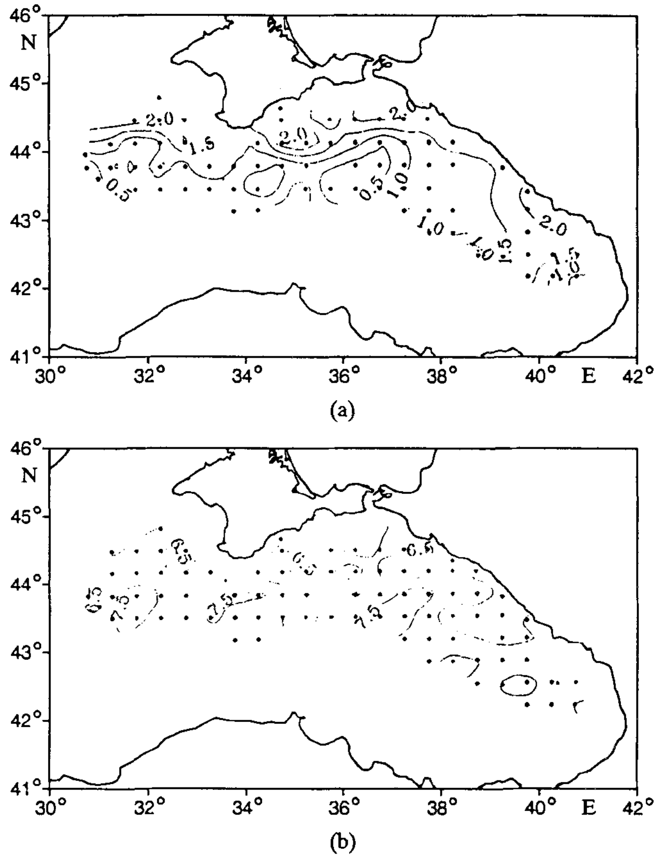

Figure 3. Phosphates spatial distribution at the (a) 15.95 and (b) 16.20 isopycnic surfaces.

column described above. It is readily visualized that phosphates distribution within the range σ_t = 14.5–16.0 is essentially non-isopycnic. The intermediate minimum layer is most markedly pronounced at the southernmost station of the transect ($\sigma_t \sim 16.0$; Fig. 4b), which is influenced, in largest measure, by the western cyclonic gyre. In that area, phosphates concentration is smallest within the intermediate minimum layer being 0.24 μmol·l^{-1}. As one moves northward, the position of the intermediate minimum layer, relative to conventional density, changes insignificantly, with the minimal concentration gradually increasing up to 0.8 μmol·l^{-1}. In the Black Sea rim current area, the intermediate minimum layer becomes wider, with the phosphates content concurrently growing, and then vanishes (Fig. 4b). The vertical distribution of this biogenic element, relative to conventional density north of 44.33° N, exhibits enhanced phosphate concentrations in the 14.5–16.2 isopycnic field (Fig. 4).

Coinciding of the location of the areas with the smallest phosphate concentrations within the intermediate minimum layer, at σ_t = 15.95, with the areas displaying the largest phosphate concentrations within the maximum layer, at σ_t = 16.20, supports the mechanism suggested for their occurrence in ref. 5, which implies phosphates adsorption on iron hydroxides from the layer of waters with $\sigma_t \sim 15.95$, and their subsequent precipitation as metal hydroxides dissolve in the upper part of the anoxic zone.

