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Original paper

Variability of Parameters of the Carbonate System of the Northern Black Sea Surface Waters During Coccolithophorid Blooms

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Abstract
The paper studies dynamics of carbonate system parameters during the spring-summer coccolithophores bloom using data on temperature, salinity, carbonate system parameters (CO_2, pH and alkalinity) and backscattering index (b_{bp}(550), m^{-1}) for the northern Black Sea surface waters during the 127th and 131st cruises of R/V *Professor Vodyanitsky*. Within the studied periods (June 2023, May–June 2024) coccolithophores concentrations exceeded 1.00 million cells/L, while high pCO_2 (mean 486 ± 18 µatm) was also observed. The surface water layer was oversaturated with CO_2 compared to the atmosphere, with a mean water CO_2 supersaturation of 14% (58 µatm). However, no pronounced relationship was found between coccolith concentrations and pCO_2, pH and alkalinity values, which may indicate a non-core contribution of the bloom to CO_2 concentrations in the surface waters. It was found that even during the coccolithophores blooming period, temperature is the key factor determining the surface waters pCO_2. The spatial distribution of suspended matter concentration represented by coccoliths was determined by water dynamics and current structure in the Black Sea.

Keywords: carbonate system, carbon dioxide partial pressure, coccolithophores, Black Sea

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Изменчивость параметров карбонатной системы поверхностного слоя вод северной части Черного моря в период «цветения» кокколитофорид

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Аннотация
Рассмотрена динамика параметров карбонатной системы в период весенне-летнего «цветения» кокколитофорид с использованием данных о температуре и солености, параметров карбонатной системы (CO_2, pH и щелочности) и показателя рассеяния назад взвесью ($b_{bp}(550)$, м$^{-1}$) для поверхностного слоя вод в северной части Черного моря в 127-м и 131-м рейсах НИС «Профессор Водяницкий». В исследуемые периоды (июнь 2023 г., май – июнь 2024 г.) концентрации кокколитофорид превышали 1.00 млн кл/л, также отмечено высокое значение pCO_2 (среднее 486 ± 18 мкатм). Поверхностный слой вод был пересыщен CO_2 по сравнению с атмосферой, среднее пересыщение вод CO_2 составило 14 % (58 мкатм). Однако выявлено отсутствие выраженной связи между концентрациями кокколитов и величинами pCO_2, pH и щелочности, что может указывать на неосновной вклад «цветения» в концентрации CO_2 в поверхностном слое вод. Установлено, что даже в период «цветения» кокколитофорид ключевым фактором, определяющим величину pCO_2 поверхностного слоя вод, является температура воды. При этом пространственное распределение концентрации взвеси, представленной кокколитами, определялось динамикой вод и структурой течений в Черном море.

Ключевые слова: карбонатная система, парциальное давление углекислого газа, кокколитофориды, Черное море

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Introduction

The continuous increase in atmospheric CO_2 concentrations and its further absorption by ocean waters, which are one of the main natural CO_2 sinks, has led to a decrease in the buffer capacity of those waters and a change in the hydrochemical characteristics of the World Ocean. In particular, there has been an increase in the concentration of hydrogen ions in seawater [1]. According to [2–4], over the past 250 years, the pH of surface ocean waters has decreased by approximately 0.11, which corresponds to a 30–40% increase in the concentration of hydrogen ions. In addition, there has been a decrease in oxygen concentrations and the spread of oxygen-deficient zones in the waters of the World Ocean [5, 6]. At the same time, the increase in CO_2 concentrations in water and the atmosphere, as well as changes in the hydrochemical characteristics of the ocean, have a negative impact on biological organisms, including those with carbonate skeletons [2–4, 7].

In the waters of the World Ocean, the main reserve of dissolved carbon is in inorganic form and amounts to about 38 Gt C (1 Gt = 10^9 t) [1]. The atmosphere contains significantly less carbon, and significant carbon fluxes are formed at the boundary between the surface waters and the sea-surface atmosphere [1, 7, 8]. As a result, at the boundary with the atmosphere, as well as between the surface and deeper waters, various forms of carbon, including CO_2, are redistributed [2, 3], leading to changes in its concentrations.

