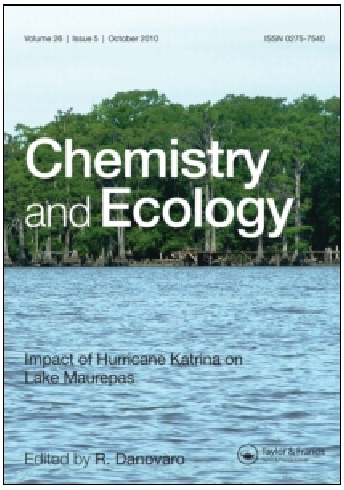

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Seasonal and interannual variability of hydrology and nutrients in the Northeastern Black Sea

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Seasonal and interannual variability of hydrology and nutrients in the Northeastern Black Sea

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The main objective of this work was to investigate the temporal variability of hydrochemical parameters in two coastal regions of the Northeastern Black Sea: the Gelendzhik bay, influenced by anthropogenic activities and the Golubaya bay an open coastal region. Dissolved oxygen, biochemical oxygen demand, pH, alkalinity, phosphate, organic phosphorus, silicates, nitrates, nitrites, ammonia, organic nitrogen, oil products and heavy metals were measured. Si/P and Si/N ratios showed that the Gelendzhik bay waters were significantly enriched in nitrogen and phosphorus compounds. Unlike the Golubaya bay, phosphates were always present in the Gelendzhik bay, and development of photosynthesis was not limited by these. Features of seasonal variability of nutrients in the Gelendzhik bay (increased concentrations and pronounced summer–autumn maximum) appeared to be a result of human impact—outflow of nutrients with shore input and recreational activities during the summer holiday season. The data obtained indicate that pollution from local spots from the coast of the Black Sea, related primarily to eutrophication, could play a large role in the nutrient balance of the sea and could affect its ecological state.

Keywords: Eutrophication; Nutrients; Coastal region; Redfield ratios

1. Introduction

The knowledge of ecological status of the coastal waters of the Black Sea, in particular in the northeastern part, is of high importance owing to increasing human activities in this area [1].

The Black Sea is the world's largest marine basin with permanent anoxia [2]. Saline water from the Marmora Sea forms the lower 1900-m layer, leaving only the upper 100 m to be influenced by fresh river water. The existence of a constant halocline leads to the appearance of a unique mechanism for seasonal vertical mixing: the annual renovation of waters in the Black Sea occurs only down to a depth of about 60–80 m, where the so-called Cold Intermediate Layer (CIL) is formed. This restriction in the oxygen supply allows oxygen to become rapidly

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exhausted from organic-matter (OM) oxidation, and anoxic OM mineralization causes the appearance of hydrogen sulfide in the water [2–4].

The upper, oxic layer of the Sea contains about 10% of the water [2], and so this sea is very susceptible to external impacts.

The chemical balance of this layer is affected by exchange with the anoxic waters, fluxes from the Seas of Marmora and Azov, and the river influx. Nearly all large Black Sea rivers flow into the north-western part of the Sea (more than 90% of the river input), while the remaining coastal areas are characterised by limited fresh water inputs.

As a part of the World's Ocean, the Black Sea undergoes the influence of natural and anthropogenic factors [2, 5, 6]. Climatic changes have been found to affect the amount of oxygen in the CIL layer, the position of the hydrogen sulfide boundary in the density field (and therefore the volume of the oxic waters of the Sea), and the amount of nutrients in the upper layer available for OM synthesis. Recent studies have revealed that interannual and interdecadal changes in large rivers influence the north-western region [7] and the redox layer [8, 9] and in particular, the inputs of phosphate and nitrate from Danube river had decreased in the last 20 years.

On the other hand, the situation in the other coastal regions, in particular the north-east coast is less well known. The seasonal variability of nutrients in the shelf area is supposed to be much more complex because of the influence of coastal influx, which is subjected to meteorological events and anthropogenic pollution. The coastal regions undergo higher levels of eutrophication that can result in hypoxia and anoxia [10].

The goal of this work was to study the peculiarities of the seasonal and interannual variability of the chemical characteristics of coastal waters of the north-eastern Black Sea, not influenced by the large rivers, in which the study of local points of pollution (e.g. related to resort businesses) is easier.

2. Material and methods

In this study, we analyse the data gathered in the Gelendzhik bay, which is influenced by significant anthropogenic stress, and in the Golubaya bay, which is the open coastal region.

The Gelendzhik bay (with an average depth of about 12 m) hosts one of the largest resort centres of the Black Sea, the town of Gelendzhik, and is characterized by a restricted water exchange with the open sea. There are several small springs that flow into this bay after rains, and in addition the bay is influenced by the town's drainage-system flow. Exploitable vineyards are situated along the northern coast of this Bay. The Golubaya bay is less wide than Gelendzhik bay and less influenced by human activities but displays a larger water exchange with the Black Sea. This bay is influenced by a small river, the Ashamba, that dries up during the summer.

A sampling program had been initiated by the Southern Branch of Shirshov Institute of Oceanology, RAS (SB SIO RAS) on a weekly basis at the shore line area of Chernomorets beach (the Gelendzhik bay) and from the head of the pier in Golubaya bay (figure 1). Studies were carried out during a period from January 2001 to the summer of 2005. The list of parameters measured included temperature, dissolved oxygen, biological oxygen demand (BOD), alkalinity, pH, phosphate, organic phosphorus, silicates, nitrates, nitrites, ammonia nitrogen, urea, organic nitrogen, oil products, and heavy metals.

Sampling was carried out from the water surface with a plastic bucket. Analytical determinations were carried out by the Laboratory of Chemistry of SB SIO RAS in accordance with standard methods of hydrochemical determinations [5, 11].