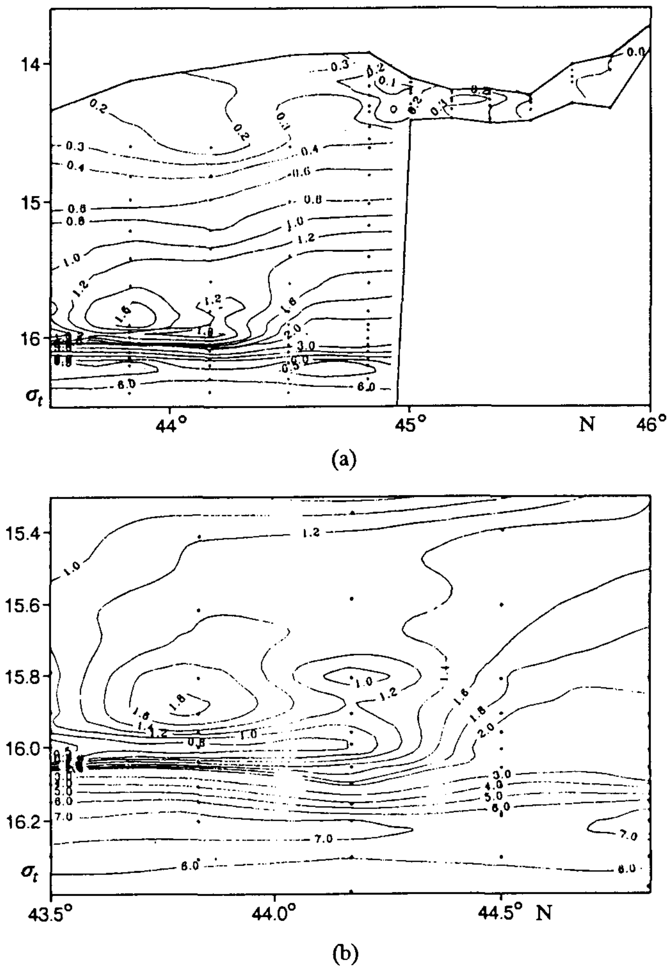

Figure 4. Phosphates distribution relative to conventional density (a) at the transect made along 32.25° E; (b) enlarger scale.

As refs 19–22 claim, during winter, the cold intermediate layer is being regenerated above the domes of the cyclonic gyres, due to the cooling of surface waters and their convective sinking down to the depth of the main pycnocline, which is closest there to the sea surface. It may be hypothesized that the intensification of convective mixing leads to washing out of the upper phosphate maximum. At the same time, an intensification of the O_2 downward flux is expected to contribute to the latter's interaction with the reduced forms of iron and manganese, to the emergence of suspended oxidized forms of metal hydroxides, to phosphate adsorption on the latter, and hence, to their transport to larger depths. Naturally, the maxima of phosphate concentration over the water column will be more pronounced, this having been observed in the course of the experiment (Fig. 3).

As one moves away from the centres of the cyclonic gyres, the intensity of the process declines. Initially, that leads to a growth of phosphate concentration in the intermediate minimum layer, and than the layer itself vanishes. In the areas housing near-shore anticyclonic vortices, only the deformation of the isopycnic surfaces and the isopycnic transport of chemical components take place, with all chemical and physico-chemical processes, for which the diapycnic transport of the reacting substances is vital, prove to be slowed down (first of all, this applies to the oxidation of H_2S and to the accompanying processes). This inference is also confirmed by the analysis of the vertical structure of the O_2, H_2S, and pH fields, with the mechanism for H_2S oxidation possibly being modified.

Phosphate concentration within the 15.6–15.8 layer of waters (Fig. 4) is maximal at the periphery of the central cyclonic gyres. This phenomenon is readily explained, as it proves impossible to identify that layer in the near-shore areas in view of the absence of an underlying intermediate phosphate minimum, notwithstanding the fact that phosphates concentration in the layer σ_t = 15.6–15.8 in those areas is larger than 2 μmol·l^{-1}. In the central part of the cyclonic gyres, the upper maximum under consideration is being washed out as a result of winter-time convective sinking of cold oxygenated surface waters, in which, however, phosphate concentration is small. That process leads to the growth of phosphate content in the upper layer, which is one of the causes of intense winter–spring-time phytoplankton blooming in the areas encompassed by the cyclonic movement of waters.

Analysis of the dataset compiled during Cruise 30 of the R/V *Professor Kolesnikov* indicates that the intermediate phosphate minimum occurs only in the central part of the sea bounded by the Black Sea rim current (Figs 4 and 5). To the right of the rim current, the intermediate minimum was not observed no matter how far away from the continental slope a station was occupied. This evidence and the data discussed above allow us to hold that the winter-time ventilation of waters above the domes of the cyclonic gyres and the location of the Black Sea rim current represent one of the major factors determining the large-scale variability of phosphates vertical distribution in the layer bounded by the ~16.5 isopycnic surface.

Thus, for the annual cycles with fairly cold winters, the basic processes responsible for the generation of the vertical structure of the phosphates fields in the Black Sea may be presented in the following form.