The exchange of CO_2 between water and the atmosphere occurs due to the diffusion of gaseous CO_2 across the phase boundary, with the total exchange being proportional to the difference in partial pressures of gaseous CO_2 in the air and seawater. Thus, it is closely related to the solubility of CO_2 in seawater (K_0), which determines the ratio of CO_2 in seawater to the partial pressure of CO_2 in the gas phase [5] at chemical equilibrium:

$$K_0 = [CO_2]_{sw}/pCO_{2,\,sw}.$$

In addition to physical transport and temperature contributions, the dynamics of CO_2 concentration in the surface waters is determined by biological processes as well as bya complex set of abiotic chemical reactions [2–4].

The combination of CO_2 dissolution and carbonic acid dissociation products forms a carbonate system, which can be described by a system of equilibria [1, 2, 4]:

$$CO_2\ (g) \leftrightarrow CO_2\ (aq) \leftrightarrow CO_2\ (aq) + H_2O \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}, \quad (1)$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3\ (s). \quad (2)$$

Hydrogen ions (H^+) (or pH) are one of the main components describing the state of the carbonate system; their concentration is closely related to the concentration of CO_2. An increase in CO_2 concentration is accompanied by an increase in the concentration of hydrogen ions and a decrease in pH:

$$pH = -\lg a_{H+}, \text{ or, conventionally, } pH \approx -\lg [H^+]. \quad (3)$$

Another important parameter of the carbonate system – one not directly dependent on CO_2 concentration – is total alkalinity (Alk), which is typically defined as the excess of proton acceptors (bases formed from weak acids) over proton donors measured relative to a reference point; formally, the acid dissociation constant pK_a = 4.5 corresponds approximately to the equivalence point of H_2CO_3 in seawater. In aerobic ocean waters, carbonate alkalinity constitutes up to 96–99% of the total alkaline reserve [9], which is expressed as:

$$Alk = [HCO_3^-] + 2[CO_3^{2-}]. \quad (4)$$

Carbonate alkalinity determines the buffering capacity of the system, and the dissolution of CO_2 primarily causes a shift in chemical equilibrium, altering the ratio of inorganic forms of carbon, while the concentration of total dissolved inorganic carbon remains nearly constant.

The primary chemical and biological processes governing the dynamics of the carbonate system in the water column are those involving organic matter – namely, its production and destruction:

$$6\,CO_2 + 6\,H_2O \leftrightarrow 6\,H^+ + 6\,HCO_3^- \leftrightarrow C_6\,H_{12}\,O_6 + 6\,O_2. \quad (5)$$

as well as the processes of carbonate formation/dissolution:

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-. \quad (6)$$

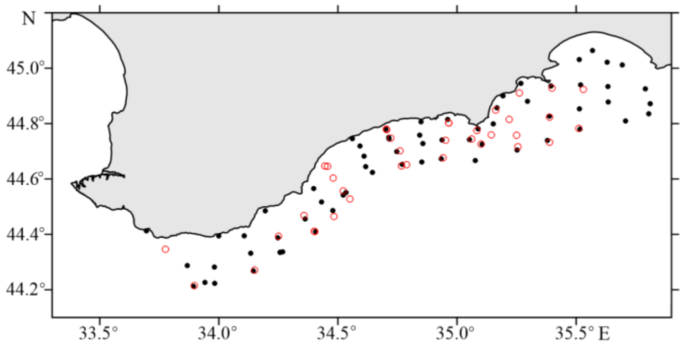
One group of marine phytoplankton involved in carbonate processes are coccolithophores. Their cells are covered with layers of plates –coccoliths – formed from calcium carbonate. The most abundant species in the Black Sea is *Emiliania huxley*, which can account for up to 99% of the total coccolithophore population. Cells of this species can shed coccoliths, a process in which the ratio of detached coccoliths to cells can reach 400:1 [11, 12]. Obviously, by possessing carbonate skeletons, coccolithophores during intense blooms (when their population exceeds 1 million cells/L [13]), significantly affect the optical and thermal characteristics of the surface waters of the World Ocean. The coccoliths cause strong light scattering, which reduces water transparency, and increase the ocean surface albedo, thereby reducing the insolation of the surface water layer [14]. An increase in backward scattering leads to higher values of upwelling sea radiance and the radiance coefficient [12]. This property enables the estimation of coccolithophore cell abundance, detached coccolith concentration, and overall carbonate concentration through the remote sensing of upwelling radiance [15]. The rate of carbonate formation, and consequently the rate of CO_2 drawdown, can increase or decrease based on limiting factors such as light intensity, temperature, nutrient concentrations, and carbon dioxide availability [16, 17].