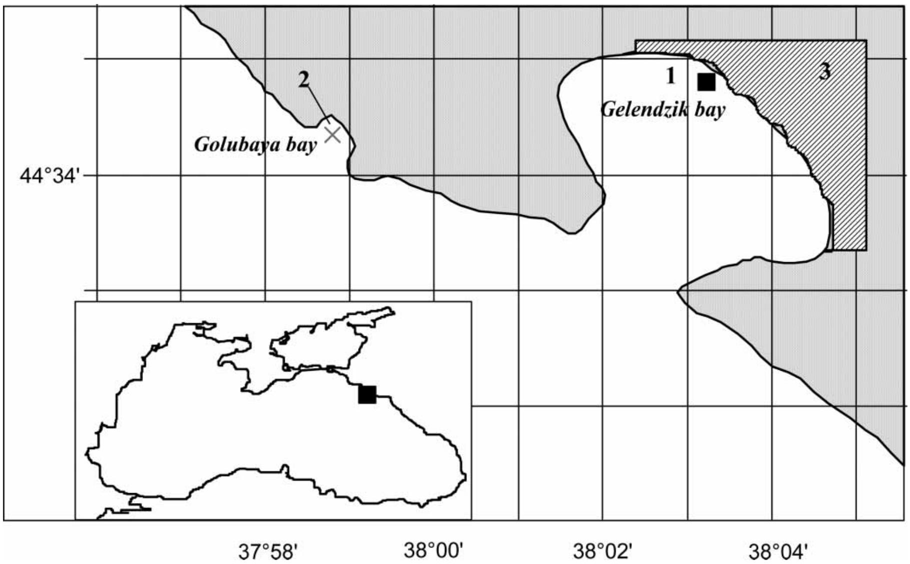

Figure 1. Position of the sampling points in the Gelendzhik (1) and Golubaya (2) bays and the town of Gelendzhik (3).

Dissolved oxygen analyses were performed using the classic Winkler method with a Jencons Digitrate automatic burette. In addition to a correction for the reagent blank, we also corrected for the oxygen content of the fixing reagents [5]. The accuracy of the Winkler technique is $0.02\,\mathrm{ml\,l^{-1}}$ (0.9 μM), and the detection limit is about $0.06\,\mathrm{ml\,l^{-1}}$ (2.7 μM).

pH was determined on the NBS scale with an 'I-500' pH meter (NPKF 'Aquilon', Russia). The precision was about 0.01 unit NBS.

The total alkalinity was determined in the coastal laboratory by direct titration with hydrochloric acid, according to Bruevich's modification [11]. The process of titration with constant venting with CO_2-free air to a pH of 5.45 was monitored using a glass electrode. The precision of this technique is about 1–2 $\mu\mathrm{eq\,kg^{-1}}$.

Phosphate was determined by the method based on that of Koroleff [12]. Absorbance was measured at 885 nm in a 50-mm cell.

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

Nitrite was measured with sulfanilamide and *N*-1-naphthylethylendiamine dihydrochloride. Nitrate was converted to nitrite using Cu–Cd columns. Absorbance was measured at 543 nm in a 50-mm cell and from 2004 nitrate was measured with AA 'Bran-Luebbe'.

Ammonium was determined by the phenol-hypochlorite reaction. The reagents (phenol and hypochlorite solutions) were added immediately after sampling in order to avoid contamination of the NH_3 from the air inside laboratory [11].

Urea was measured photometrically with diacetylmonooxim and semicarbazid [7].

Total phosphorus was determined by digestion with sodium persulfate in a water bath at 100 °C. The Valderrama technique (digestion in an autoclave) was used for analysis of total nitrogen. Organic forms of phosphorus and nitrogen were estimated as the difference between the total and inorganic (phosphate for phosphorus and nitrate, nitrate and ammonium for nitrogen).

Biochemical Oxygen Demand (BOD) was determined according to Bordovsky and Chernyakova [11] after exposure for 5 d.

The voltammetric technique was used to determine the copper and lead content. The analyses were performed in the preliminary acidic (4.4 ml HCl for 200 ml) and filtered (0.45 μm) samples of water with a voltammometer AKV-07 (produced by NPKF 'Aquilon', Russia).

Oil products and surfactants were measured with a FLUORAT-02M fluorimeter (LOMO, Russia), following the manufacturer's recommendations.

3. Results

3.1 *Temperature*

Seasonal variability of temperature in the Gelendzhik and Golubaya bays was characterized by a minimum (7–8 °C) in January to March and a maximum (24–26 °C) in July to August (figure 2) in 2005. The water temperature in the Gelendzhik bay was characterized by higher values (about 0.5–1.0 °C) compared with the Golubaya from March to July, most likely due to a greater degree of warming because of the higher degree of isolation of the Gelendzhik bay and increased impact of the shore. From September to December, in contrast, the temperature in the Gelendzhik Bay was lower, probably due to more intensive cooling in the isolated Gelendzhik Bay.