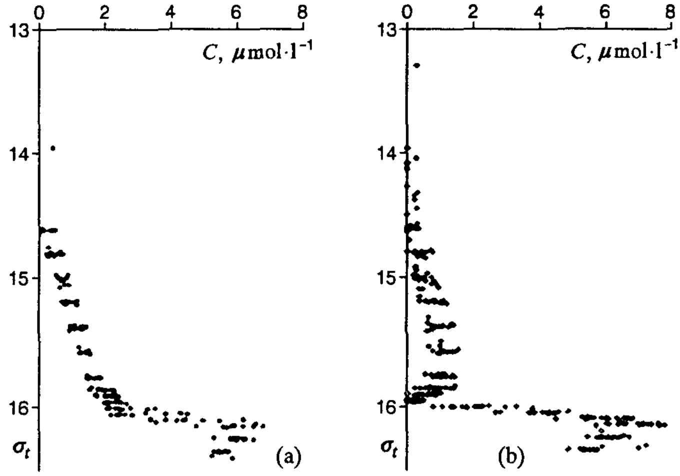

Figure 5. Phosphates vertical distribution relative to conventional density for the stations occupied (a) to the right-hand side and (b) to the left-hand side of the Black Sea rim current.

1. An intermediate minimum ($\sigma_t \sim 15.95$) occurring due to the adsorption of phosphates on manganese and iron hydroxides is observed predominantly during winter–spring season in the Black Sea areas, which are strongly impacted by the cyclonic gyres. This process depends on how severe is winter and how intense is the ventilation of waters over the domes of the cyclonic gyres as a result of their cooling and sinking, which, in turn, contributes to the turbulent diffusion of oxygen and, respectively, to the rate of oxidation of the reduced forms of manganese and iron.

2. In the marginal areas of the cyclonic gyres, the process of phosphate minimum formation by the pattern given above is weakly pronounced. It may be supposed that the peculiarity of their vertical distribution persists there primarily due to the isopycnic transport and mixing with the central Black Sea waters. The area where these phenomena take place is bounded by the Black Sea rim current, which hampers the transversal transport of waters with small phosphates content ($\sigma_t \sim 15.95$) toward the area overlying the continental slope.

3. The upper phosphates maximum ($\sigma_t \sim 15.6$) manifests itself only if the intermediate minimum layer is present ($\sigma_t \sim 15.95$). To the right of the Black Sea rim current, such vertical distribution is not observed at all, although phosphate concentrations at the isopycnic surface $\sigma_t \sim 15.6$ in these areas are larger than their counterparts to the left of the Black Sea rim current.

4. In the central part of the basin, where seawater is being ventilated over the domes of the cyclonic gyres in winter, phosphates are being washed out from the depths of the upper maximum ($\sigma_t \sim 15.6$), which may provide for their supply to the photic layer. The effect of this process, even during cold winters, is restricted by the depth of the ~ 15.7 isopycnic surface. Phosphates from the anoxic zone are not being transported to the oxic layer directly in the course of winter-time convection.

5. The lower phosphates maximum ($\sigma_t \sim 16.2$) evolving as a result of reduction, dissolving of the suspended hydroxides of Fe (III) and Mn (III, IV), and releasing of the adsorbed phosphates, is most pronounced in the central part of the basin. The available data allow us to claim that it is in that area that the lower phosphate maximum basically occurs during the winter–spring period. However, in contrast to the phosphate minimum ($\sigma_t \sim 15.95$), isopycnic transport in the layer of the lower maximum ($\sigma_t \sim 16.2$) facilitates the conservation of that specific feature of the phosphates vertical distribution throughout the abyssal part of the Black Sea.

NITRATES

Nitrates vertical distribution relative to conventional density, shown in Fig. 2b, is characterized by the occurrence of a maximal concentration at $\sigma_t = 15.4–15.6$. As in the case of phosphates vertical distribution, nitrates concentration within the layer of maximum is subject to appreciable fluctuations. Matching up the data compiled in the expeditions of the R/Vs *Atlantis-II* and *Knorr* in 1969 and 1988, respectively, the authors of ref. 16 have deduced that nitrates content maximum concentration within the layer of a maximum had essentially increased over the time that had passed between the two cruises. This phenomenon is accounted for by the eutrophication of the Black Sea surface waters as a result of the influx of various forms of nitrogen brought by the river discharges.