Thus, by participating in the carbon cycle, these algae influence the oceanic CO_2 budget. However, accounting for all relevant factors and establishing a direct link between coccolithophore abundance/biomass and their carbon fixation rate remains highly challenging [18].

The study aims to evaluate the relationship between carbonate system parameters and coccolithophore blooms in the late spring. To this end, we investigate the spatiotemporal dynamics of temperature, salinity, carbonate system parameters (CO_2, pH, and alkalinity), and backscattering coefficient ($b_{bp}(550)$, m^{-1}) in the surface layer of the northern Black Sea.

Materials and methods

The data were obtained during the 127th (June 14, 2023–July 7, 2023) and 131st (May 27, 2023–June 21, 2024) cruises of R/V *Professor Vodyanitsky* off the southeastern coast of Crimea (Fig. 1).



F i g . 1 . The scheme of stations of points where the carbonate system parameters and optical characteristics were determined. The red circles stand for stations surveyed in the 127th cruise of R/V *Professor Vodyanitsky*, the black ones stand for those surveyed in the 131st cruise

The temperature and salinity of the surface water layer were measured using Sea-Bird 911plus CTD or IDRONAUT OCEAN SEVEN 320 PlusM sounding complexes; at shallow stations (depth less than 50 m), a SeaSun CTD48M hydrological CTD probe was used.

Water samples were collected from a depth of 1.5–3.0 m using a submersible pump. Atmospheric air was collected at a height of 10 m above sea level, ensuring the absence of local CO_2 sources.

CO_2 concentration was determined using a LI-7000 infrared analyzer with a CO_2 concentration range of 0–3000 μmol/mol. A special module (equilibrator) was used to determine the CO_2 concentration in water, ensuring contact between the analyzed water and air to achieve equilibrium pCO_2 in the gas phase.

The device was calibrated using argon (volume fraction of CO_2 = 0 μmol/mol) and a calibration mixture with a CO_2 concentration of 440 μmol/mol. The measurement uncertainty of this method is 1% [19]. Argon was used as the carrier gas.

The pH value was measured using I-160 and I-160MP ionometers calibrated on the NBS scale with buffer solutions [20]. Total alkalinity was determined by direct titration with potentiometric termination, titrating 50 ml of seawater with a 0.02M [1)] solution of hydrochloric acid. The titration was performed using a high-precision Metrohm Dosimat 765 piston burette, and the endpoint was determined with a Hanna HI-2215 pH meter. All measurements were made according to the established methodology [2)].

[1)] Bordovsky, O.K., ed., 1978. [*Methods of Hydrochemical Research of the Ocean*]. Moscow: Nauka, 267 p. (in Russian).

[2)] Dickson, A.G. and Goyet, C., eds., 1994. *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water. Version 2.* Oak Ridge, Tennessee: DOE, 187 p. (ORNL/CDIAC-74).