The distributions of surface water temperature in the Gelendzhik bay in both winter and summer were characterized by a spotted type of meso- and micro structure, associated with

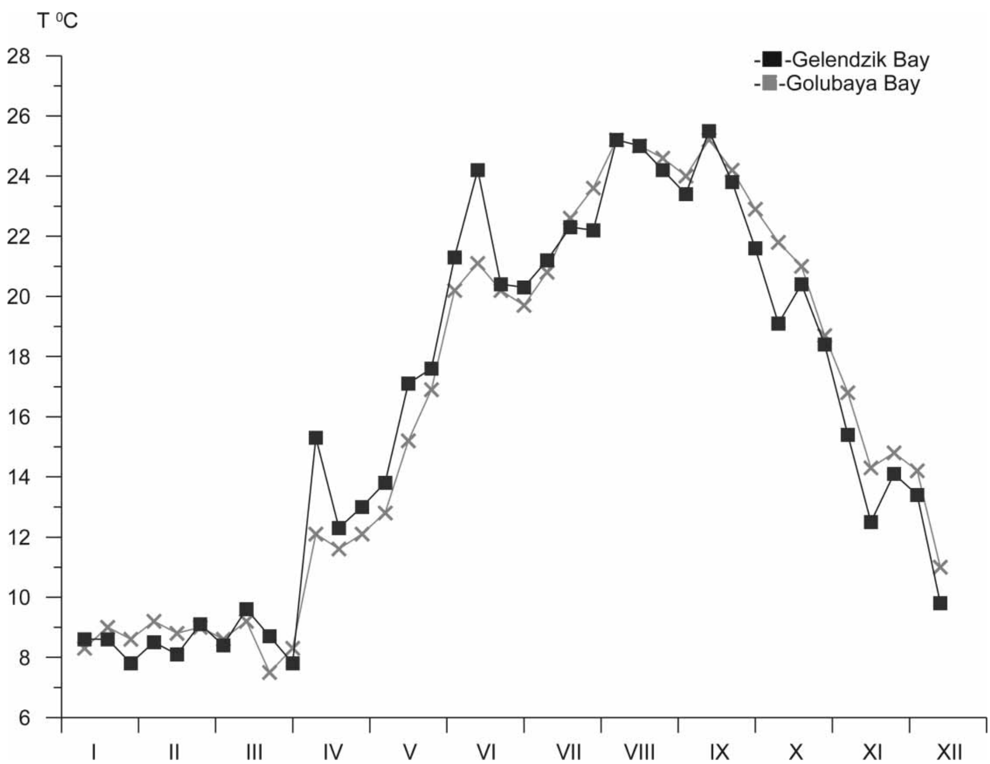

Figure 2. Seasonal variability of temperature in Gelendzhik and Golubaya bays.

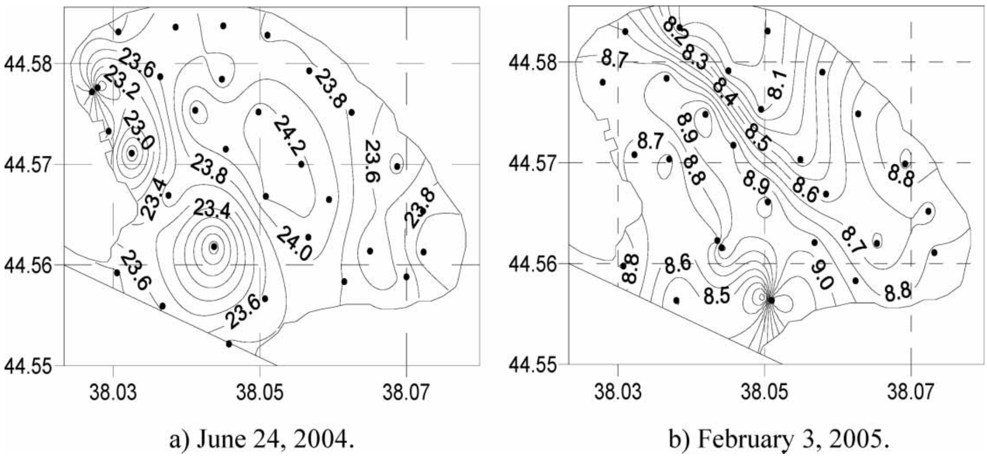

Figure 3. Distribution of temperature (°C) in the Gelendzhik bay in summer (a) 24 June 2004 and winter (b) February 2005.

the influence of weather, absence or presence of Black Sea rim current coastal anticyclonic eddies near the bays, and the coastal influx. In some cases, the coastal and marine waters were separated by a frontal zone oriented according to the wind direction. Examples of the observed winter and summer hydrophysical structures are shown in figure 3. A similar spatial structure was typical for the distribution of all chemical variables. Therefore, the weekly changes of concentrations analysed below may reflect both temporal and spatial variability.

3.2 *Dissolved oxygen*

Observations of seasonal variability of oxygen had shown that its maximal values in both bays occurred during the winter–spring period (figures 4 and 5), because of the greater degree of solubility of oxygen and slowed decay of OM at low temperature and the spring phytoplankton bloom. The summer was characterized by decreased oxygen concentrations, related to an intensification of OM decay and respiration of living organisms at higher temperatures. The amplitude of seasonal variability of oxygen was greater in Gelendzhik (320 μM in 2003) than in Golbaya bay. Brief decreases of oxygen concentration, most intensive in 2003, were related to a period of showery rains, when the bay was subject to intensive shore outflow. In the Golubaya bay, these increases were smoother, most likely due to relatively low concentrations of nutrients in the waters of Ashamba river flowing into the Golubaya bay, compared with streams of the Gelendzhik bay. Also, the Golubaya bay is more open for water exchange.