The explorations conducted on board the R/V *Professor Kolesnikov* have allowed us to rationalize the variability of nitrates concentration within the layer of maximum and to outline the mechanism for their input to the photic layer from the abyssal waters.

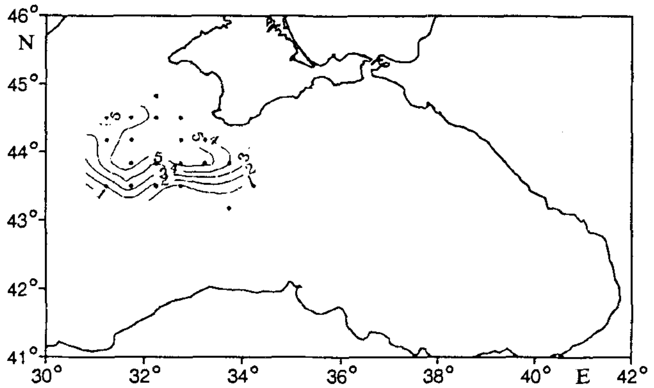

Figure 6. Nitrates spatial distribution on the 15.40 isopycnic surface.

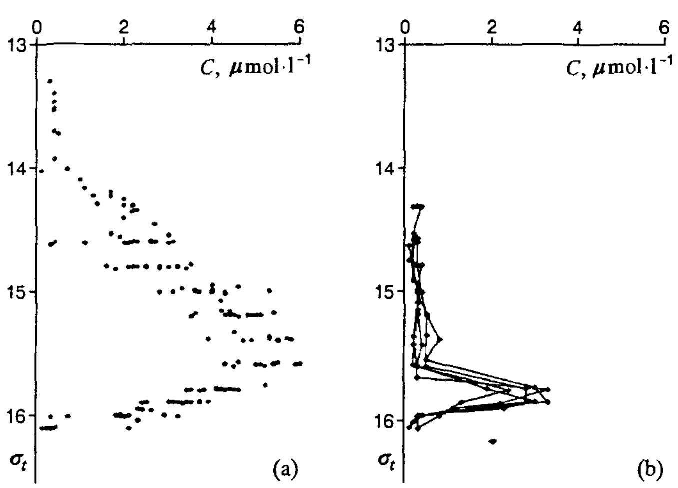

Figure 7. Nitrates vertical distribution relative to conventional density for the stations occupied (a) to the right-hand side of the Black Sea rim current and (b) in the central sea.

Figure 6 shows the spatial distribution of nitrates concentration at the 15.4 isopycnic surface. Small concentrations are characteristic of the central sea, that is, the area strongly influenced by the western cyclonic gyre. This fact allows a supposition that processes of winter-time convective mixing resultant from the descending of cool surface waters over the domes of the cyclonic gyres play the principal role in the formation of the nitrates vertical structure during that period.

Figure 7 demonstrates two groups of stations occupied in the areas impacted by the anticyclonic quasi-stationary vortices to the right of the Black Sea rim current and in the central part of the basin. It is manifest that for the stations indicated in Fig. 7a, nitrates distribution did not differ from the distributions given in refs 12 and 16. The different vertical nitrates distribution in the central part of the sea (Fig. 7b) allows us to vividly show the result of winter-time ventilation of waters over the domes of the cyclonic gyres. It is readily seen that it is the upper part of the maximal nitrates concentration that is destroyed (σ_t = 14.0–15.7), while the structural characteristics of its lower part

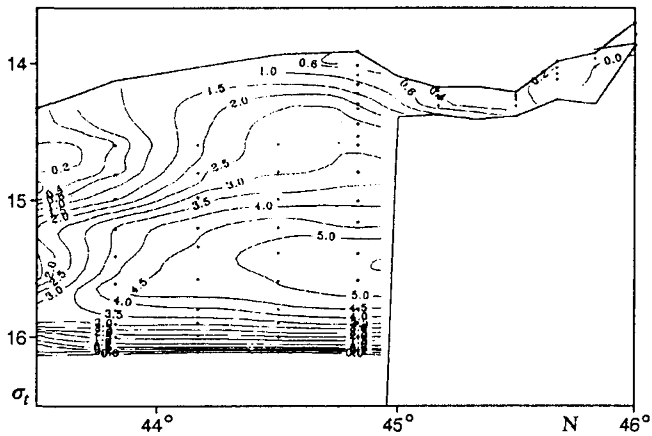

Figure 8. Nitrates distribution relative to conventional density at the transect made along 32.25° E.