Optical characteristics

The backscattering coefficient at a wavelength of 550 nm ($b_{bp}(550)$, m^{-1}) was calculated based on data from measurements of the spectral reflectance coefficient of the water column in the visible range using a semi-analytical algorithm [21]. A spectrophotometer developed in the laboratory of the Department of Marine Optics and Biophysics of the FRC MHI was used to determine the reflectance coefficient [22]. The measurement methodology is consistent with NASA protocols for sub-satellite measurements [3)]. To convert backscattering to the number of separated coccoliths N_c (pcs/m^3), an empirical relationship from [23] was used:

$$b_{b_{\mathrm{cocc}}}(546) = 1.1 \cdot 10^{-13} N_c, \qquad (7)$$

where $b_{b_{\mathrm{cocc}}}(546)$ is the backscattering coefficient of a coccolith suspension at a wavelength of 546 nm.

Changes in scattering within 5 nm range are neglected in this work.

It should be noted that eq. (7) was derived from the Black Sea data in the 1990s; consequently, the coefficients may not be directly applicable today. As shown in [24], these coefficients can vary significantly over a few days in a single area, although the linear relationship itself remains consistent. Therefore, the concentrations of suspended coccoliths and coccolithophore cells reported here should be regarded as estimates accurate only to a coefficient. This coefficient is introduced for convenience, particularly as the water also contains terrigenous suspended matter, which is difficult to estimate precisely.

To calculate the number of cells N_{cocc} (million cells/liter), we used the formula from [25], which was also obtained based on data from 1996–1998:

$$N_{\mathrm{cocc}} = 160\, b_{bp}(555) - 0.32 \qquad R^2 = 0.82, \qquad (8)$$

where $b_{b_{\mathrm{cocc}}}(555)$ is the backscattering at a wavelength of 555 nm.

Results

According to the calculations, the backscattering coefficient $b_{bp}(550)$, during the late spring hydrological season ranged from 0.008 to 0.020 m^{-1} (in 2023) and from 0.004 to 0.021 m^{-1} (in 2024). In other seasons, values of 0.003–0.009 m^{-1} are typical for the Black Sea [26]. This indicates that suspended matter of coccolithophore origin contributed at least half of the total backscattering.

The calculated number of coccoliths and coccolithophore cells, derived using this parameter (following formulas (8) and (9) [23, 25]), is presented in Table 1. The ratio of cells to coccoliths at the measured scattering levels averaged approximately 88 and 94 in the 127th and 131st cruises, respectively. This result implies that the formulas assume a relationship between elevated backscattering and an increase in the number of detached coccoliths per cell.

[3)] Zibordi, G., Voss, K.J., Johnson, B.C. and Mueller, J.L., 2019. *Ocean Optics and Biogeochemistry Protocols for Satellite Ocean Colour Sensor Validation. Vol. 3: Protocols for Satellite Ocean Colour Data Validation: in situ Optical Radiometry*. Dartmouth, NS, Canada: IOCCG, 67 p. http://dx.doi.org/10.25607/OBP-691

T a b l e 1. Data of hydrological-hydrochemical and bio-optical characteristics of the Black Sea surface waters in late spring period

Parameter	127th cruise (14 June 2023–7 July 2023)*		131st cruise (27 May 2023–21 June 2024)	
	Average	Value range	Average	Value range
T, °C	23.0 ± 0.8	20.7–24.6	20.2 ± 1.5	16.8–25.7
S, ‰	17.88 ± 0.11	17.63–18.35	18.38 ± 0.14	17.99–18.62
$pCO_{2\ sea}$, μatm	480 ± 7	460–501	498 ± 23	449–546
$pCO_{2\ air}$, μatm	421 ± 5	411–441	435 ± 3	423–448
ΔpCO_2, μatm	59 ± 9	36–79	70 ± 31	15–117
N_{cocc}, million cells/L	1.39 ± 0.28	0.87–2.95	1.16 ± 0.55	0.32–2.97
$N_c \cdot 10^9$, pcs./m^3	112 ± 19	82–225	102 ± 37	44–226
Alk, mmol/L	3.224 ± 0.019	3.170–3.279	3.250 ± 0.033	3.137–3.296
pH	8.30 ± 0.02	8.25–8.37	8.27 ± 0.02	8.23–8.32

* The bio-optic and pCO_2 measurements were synchronized using the period of 14–26 June.