3.3 *Phosphate*

During the winter period, when consumption of phosphate was insignificant, the concentration fluctuated from 0.1 to 1 μM (figures 4 and 5). Exhaustion of phosphate in the summer period in 2000 and 2003 coincides with such seasonal features as a lack of precipitation and absence of intensive mixing. Only by the end of the summer period did the concentration of phosphates in both bays increase. While the seasonal trend in both bays consisted of many concentration peaks, they are more pronounced in the Gelendzhik bay. Phosphate background was significantly higher here as well, most likely a result of a large quantity of organics in the intake of the Gelendzhik bay and hindered water exchange. The permanent presence of phosphate in the Gelendzhik bay, as distinct from Golubaya, could not limit the development of photosynthesis,

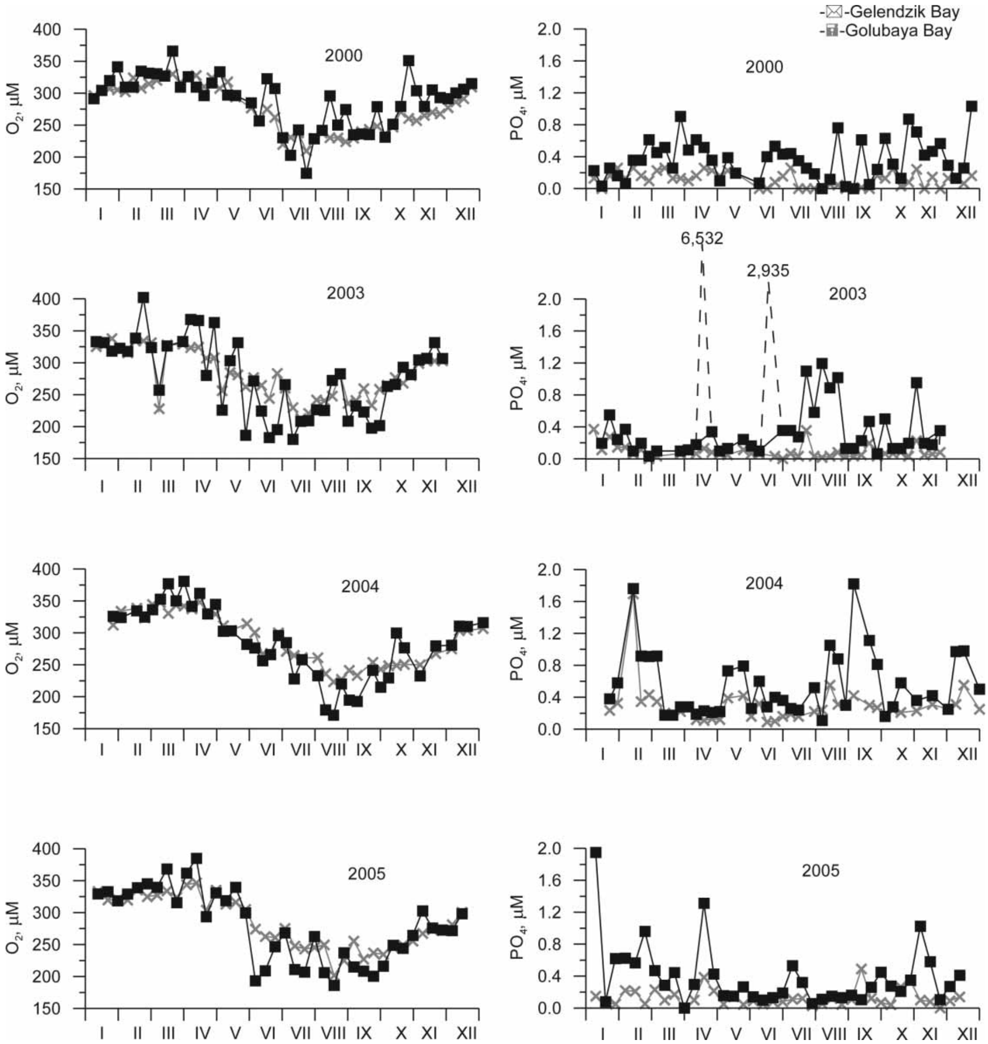

Figure 4. Seasonal variability of oxygen and phosphate in Gelendzhik and Golubaya bays in 2000–2005.

leading later to processes of intensive eutrophication. Analysis of the interannual distribution of phosphorus shows a gradual increase in concentrations. Abnormal peaks (e.g. 6.5 μM) of mineral phosphorus were observed in May and August 2003. In the same periods, the contents of nitrate (more than 18 μM) and ammonia (more than 24 μM) were very high. Such abnormal peaks are most likely the result of wastewater that pollutes the bay inflow, since at this time meteorological cataclysms take place, e.g. local floods and waterspouts damaging the coast. A comparison of phosphate concentrations in the summer period in 2004–2005 suggests a general tendency towards an increase in phosphate concentration from year to year.

3.4 *Inorganic nitrogen compounds*

As for oxygen and phosphate, the seasonal variability of all the nitrogen compounds was somewhat changeable, by the presence of many concentration peaks (figure 6).

The highest concentrations of nitrate (3–8 μM) in both bays were observed in the winter period, which is explained by the increase in coastal water influx due to rains and decrease

