Seasonal Changes in the Hydrochemical Structure of the

THE BLACK SEA
Redox Zone

BY EVGENIY V. YAKUSHEV, OLEG I. PODYMOV, AND VALERIY K. CHASOVNIKOV

The Black Sea is the world's largest marine anoxic basin. The Black Sea's water below a depth of ~100 m is enriched with hydrogen sulfide that formed after the intrusion of seawater as a result of sea-level rise about 8,000 years ago (Deuser, 1974). Winter mixing in this sea results in the formation of an oxygen-rich cold intermediate layer (CIL), which is observed at depths of about 60 to 100 m. Transport of oxygen to the underlying water is connected with very weak processes of vertical turbulent exchange, which results in a very smooth decrease of redox potential. Therefore, the different oxidation-reduction reactions that occur there in narrow water layers form features that are characteristic hydrochemical structures (e.g., maxima and minima, and onset points). We call these features "chemotropic," the connection between water density and the chemical struc-ture's properties (analogous to baro-tropic, the connection between density and pressure). The position of these chemotropic features in the density field is very stable (Vinogradov and Nalban-dov, 1990; Turgul et al., 1992; Murray et al., 1995). The chemotropy of the Black Sea redox layer is well known, and this sea is successfully used as a natural labo-ratory to study processes that occur at the oxic/anoxic interface.

Over the past few decades, the Black Sea has been seriously perturbed by climatic change and intensive anthro-pogenic contamination. Some nutri-ents have increased (e.g., nitrate [NO_3^-] due to eutrophication), while others have decreased (e.g., silicon [Si] due to dam construction or increased diatom-blooms) (Konovalov and Murray, 2001). Organisms imported as part of interna-tional shipping (e.g., *Mnemiopsis* and *Beroa*) have contributed to modification of the natural ecosystem (Kideys et al., this issue). Because of these changes, and others, questions about the tempo-ral variability of the Black Sea's chemi-cal system and the processes that occur at the redox boundary are acute. Ulti-mately, the goal is to understand which changes in the Black Sea are due to anthropogenic effects, and which are due to normal seasonal variability.