Table 1 presents the main hydrological characteristics and parameters of the carbonate system in the surface waters of the Black Sea, as measured during the 127th and 131st cruises of R/V *Professor Vodyanitsky*.

As shown in Table 1, coccolithophore blooms of varying intensity occurred during the study period, with an average coccolith concentration exceeding $100 \cdot 10^9$ pcs/m^3. In this study, we focus on the coccolith concentration (N_c) as the most reliable metric. This is because optical methods allow for its direct calculation, unlike the ratio of cells to coccoliths, which varies with the bloom stage. On average, this ratio was approximately 90 coccoliths per cell, as noted previously. Furthermore, we posit that coccoliths likely contribute more significantly to the CO_2 concentration than coccolithophore cells, in accordance with equation (6).

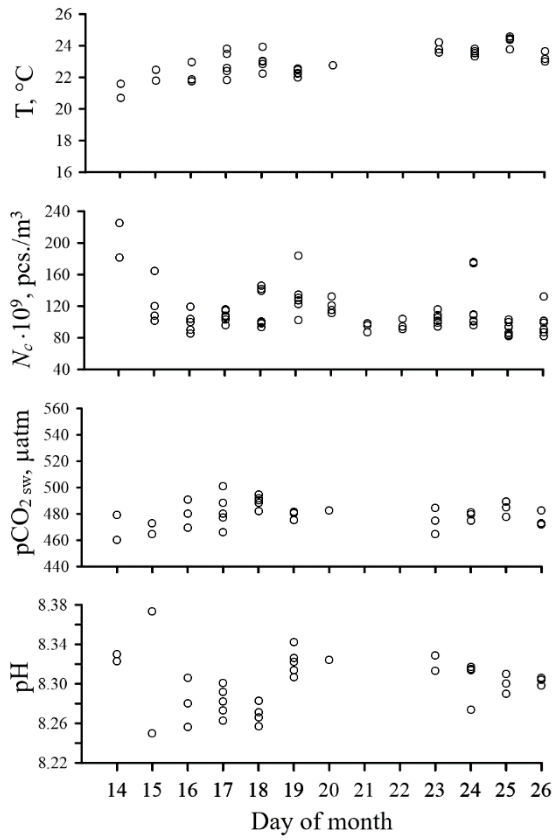
In all cases, the surface waters were oversaturated with CO_2 relative to the atmosphere (Table 1), indicating that it acted as a source of carbon dioxide to the atmosphere.

In June 2023, coccolithophore cell density reached 2.95 million cells/L, with a mean value of 1.39 million cells/L. The concentration of coccoliths averaged $112 \cdot 10^9$ pcs/m^3 (Table 1). The predominance of carbonate-based cells drove high pCO_2 levels – a result of CO_2 formation according to equation (6)) – leading to oversaturation of the surface waters with CO_2 relative to the atmosphere. The mean pCO_2 in the surface layer was 480 ± 7 µatm, ranging from 460 to 501 µatm. Elevated surface water temperatures (reaching 24.6°C with a mean of 23.0 ± 0.8°C) also contributed to the high pCO_2 values, as indicated by the average nature of the relationship between these parameters – the correlation coefficient of pCO_2 with temperature in the surface waters is 0.52.