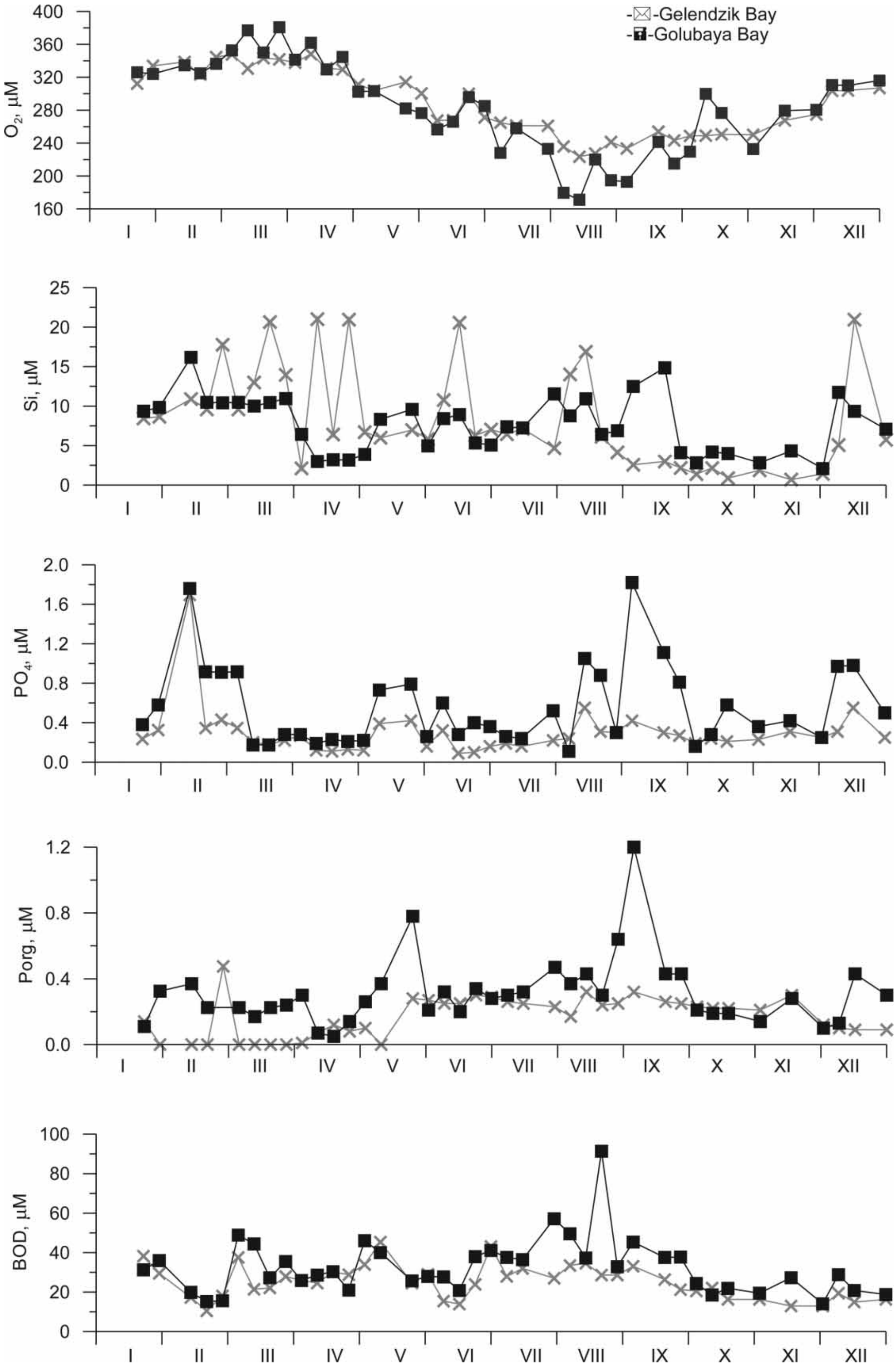

Figure 5. Seasonal variability of dissolved oxygen, silica, phosphate, organic phosphorus, and BOD in the Gelendzhik and Golubaya bays in 2004.