The northeastern Black Sea region near Gelendzhik (Figure 1) is far from the influence of the Bosporus Strait's input and Danube River inflow. There-fore, the vertical hydrochemical structure in this region is more stable and reflects "integrated" rather than local changes in the sea. Data obtained in this region from regular sampling expeditions from 1989 to 2005 can be used for studying changes connected to temporal variabil-ity on a seasonal scale.
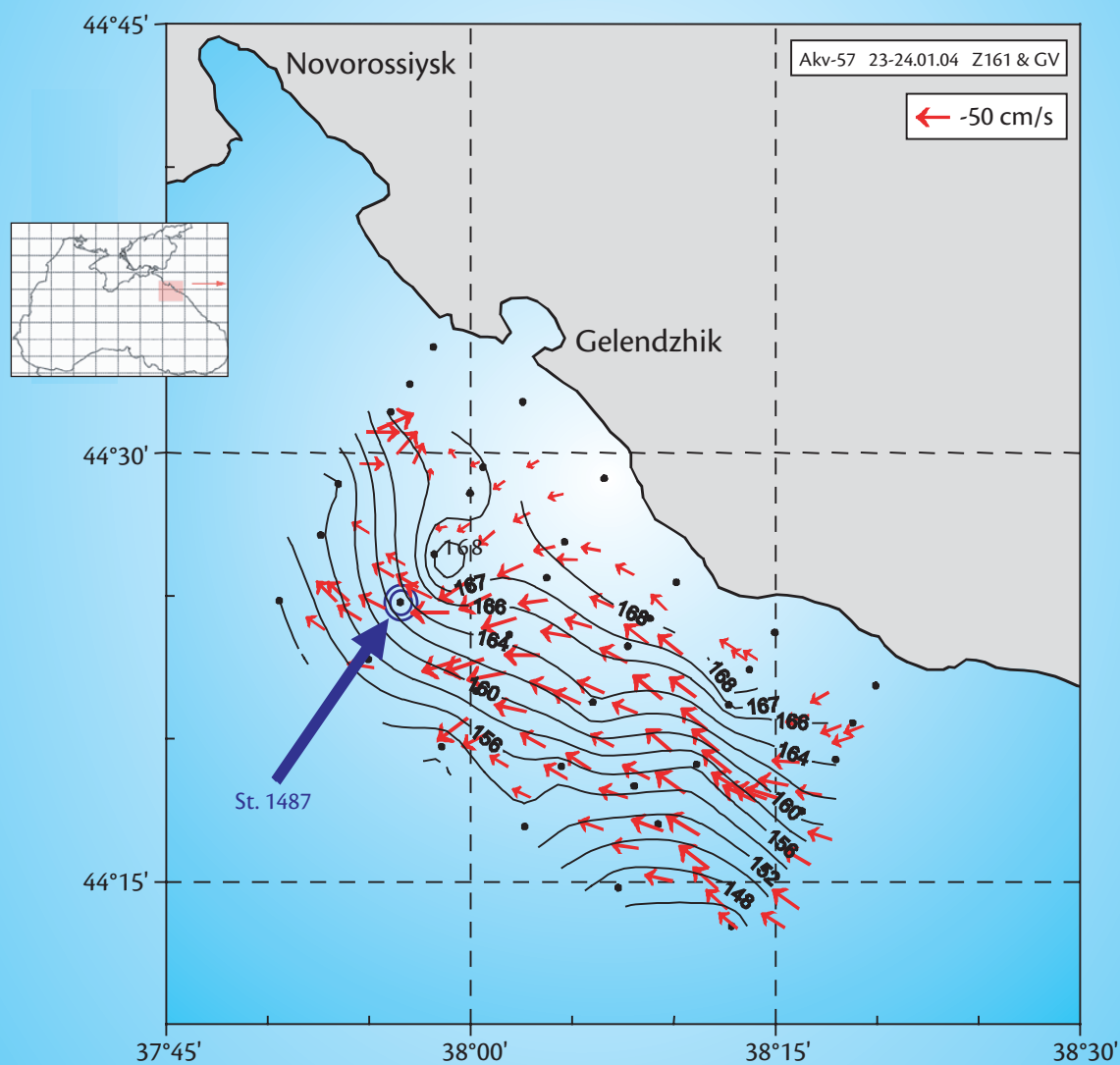
Figure 1. Position of the station 1487 and the velocity field of the R/V *Akvanavt* survey in January 24-25, 2004, calculated using the geostrophic method (Yakushev et al., in press).

MATERIAL AND METHODS

We studied the hydrochemical structure of the redox layer in the northeastern Black Sea during scientific expeditions aboard the R/V *Akvanavt* and R/V *Ashamba* from 2000 to 2004. During these expeditions, we measured dissolved oxygen, phosphate, silicate, nitrate, nitrite, ammonium, urea, total phosphorus, total nitrogen, pH, alkalinity, hydrogen sulfide, and total manganese. Water samples for chemical measurements were collected with 5L Niskin bottles on a Rosette attached to a Sea Bird CTD probe.

Analytical methods used to determine each parameter were according to Russian standards (Bordovskiy and Chernyakova, 1992). We measured dissolved oxygen by Winkler titration, and determined phosphate concentrations by the Murphy-Riley method. We measured absorbance at 885 nm in a 50 mm cell.

For silicate, we used the method introduced by Koroleff based on the formation of B-1:12 silico molybdic acid and its partial reduction to a blue heteropoly acid. We measured absorbance at 880 nm with a 10 mm cuvette.

We measured nitrite with sulfanilamide and N-1-naphthylethylendiamine dihydrochloride, and converted nitrate to nitrite using Cu-Cd columns. We measured absorbance at 543 nm in a 50 mm cell. We determined Ammonium concentrations by the phenol-hypochlorite reaction (Solorzano, 1969). We added the reagents (0.5 ml of phenol solution and 0.5 ml of hypochlorite solution) on the ship's deck to avoid NH_3 contamination from the air inside ship. We measured urea photometrically with diacetylmonooxim and semicarbazid (Sapozhnikov et al., 1988).

We determined total phosphorus by digestion with sodium persulfate in a water bath at T=100 degrees C. We used the Valderrama technique (digestion in and autoclave) for analyzing total nitrogen. We estimated organic forms of phosphorus and nitrogen as the difference between the total and inorganic species (phosphate for phosphorus and nitrate, nitrate and ammonium for nitrogen).