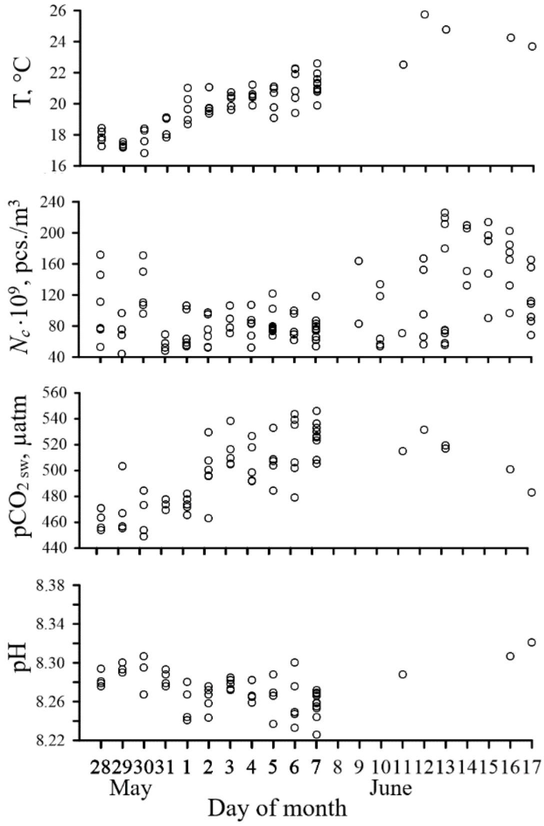
Fig. 2 presents the dynamics of the studied parameters during the 127th cruise. The principal trends observed include an increase in temperature and pCO_2 alongside a decrease in coccolith concentration.

Fig. 3 illustrates parameter changes at the end of the spring hydrological season of 2024 (late May–June). During this period, coccolithophore blooms occurred again, with cell densities averaging 1.16 million cells/L with a range of 0.32–2.96 million cells/L. The concentration of coccoliths averaged $102 \cdot 10^9$ pcs/m^3 (Table 1).

As expected, the surface waters were also significantly oversaturated with CO_2 compared to the atmosphere (the pCO_2 gradient could reach more than 100 µatm), and deep evasive conditions were observed in the surface waters of the Black Sea (CO_2 flux directed from water to the atmosphere). The average pCO_2 value in the surface layer of water was 498 µatm, with a pCO_2 range of 449 to 546 µatm (10%). The surface water temperature reached 20°C, with an increase in pCO_2 observed along this temperature rise, with maximum pCO_2 values corresponding



F i g. 2. Changes in pH, pCO_2, coccoliths and temperature of the surface waters in June 2023 (127th cruise of R/V *Professor Vodyanitsky*)



F i g . 3 . Dynamics of pH, pCO_2, coccoliths and temperature of the surface water layer in May–June 2024 (131st cruise of R/V *Professor Vodyanitsky*)

to the highest recorded temperatures (Fig. 3). The correlation coefficient between pCO_2 and surface water temperature was 0.68, indicating that temperature played a significant role in controlling the CO_2 concentration.

The maximum pCO_2 values in the water corresponded to the maximum temperatures of the surface layer of water (Fig. 3).

The pH values (Figs. 2, 3) and total alkalinity varied within narrow limits during the study periods. The average pH was 8.30 ± 0.02 in 2023 and 8.27 ± 0.02 in 2024 (Table 1), consistent with long-term observational data for this period.

Alkalinity exhibited minimal interannual variability, with values of 3.224 ± 0.019 in 2023 and 3.250 ± 0.033 in 2024. However, significant spatial heterogeneity was observed. This heterogeneity was primarily attributed to the influence of salinity (correlation coefficient 0.73), rather than to physicochemical processes associated with organic matter transformation or blooms.

Discussion

During the spring-summer phytoplankton bloom (late May–June), coccolithophores comprise the majority of the biomass (50–60%) [11, 13, 27]. Their development in this period is determined by a combination of abiotic factors – including light, temperature, and nutrient concentration – as well as biotic factors such as grazing by microzooplankton [11].

During the study perio ds, coccolithophore concentrations exceeded 1.0 million cells/L (Table 1), indicating a bloom state. High pCO_2 (average 486 ± 18 µatm) was also observed in the surface waters , with an average value of 442 ± 44 µatm (according to our data for 2015–2024, covering the period from March to December).