($\sigma_t \sim$ 15.7–16.1) remain practically unaltered. The latter allows an assumption that the ventilation of subsurface waters described above represents the basic mechanism for the influx of phosphates and nitrates to the photic layer from the cold intermediate layer. Nitrates at the depths of maximal concentration are not consumed then for oxidizing the reduced forms of iron, manganese and, hence, hydrogen sulphide [14], but act as a subsurface source of biogenic elements for the photic zone. At the same time, it is seen that the depth of convective ventilation is restricted by the position of the 15.7–15.8 isopycnic surface. Hence, an efflux of the biogenic elements from the anoxic zone does not take place [23].

The evidence depicted in Fig. 7 allows one to explain why the scatter of nitrates concentrations on the isopycnic surfaces in the vicinity of the maximum was so large during Cruise 30 of the R/V *Professor Kolesnikov*. The data in Fig. 2b reflect the diverse profiles of nitrates distribution in the Black Sea in spring. With the exception of the limiting cases shown in Fig. 7, Fig. 2 also demonstrates the intermediate cases when the effect of winter-time ventilation reached the isopycnic surfaces, whose conventional density was less than 15.7.

The processes under consideration can be presented in a more emphatic fashion by analysing nitrates vertical distribution at the transect made along 32°25′ E (Fig. 8). The effect of winter-time ventilation (during 1992–1993) above the domes of the cyclonic gyres reached the depth of the conventional density 15.7. This is readily seen from the shape of the nitrate concentration isolines (Fig. 8). At the southernmost station of that transect, the isopycnic nature of nitrates distribution within the layer of maximal nitrates concentrations was violated up to σ_t = 15.7–15.8. Maximal nitrates concentration at that station amounted to 3.1 μmol·l^{-1}. Maximal concentrations tended to increase along the transect in the northward direction, attaining 5.4 μmol·l^{-1} in the domain of a quasi-stationary anticyclonic eddy.

The acquired data allow us to evaluate not only the volume of waters participating in the process, but also the amount of nitrates (Σ) brought to the active layer of the sea. For the respective calculations to be performed, we assume the nitrates vertical distribution during summer–autumn period to be isopycnic for the larger part of the sea and to coincide in its qualitative characteristics (maximal concentration and the structure of maximal nitrates concentration) with those obtained for the station having coordinates 44.50° N and 32.25° E. Nitrates vertical distribution in spring, following the winter-time convective ventilation, will be taken to be similar to the distribution reproduced at the transect along 32.25° E (Fig. 8). For simplicity, the surfaces bounding waters with concentrations 5, 4, 3, 2, and 1 $\mu mol \cdot l^{-1}$, will be assumed to be flat, displaying an identical inclination at the section between 43.50 and 44.50° N. By variation of the respective specific volumes of water, we assessed a drop in the amount of nitrates within the layer of large nitrates content, as compared with autumn. For a 1° × 1° square, that quantity equalled nearly 43 700 tons. On the assumption that such processes of winter-time convective ventilation encompass, at least, five 1° × 1° squares, we obtain $\Sigma \geq 200\,000$ tons.

The amount of nitrates discharged by the Danube (80% of the total river run-off to the Black Sea) averages 1.5×10^7 kg per month [24]. Thus the overall annual input of nitrates to the Black Sea by the river run-off is assessed to be approximately 200 000 tons. Obviously, the amount of nitrates brought to the Black Sea by the river run-off and in the course of winter-time convective ventilation of waters over the domes of the cyclonic gyres are comparable. However, in calculating their likely influx due to winter-time ventilation, we started from the minimal estimates of the scale of that phenomenon. Hence, during fairly cold winters, that process may turn out to be the principal mechanism for 'pumping' biogenic elements into the photic layer, providing for a definite level of ecosystem functioning. It should be appropriately noted that the process at issue appears to be irregular which, in contrast to the relatively even influx of the biogenic elements brought by the river run-off in the course of the year, is realized over a space of 1 or 2 months.