We defined pH on the NBS scale with a pH-meter I-500 (NPKF Aquilon, Russia). The precision was approximately 0.01 unit NBS. Alkalinity samples were collected into 250 ml glass bottles. We determined total alkalinity in the coastal laboratory by direct titration with hydrochloric acid according to Bruevich's modification (Bordovskiy and Chernyakova, 1992). We monitored the process of titration, with constant venting with CO_2-free air, to a pH value of 5.45 using a glass electrode. The precision of this technique is about 2 µeq/kg.

We determined the hydrogen sulfide content of the upper part of anoxic zone photometrically with paraphenilendiamin. Absorbance was measured at 670 nm with a 10 mm cuvette.

We took samples for methane from Niskin bottles and placed them in 120 ml glass bottles using silicon tubing. We left a head space of about 4 ml in each bottle. We made the bottles gas tight using a screw lid with a rubber membrane. We shook the samples and then left them standing without shaking to establish temperature and gas-phase equilibrium. We used a syringe through the rubber membrane and a hole in the lid to take as sample of the gas phase for analysis. We used a gas chromatograph (LHM-80) with a flame-ionization detector for determining the methane content of the gas phase. The accuracy of determination was 0.05 ppm. We calculated methane concentrations in the water samples following Bol'shakov and Egorov (1987), assuming that the initial methane content in the gas phase was equal to that in the atmosphere and had a value of 1.8 ppm.

We used formaldoxime to determine manganese concentrations (Peshkova and Ovsyannikova, 1937).

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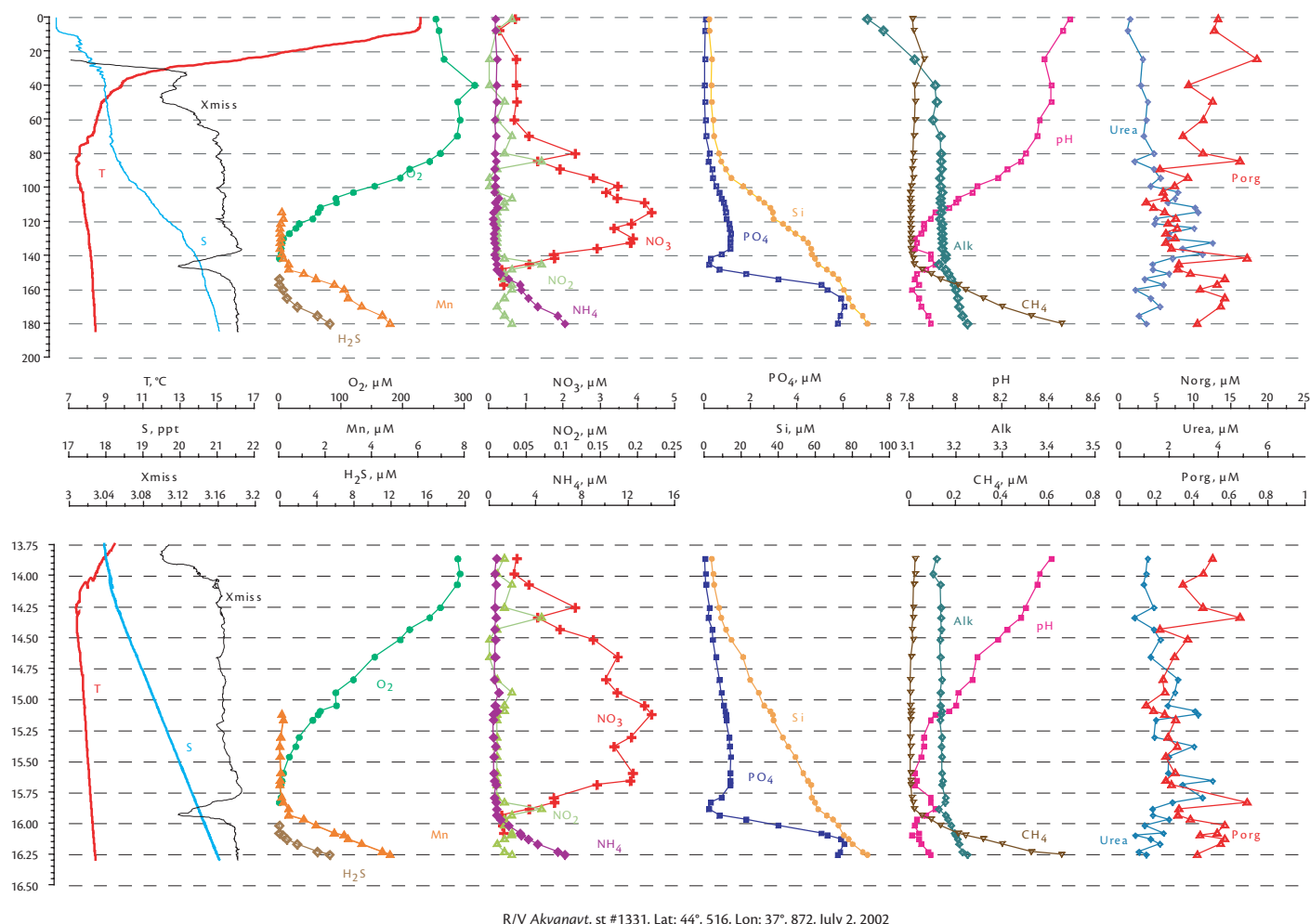
Figure 2. Vertical distribution of temperature (T), salinity (S), density (σ_θ), transmission (Trans), oxygen (O_2), hydrogen sulfide (H_2S), total manganese (Mn^{2+}), silicates (Si), nitrates (NO_3), nitrites (NO_2), ammonia (NH_4), urea (Urea), phosphates (PO_4), and organic phosphorus (P_{org}) at a summer station near Gelendzhik (Station 1331). Concentrations of chemical parameters are in µM.