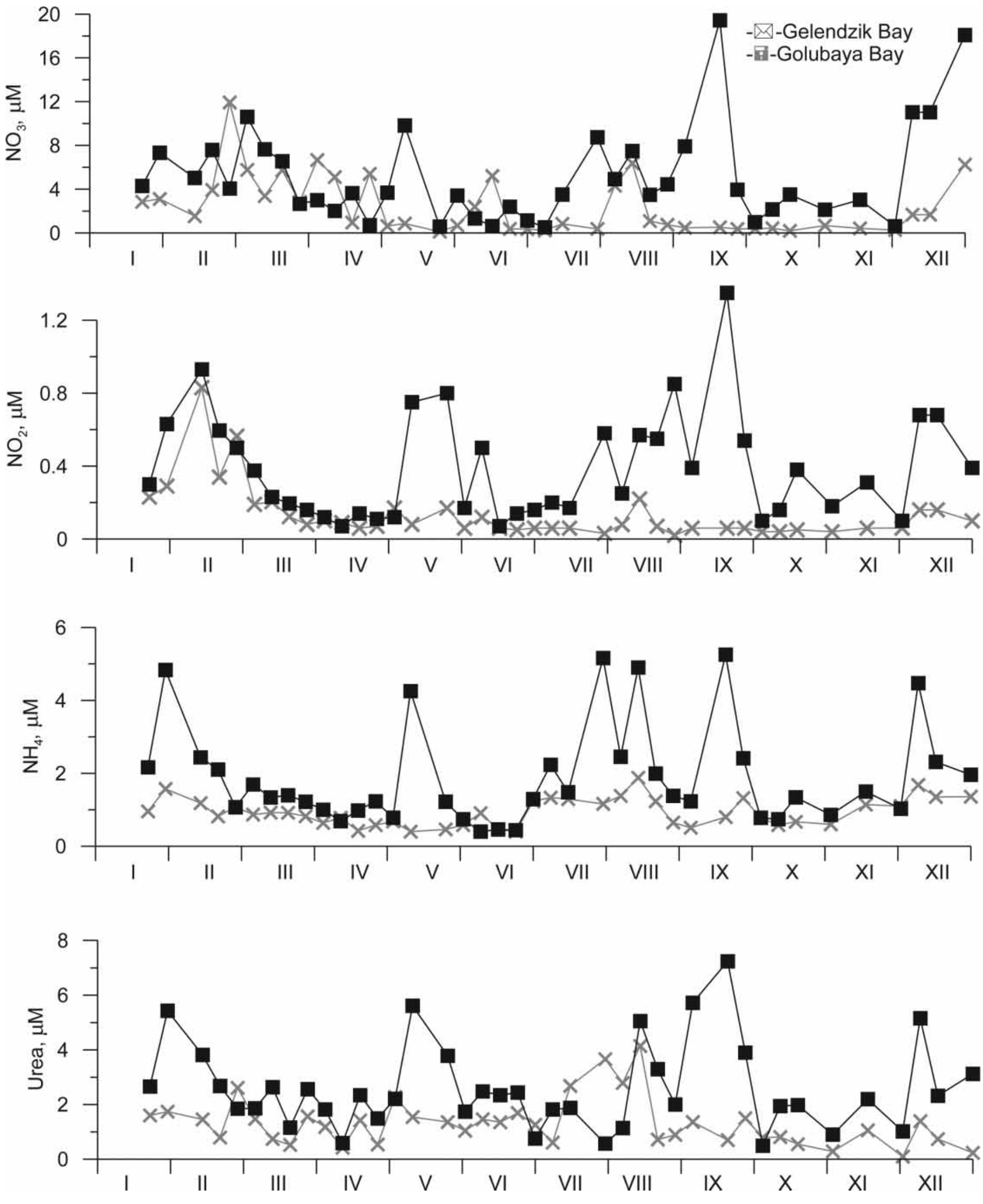

Figure 6. Seasonal variability of the nitrogen species in Gelendzhik and Golubaya bays in 2004 (nitrate, nitrite, ammonia, urea, organic nitrogen).

in phytoplankton activity. The background concentrations in other months of the year were lower, 0.1–4 μM.

In the Golubaya bay, the observed concentrations of nitrate decreased to 0.1–0.7 μM in July to September, while from the middle of February to the end of June, concentrations were significantly higher, and their variability was of a stepwise nature. A relatively small increase (up to 7.1 μM) in concentration was observed in 2004 from the end of September to October. A maximum was reached at the end of April. Concentrations in the Gelendzhik bay during July decreased as well, although they were still greater than those in the Golubaya bay. During stepwise increases in concentrations in the spring (beginning of April) and at the end of the summer-to-autumn period (end of July, September, October, and November) concentrations of this variable temporarily increased to 13–19 μM. These concentrations are abnormal even for nearshore surface waters and can be related only to shore outflow. Large peak values in the Gelendzhik bay compared with the Golubaya bay witness a significant pollution of this water mass with organic pollutants. Also, as in the previous year, concentration peaks of nitrate nitrogen fall in April, but as we observed in 2005, the distribution of this parameter in the bays varies significantly. Practically every time, the nitrate concentration in the surface waters of the Golubaya bay was less than in the Gelendzhik bay.

The type of nitrite variation (NO_2) in both bays was more or less similar to a period from January to June (stepwise distribution: 0.1–0.5 μM in the Golubaya bay and 0.2–0.75 μM in the Gelendzhik). Concentrations are minimal in the Golubaya bay (0.07 μM) in July to August, while in the Gelendzhik bay, on the contrary, an increase is observed (up to 0.78 μM). Maximal concentrations concur with nitrate peaks (maximum at the end of October, 1.43 μM). During 2004, the summer maximum of nitrates drew close to 1 μM, while during the summer months of this year, the maximum concentrations were 0.7 μM. Rather high concentrations of nitrites in the Gelendzhik bay prove the active mineralization of organic matter.

Ammonia nitrogen was characterized by a similar variability (the winter maximum gradually gives way to the spring decrease in concentrations). In both bays, there were minimal concentrations in the middle of April (about 0.55 μM), in the first half of the summer, and in the autumn (more than 0.08 μM). Differences between two bays, in general, coincide with the amplitude difference of distribution for other forms of nitrogen. The annual trend of ammonia nitrogen had no significant changes (figure 6).

3.5 *Silicate*

During the cold time of the year, values of silicate (figure 5) are increased and on average make up to 9–20 μM, while in the summer months and at the beginning of the autumn, decreases are observed (down to 0 μM in the Golubaya bay and to 0.5 μM in the Gelendzhik bay). The seasonal trend of silicate is different in both bays as well. It may be worth noting that in the Golubaya bay, several maxima, not observed in the Gelendzhik bay, can be distinguished (from December to April). While in the Gelendzhik bay, several maxima are observed for August to October that are not noticed in the Golubaya. The latter peaks coincide with the maxima of nutrients, primarily for phosphate and all inorganic nitrogen species.

3.6 *Organic forms of nutrients*

The annual variability of urea (with background concentrations of 1–3 μM and peak concentrations of about 5–8 μM) was very similar to that of nitrite and ammonia (figure 4). All the peaks of maximum concentrations were found in the urea variability curves.

Meanwhile, the seasonal variability of organic nitrogen did not reproduce a peak of increased concentrations in the late summer. The maximum values for organic nitrogen were reached in the winter (about 25 μM in the Golubaya bay and 45 μM in the Gelendzhik bay), while during the rest of the year the values lay within the range of 5–20 μM in both bays.

In contrast to this, in the Gelendzhik bay organic phosphorus showed the largest maximum in August to September (1.3 μM compared with 0.2–0.4 μM in other periods of the year). The content of organic phosphorus in the Golubaya bay was significantly lower (0–0.1 μM), especially in June to October.

From the BOD variability, one can mark out a period from June to September that was characterized by larger values (20–40 μM in the Golubaya and 30–90 μM in the Gelendzhik bay) compared with the background values (10–40 μM). The peaks of increase in concentrations in inorganic phosphorus and nitrogen species clearly seen during the cold part of the year were not well defined in the BOD variability.