The average CO_2 oversaturation of the water relative to the atmosphere was 14% (58 μatm). It can be assumed that the high pCO_2 values were contributed to by coccolithophore bloom, which is accompanied by CO_2 production (equation (6), right to left). In addition, the increase in the sea surface temperature (Table 1) contributes to the shift of the carbonate equilibrium system towards CO_2 accumulation (equation (1)), as well as the intensification of organic matter destruction (equation (5), right to left) formed during the spring phytoplankton bloom.

In June 2023 (127th cruise of R/V *Professor Vodyanitsky*), the average coccolithophore content was 1.39 million cells/L, corresponding to $112 \cdot 10^9$ coccoliths/m^3 (Table 1). However, a decrease in the number of coccoliths was observed during the month (see Fig. 2). This may indicate the attenuation of the bloom and the gradual dissolution of carbonates, occurring according to the scheme of equation (6) (direction from left to right). This process should be accompanied by a decrease in CO_2 concentration and an increase in bicarbonate concentration, which in turn leads to an increase in pH; according to equations (4) and (6), alkalinity should also increase. However, no such trend was observed either spatially or seasonally: according to long-term observations for this region in the absence of coccolithophore blooms (March), the average alkalinity values are 3.281 ± 0.062 mmol/dm^3, and pH is 8.26 ± 0.09, which are statistically indistinguishable from their late spring values (Table 1). At the same time, the waters were significantly undersaturated with CO_2 compared to the atmosphere (average pCO_2 gradient = −46 ± 21 μatm). Thus, it can be assumed that this biological process is not decisive for the dynamics of CO_2 or for the dynamics of other hydrochemical characteristics (pH and alkalinity). This is also confirmed by correlation analysis data: the correlation coefficient between pCO_2 and the number of coccoliths is −0.22, indicating a weak relationship. The closest relationships were between pCO_2 and temperature (correlation coefficient 0.52) and pH (correlation coefficient −0.53).

At the end of May–June 2024, coccolithophore blooms were also observed (1.16 million cells/L; Table 1), corresponding to $102 \cdot 10^9$ coccoliths/m^3. Based on the dynamics of the studied hydrochemical and bio-optical parameters, two periods can be distinguished: May 28–June 7 and June 11–17 (Fig. 3). Thus, the change in the number of coccoliths indicates the development of the bloom during the voyage from May to June. In the first period, the average number of coccoliths was $(83 \pm 20) \times 10^9$ pcs/m^3, and in the second, $(131 \pm 49) \times 10^9$ pcs/m^3, with maximum values reaching 226×10^9 pcs/m^3.

In the first period, against the backdrop of rising sea surface temperatures and no visible trend toward an increase in the number of coccolith particles, there was an increase in pCO_2 and a decrease in the pH of the surface waters (Fig. 3). This may indicate the beginning of coccolith formation and gradual accumulation, accompanied by an increase in pCO_2 (equation (6) from right to left) and a decrease in pH (Fig. 3). The following period (June 11–17) is characterized by an increase in the number of coccoliths, a decrease in pCO_2, and an increase in pH (Fig. 3). The increase in the number of coccoliths and the concentration of coccolithophores (the average concentration during this period was 1.66 million cells/L) indicates blooming.

However, the gradual decrease in pCO_2 and increase in pH observed at this time most likely indicate the presence of an additional factor contributing to CO_2 binding. In this case, coccolith formation is not the main process determining the concentration of CO_2 and hydrogen ions.