RESULTS

We studied the vertical hydrochemical structure of the northeastern Black Sea on a regular basis from 1999 to 2004. We took hydrochemical measurements in the redox layer at approximately 600 stations, including about 30 stations with 2- to 3-m grid sampling in the redox zone. Because winter hydrochemical measurements were rarely collected as compared with those of the summer, it was difficult to detect the seasonal variability of parameters in the redox layer.

Figure 2 shows a typical summer vertical distribution of hydrochemical constituents. Figure 3 shows the results of the winter observations obtained in the northeastern Black Sea coastal waters on January 26, 2004 (Station 1487, R/V *Akvanavt*, cruise 57). We calculated the geostrophic current shown in this figure using hydrophysical data collected during the first stage of this cruise (January 24-26, 2004) (Yakushev et al., Submitted).

The summer distribution (Figure 2) included a 10-to-20 m, high-temperature (25 to 26 degrees C) upper mixed layer.
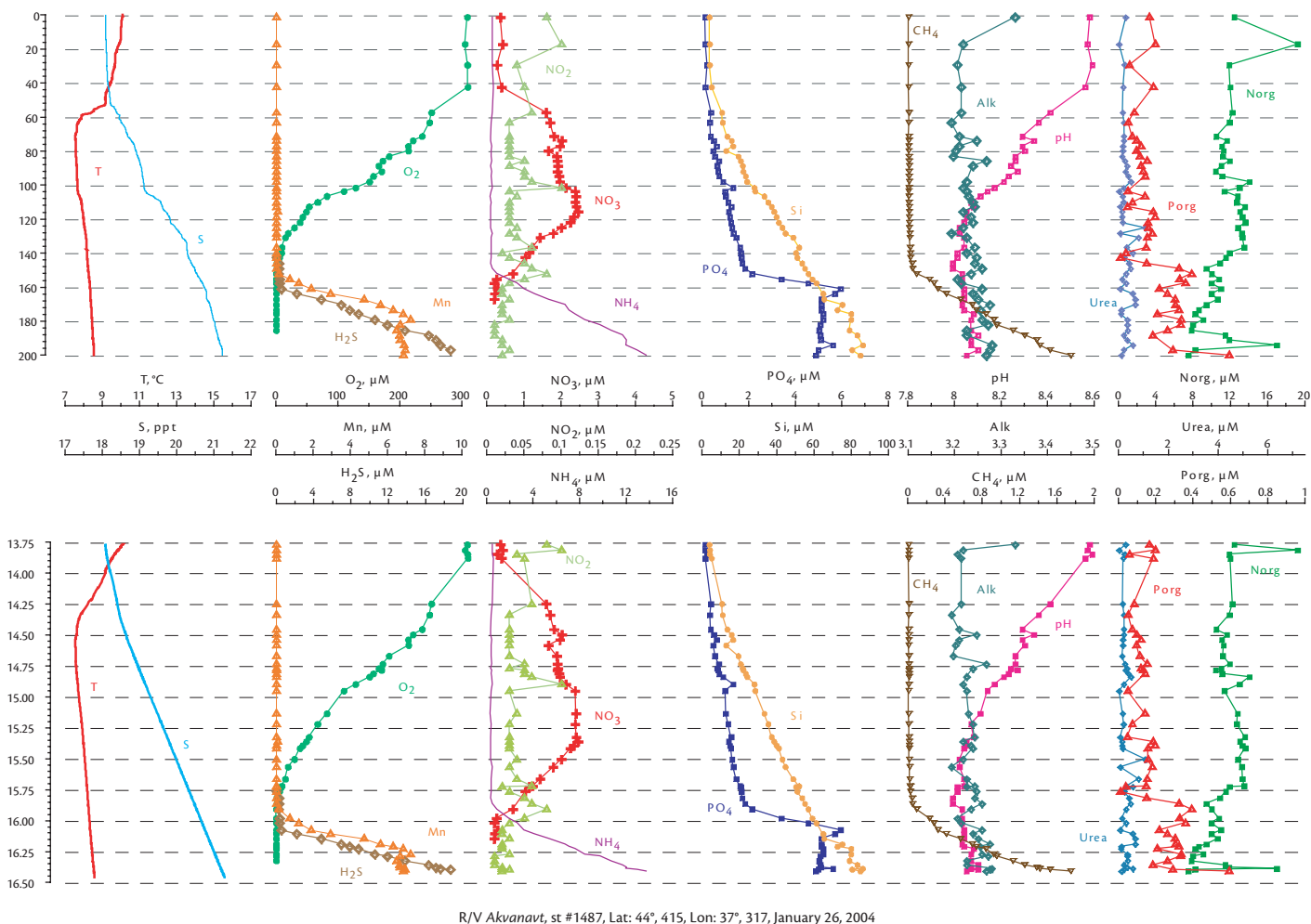
Figure 3. Vertical distribution of temperature (T), salinity (S), density (σ_θ), oxygen (O_2), hydrogen sulfide (H_2S), total manganese (Mn^{2+}), silicates (Si), nitrates (NO_3), nitrites (NO_2), ammonia (NH_4), urea (Urea), phosphates (PO_4), and organic phosphorus (P_{org}) at a winter station near Gelendzhik (Station 1487). Concentrations of chemical parameters are in μM.