3.7 *Heavy metals, oil products, and surfactants*

During observations from July 2004 to January 2005, we found that the average concentrations of copper in the Gelendzhik bay (4.1 $\mu g\, l^{-1}$) are half as much again as those of the Golubaya bay (2.8 $\mu g\, l^{-1}$). In November 2004, this excess was 7.8 $\mu g\, l^{-1}$. The average lead concentrations in the Gelendzhik bay (5.2 $\mu g\, l^{-1}$) were 2.5-fold higher than in the Golubaya bay (2.2 $\mu g\, l^{-1}$). The difference in metal concentrations in the observed bodies of water is a result of anthropogenic pollution and stress in the area of the Gelendzhik bay.

There are similar patterns with pollution centres located mostly in the area of the Gelendzhik bay, associated with oil products and surface-active material. Maximal concentrations of oil products were reported during the summer in the south-east and north-west areas of the bay (1–3 $\mu g\, l^{-1}$ compared with background concentrations of 0.4–0.8 $\mu g\, l^{-1}$) due to industrial and municipal sewage [1, 10]. Also the concentrations of surface-active material are comparable (4-6-4 $\mu g\, l^{-1}$ and 0.37–0.39 $\mu g\, l^{-1}$ for cation and anion surfactants correspondingly, compared with background concentrations of 2–4 $\mu g\, l^{-1}$ and 0.36–0.37 $\mu g\, l^{-1}$). The major sources of pesticides, and thus heavy metals, are the vast vineyard areas (along the northern coast of the Gelendzhik bay) [1]. As a result of recent reductions in areas of exploitable vineyards, zinc and lead concentrations in 2005 have decreased also.

4. Discussion

The seasonal variability of all the parameters we studied was accompanied by low timescale changes, related to hydrophysical and meteorological factors that led to the formation of a spotted-type meso- and microstructure (figure 2). From this point of view, we should consider abrupt changes in concentrations of practically all the observed parameters during all the year.

Silicate appeared to be a good tracer of fresh coastal origin water, and the annual variability of this parameter allowed us to outline the events of an intensive coastal influx (figure 5). These events, as peaks of increased concentrations, are more frequent in the cold period of year and are better pronounced in the Golubaya bay, because of the influence of Ashamba river. Only in August were the silicate concentrations in the Gelendzhik bay significantly higher.

The results of observations for all sets of organic and inorganic nutrients in 2004 allowed us to mark out the periods of peaks of increased concentrations in February, May, July to August, and September.

The most pronounced peak in July to August of 2004 in the Gelendzhik bay was first observed in BOD and organic nitrogen (to a lesser degree), then in organic phosphorus and urea, and then in concentrations of phosphate, ammonia, nitrite, and nitrate. This consequence corresponds to the general hypothesis of mineralization of organic matter. During these days, we also observed the year-minimal concentrations of dissolved oxygen (less than 200 μM, figures 4 and 5). Probably, these data reflect the process of mineralization of excessive organic matter that entered the water of the bay.

The seasonal variabilities in Redfield ratios are presented in figure 7. The year-averaged values of the N/P ratio (calculated as $(NO_3 + NO_2 + NH_4)/PO_4$) were close to theoretical values (correspondingly 15.2 and 16.8 in the Golubaya and Gelendzhik bays). However, the N/P values were higher during the cold period of the year and less than theoretical values in the summer. The absolute maximum was reached in the Gelendzhik bay in August (>60), when