With the depth of the photic layer assumed to equal 40 m over the entire area under study, we obtain that the calculated amount of nitrates inflowing to the photic layer may lead to the rising of their content in the layer overlying the domes of the cyclonic gyres by 0.7 $\mu mol \cdot l^{-1}$. The real concentration will depend on the area where the phenomenon is taking place and on the intensity of winter-time convective ventilation, quantitative parameters of the layer of nitrates maximal concentration during the autumn period and on the rate of their transportation within the photic layer proper. In any case, it is obvious that this source of nitrates represents one of the causes of spring-time phytoplankton blooming in the central part of the Black Sea during early spring, and the aspect that controls the bloom intensity.

In studying the inter-annual variability of the nitrates concentration within the layer where its content is largest, it should be borne in mind that during warm winters, convective ventilation above the domes of the cyclonic gyres normally does not reach the depth layer where nitrates concentration is minimal. After such winters, nitrates concentration may be expected to grow in the layer of nitrates maximal concentration. In such a situation, the layer of nitrates maximal concentration, by the onset of the next winter, will display an increased nitrates concentration, with respect to some mean values. The recurrence of several warm winters would enhance that phenomenon by many times, while the recurrence of severe winters is expected to decrease the maximal values observed. It is likely that process accounts for the considerable difference between the nitrates concentrations observed during the expeditions of the R/Vs *Atlantis-II* and *Knorr* conducted in 1969 and 1988, respectively.

Nitrates concentration within the layer of the largest content tends to increase away from the centre of the cyclonic gyre, being maximal in the vicinity of the anticyclonic eddy and continental slope (Fig. 8). Moreover, the entire area impacted by the anticyclonic eddy displays not only the largest nitrates concentration, but also their isopycnic distribution. Thus, the presence of the anticyclonic gyre does not notably affect the nitrates vertical distribution relative to conventional density. This phenomenon can be rationalized if we assume the formation of anticyclonic gyre waters to be isopycnic. In this case, during the development of anticyclonic eddies, the form of isopycnic surfaces gets modified, with the intensity of diapycnic fluxes of substances being likely to persist till the time when the anticyclonic eddy would start to interact with the surface of the continental slope.

Analysis of the data submitted in Fig. 8 allows us to assess the likelihood of an influx of nitrates from the north-western shelf area to the abyssal part of the sea. It is readily seen that nitrates content in the eastern section of the shelf area is 0.4 μmol·l^{-1}, at most. Only near the continental slope break does nitrates concentration increase up to 0.6–0.8 μmol·l^{-1}, at the upper depth levels, and up to 1.0 μmol·l^{-1}, in the near-bottom layer. That distribution of nitrates allows one to hold that the eastern part of the shelf does not represent a major source of nitrates for the deep-water part of the sea. Naturally, we ignore the western area influenced by the Danube, Dnieper, Dniester, and Bug discharges.

CONCLUSIONS

1. Spatial isopycnic analysis is a convenient and efficient tool for the study of the variability of the vertical structure of various chemical fields. Supposedly, it will prove to be most efficient in analysing highly stratified waters. The principal advantage of the method consists in the possibility of separating the influences of various hydrophysical processes and the processes having a different nature upon the generation of chemical structures. We obtain then a chance to identify the areas where chemical substances exchange at depths by a diapycnic mechanism.

2. Spatial isopycnic analysis has enabled us to conduct a pioneering study of the evolution of vertical phosphates and nitrates distribution in the Black Sea, with respect to conventional density, as well as to explain the major causes and dynamics of that process.

3. It has been found that the convective ventilation of waters above the domes of the cyclonic gyres during winter period leads to the destruction of the layer of the upper phosphates maximum ($\sigma_t \sim 15.6$) and nitrates maximum ($\sigma_t \sim 15.4$). During fairly cold winters, these processes may lead to the influx of biogenic elements to the photic layer of the sea. In the case of nitrates, the total flux amounts to about 200 000 tons, which is comparable with the overall annual input of that biogenic element by the total river run-off. Concurrently, winter-time convective ventilation facilitates the elimination of phosphates from the layer of phosphates minimal concentration ($\sigma_t \sim 15.95$) and their transport to the layer of maximal concentration ($\sigma_t \sim 16.20$–16.30). For the annual cycles with sufficiently cold winters, an occurrence of three maxima on the phosphates vertical profile in spring is observed in the central basin, with the dynamic boundary being represented by the Black Sea rim current.

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