This layer was characterized by minimum concentrations of nutrients (less than 0.01 μM PO_4, less than 0.27 μM NO_3^-, less than 2.5 μM Si), maximum pH values, and significant concentrations of oxygen (250 μM) that increased to 290 to 300 μM in the upper part of the CIL. A sharp growth in phosphate and nitrate concentrations, and a decrease of oxygen content, marked the limits of the CIL and below it.

During winter (Figure 3), an upper layer (0 to 40 m) was characterized by low temperature (9 to 11 degrees C) and by a decrease in temperature with depth, with small vertical gradients. The vertical distribution of temperature and salinity revealed several 5-m lenses of uniform density water at 135 m and 165 m below the CIL. Maximum dissolved oxygen concentrations (300 μM), high pH values, and the minimum nutrient concentrations (0.10-0.18 μM PO_4, 0.25-0.5 μM NO_3^-, 3.5-3.8 μM Si) were observed in the surface layer. Compared with the summer period, nutrient concentrations were higher.

As opposed to the warm periods of the year, organic phosphorus, organic nitrogen, and urea maxima were not observed at the lower boundary of this layer in the vicinity of the CIL's core (σ_θ=14.6 kg/m^3), where the increase in phosphate, nitrate, and silicate begins.

The maximum nitrate concentrations (~110 m, σ_θ=15.25 kg/m^3) did not exceed 2 to 2.5 µM, which is significantly less than the values observed during the summer (about 4.5 to 5 µM). Nitrate disappeared at the same density (σ_θ=16.00 kg/m^3), as has been observed elsewhere (Murray et al., 1995). The nitrite concentrations were low compared with those observed in summer.