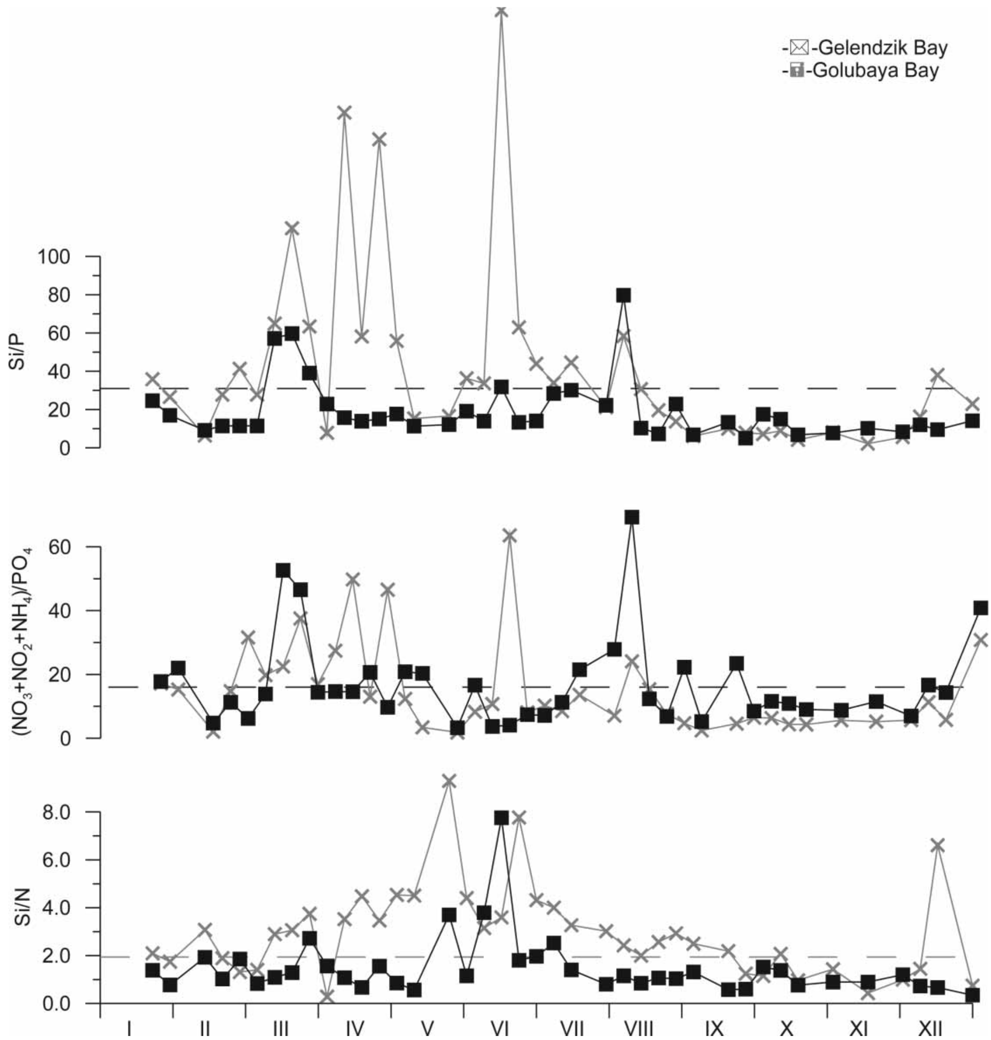

Figure 7. Seasonal variability of Si/P, N/P and Si/N ratios in Gelendzhik and Golubaya bays in 2004. Theoretical values are shown as dotted lines.

a peak of abnormally high concentrations of organic and inorganic nutrients was observed. The absolute values of N/P ratio were less than 7 from August to November in the Golubaya bay and during shorter periods in the Gelendzhik bay. Usually, this value is considered as a minimum value for the beginning of nitrogen fixation [2].

Year-averaged Si/P values were significantly different in the Gelendzhik (19) and Golubaya (41) bays and very much different from the theoretical values (31). The same picture was observed for the Si/N ratio that was lower in the Gelendzhik bay (1.5) and higher in the Golubaya bay (2.9) than the theoretical ratio (1.9).

This indicates that the water that flows into the Gelendzhik bay is significantly enriched in phosphorus and nitrogen compounds in comparison with the Golubaya bay.

It can be concluded that the seasonal variability in hydrochemical parameters in the coastal regions of the north-eastern part of the Black Sea is characterized by distinct changes in the amount of organic and inorganic nutrients. Large concentrations of nitrites and decreases in oxygen content, especially in the Gelendzhik bay, demonstrated active OM mineralization reactions. Spring–summer development of autotrophic organisms does not lead to the exhaustion of nitrogen or silicon. Exhaustion of phosphate in the Golubaya bay during summer is possible if a lack of precipitation and intensive mixing occurs, and photosynthesis is limited by this element (concentrations are lower than $0.15\ \mu M\ PO_4$). Studies in the Romanian coastal waters also revealed that frequent cases of phosphate reduction below the detection limit during the summer season grant phosphorus the role of limiting factor of primary production in the marine coastal areas [13].

An interannual variability was clearly seen during our observations. The general tendency towards an increase in phosphorus and nitrogen content associated with eutrophication was accompanied by the influence of meteorological conditions, e.g. waterspouts in 2003. The increase in ammonia forms at and even above the level of nitrates also represents a peculiarity of the Romanian coastal waters in the last decade [13]. Our estimates of urea concentration correspond to those observed in the coastal water of such regions of the World as the Baltic Sea, South Africa, Korea, but less than those in Chesapeake Bay, for instance [6].

We suppose that the results of our investigation in the Gelendzhik and Golubaya bay can be representative of a larger area as the north-eastern coast of the Black Sea is characterised by similar anthropogenic activities. This is the primary area for resort businesses, resulting in sources of pollutants at spots directly on the coast. The hydrophysical structure is also similar: the Black Sea rim current forms antycyclonic eddies that influence the exchange of coastal and marine waters and the appearance of small-scale temporal and spatial changes [14].

5. Conclusions

The number of investigations on hydrology and nutrients along the water column in the Gelendzhik and Golubaya bay has largely increased in the last few years. Various natural and unique recreational resources of this region are very important. Observations of the dynamics of hydrochemical characteristics in the relatively clean Golubaya bay and anthropogenically polluted Gelendzhik bay allows prompt and adequate estimation of the ecological conditions in the north-eastern sector of the Black Sea. Our results on the seasonal variability of nutrients suggest that Golubaya bay is a typical region of the Black Sea not affected by human activities, whereas the Gelendzhik bay represents a region strongly influenced by anthropogenic activities.

The Gelendzhik bay in its different parts is characterized by a strong variability of concentrations of hydrochemical parameters. Above all, it relates to a complex structure caused by the impact of wind. Parts of the bay filled with nearshore and sea waters are clearly different from each other. In the Gelendzhik bay, due to the limited water exchange with the open sea and the increase of human activities. The seasonal variation of the physical-chemical parameters suggests that:

- The variability of temperature during the autumn–winter period is characterized by brief fluctuations with increasing amplitude in comparison with the Golubaya bay and greater decreases in temperature.
- On the basis of Si/P and Si/N ratio analysis, it was shown that the Gelendzhik bay waters are significantly enriched with nitrogen and phosphorus compounds.
- Unlike the Golubaya bay, phosphates are always present in the water of the Gelendzhik bay, and development of photosynthesis is not limited by nutrients only. It may lead to processes of intensive eutrophication.
- It seems that the features of seasonal nutrient variability in the Gelendzhik bay (increased concentrations and a pronounced summer–autumn maximum) are caused by human

impact—the outflow of nutrients with shore input and recreational activities during the summer holiday season.

The conclusions obtained from our study testify that the pollution from local spots of the coasts of the Black Sea, primarily associated with eutrophication, can play a large role in the nutrient balance of the sea and affect its ecological state.

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