The main characteristic feature of the phosphate distribution is the presence of sequential maximum (at about σ_θ=15.55 kg/m^3) and minimum (at about σ_θ=15.92 kg/m^3), that was named by Shaffer (1986) as a "phosphate dipole." This phosphate dipole was well defined during the summer period (Figure 2). The shallower phosphate minimum was observed as a 0-µM concentration in a 3-m-thick layer, at about 140 to 150 m depth, in July 2002. Under normal summer conditions, it forms of a sharp peak with concentrations of 0 to 0.8 µM. In winter, the shallower phosphate minimum at this depth was absent (Figure 3), and phosphate everywhere increased with depth. An increase in the vertical gradient of phosphorus began at about σ_θ=15.90 kg/m^3.

During the winter, hydrogen sulfide appeared at 161 m (σ_θ=16.10 kg/m^3) (Figure 3). Its boundary was gentler than distributions typically seen.

The disappearance of the shallower phosphate minimum and upward shift of the hydrogen sulfide boundary to σ_θ=16.02 kg/m^3 were observed at Station 2002, where the measurements were carried out in a coastal eddy in December 2004 (not shown).

The onset of increasing ammonium and total manganese was found in winter at the same density as usual (σ_θ=15.90 kg/m^3) and methane started to increase at σ_θ=15.85-15.90 kg/m^3. The upper boundary of all these chemicals was smooth relative to that usually observed in other times of the year.

The vertical gradients of the total dissolved manganese and hydrogen sulfide were equal in the vicinity of the onset of hydrogen sulfide (Figure 3), and in the shallower layers, the vertical gradient of manganese decreased. A different picture is usually observed—the vertical gradient of Mn is usually less than the vertical gradient of hydrogen sulfide at its depth of onset, and in the shallower layers, the vertical gradient of Mn starts to increase (Yakushev et al., 2003).

As previously seen (September 2001, July 2002, July and August 2003), total organic nitrogen decreases from 10 to 14 µM at σ_θ=15.75 kg/m^3, to 8 to 10 µM at σ_θ=15.90 kg/m^3. Total organic phosphorus slightly increased from 0.1 to 0.2 µM at σ_θ=15.75 kg/m^3, to 0.2 to 0.4 µM at σ_θ=15.75 kg/m^3. The absence of a urea maximum in the vicinity of the H$_2$S onset was another distinctive characteristic of the winter period. As a whole, the concentrations of urea were lower than observed in summer (1 µM compared with 2 to 4 µM). The pH values in the redox zone were lower in winter than in summer (Figures 2 and 3).

The preceding results are based mainly on data from two stations. We found that one of the best criteria of the seasonal variability estimates is the character of phosphate distribution. To better understand the seasonal variability of phosphate, we performed statistical analysis of seasonal variability of the shallower phosphate minimum in the northeastern part of the Black Sea. Coastal zone (up to about 40 nautical miles from the shore) stations and open sea zone (40 to 100 nautical miles) stations were examined separately. We used the 15.80 to 15.90 kg/m^3 density layer for analysis because the local phosphate minimum that appeared just above the

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suboxic zone fell into this interval.

According to the results of statistical estimations (Figure 4), concentrations of phosphate in the shallower phosphate minimum zone in the northeastern part

of the Black Sea are greater along the coast than in the open sea during both winter and summer periods. Our data do not show distinct seasonal variability in the open sea stations, but due to the relatively small amount of winter data, we cannot state it for sure. At the coastal stations, phosphate concentrations during the winter were greater than in summer by 0.2 to 0.5 μM, and showed an increasing trend during the winter periods from 2001 to 2004 (from 0.8 to 1 μM to 1.2 to 1.6 μM).

CONCLUSIONS

Vertical distributions of hydrochemical parameters of the Black Sea redox layer observed in winter were significantly different from those observed in summer. A pronounced example of the winter season structure was observed at Station 1487 where enhanced mixing was connected with an anticyclonic eddy. This station was near an anticyclonic eddy (Figure 1) in a region with increased horizontal velocities in the redox layer and where the intensity of mixing in the redox layer was greater than in the surrounding waters.

In summary, the main differences between winter and summer distributions are:

- The vertical distribution of phosphate in winter is characterized by the absence of the shallower minimum (Figure 3).
- Concentrations of nitrate at the nitrate maximum were lower in winter (2.5 μM) than in other times of the year (greater than 4.5 μM).
- The organic phosphorus maxima and urea content at the onset of hydrogen sulfide, which are typically observed in summer, are absent in winter.
- Concentrations of organic nitrogen were lower in winter than in summer. These observations may be related to the decrease in the number of bacteria and a reduction of the rates described by Sorokin et al. (1992).
- pH values were lower in winter than in the summer.
- Changes of the vertical gradients of hydrogen sulfide, ammonium, manganese, and methane at their onset depths were smoother in the winter than in summer.
- The vertical gradient of total manganese in the layer upper above the onset of hydrogen sulfide increased in winter instead of decreased.

Two factors seem to affect the seasonal variability of the hydrochemical struc-
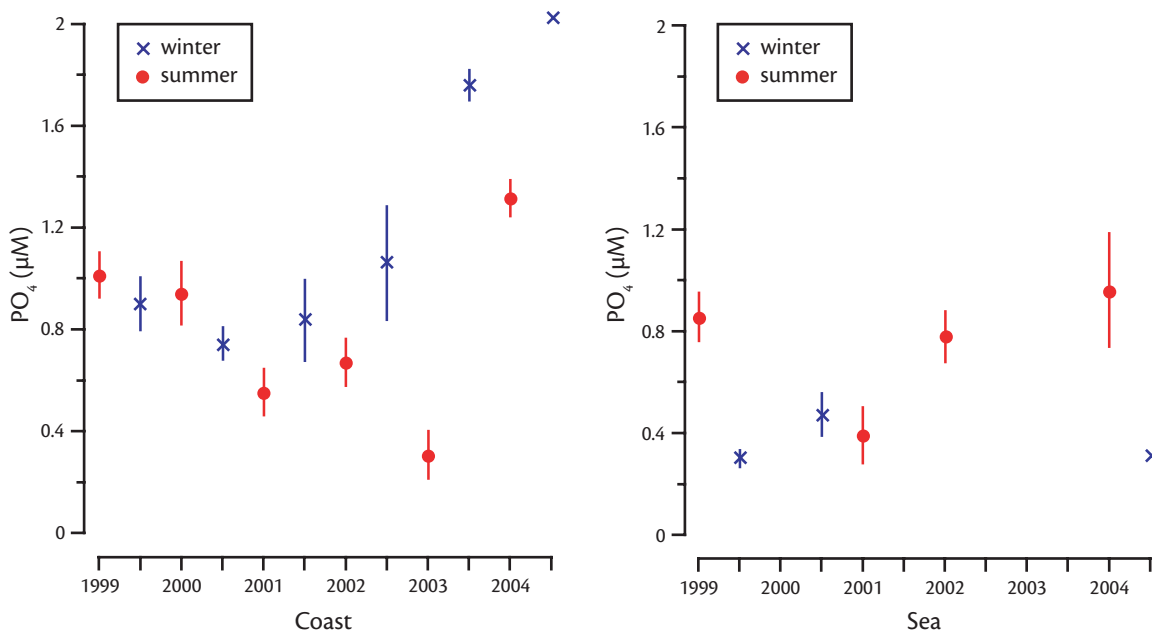

Figure 4. Results of statistical analysis of mean observation of the phosphate in the density layer of $\sigma_\theta = 15.8$ to 15.9 kg/m^3. Calculations in the coastal area are shown on the left, and the open sea is shown on the right. Vertical line displays the value of standard deviation.

ture of the oxic/anoxic interface: seasonality of organic matter production and seasonality of mixing intensity. The winter decrease of OM flux can result in decrease of number of bacteria and slowing down of reaction of biogeochemical transformation because OM is a substrate for many reactions mediated by heterotrophic bacteria. During the same season, an enhanced mixing connected with anticyclonic eddies leads to smoothing of vertical gradients and extrema, resulting in changes in biogeochemical reactions such as formation of the phosphate dipole.

These estimates were obtained in the coastal waters of the northeastern Black Sea, which are affected by the Rim Current. Similar variability should be observed in all the Black Sea coastal waters. Statistical analysis of the phosphate minimum distribution and variability shows that the central part of the sea, which has a more stable hydrophysical structure, seems unaffected by significant seasonal changes. These changes should be taken into consideration while analyzing the consequences of anthropogenic influence.

> Data obtained in this region from regular sampling expeditions from 1989 to 2005 can be used for studying changes connected to temporal variability on a seasonal scale.

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