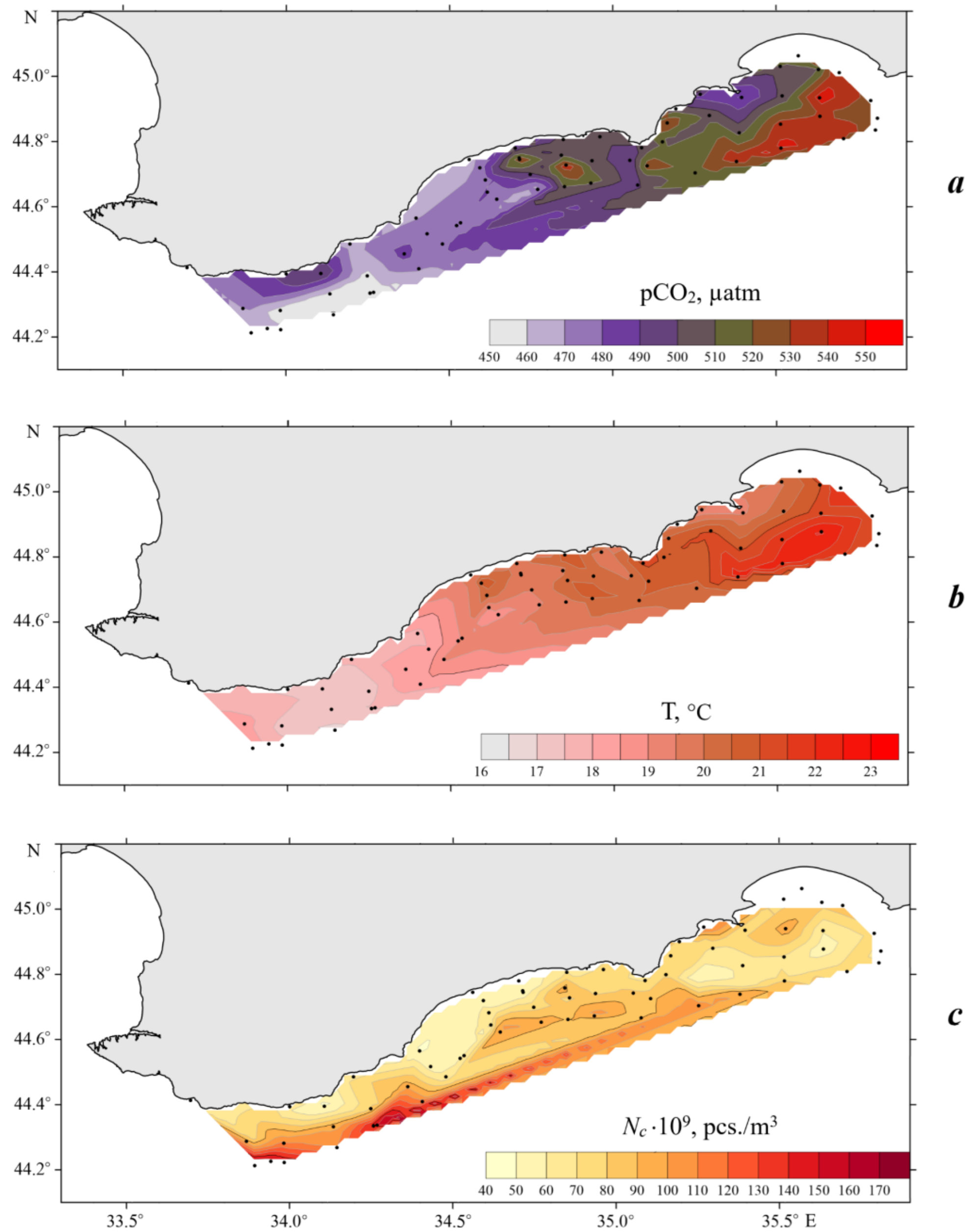
Thus, based on the dynamics of coccolith numbers in late spring, three periods can be distinguished: the beginning of the bloom and gradual accumulation of coccolithophores (late May – early June; average number of coccoliths $83 \cdot 10^9$ pcs/m^3), their accumulation and bloom outbreak during June (average number of coccoliths $131 \cdot 10^9$ pcs/m^3), and then the attenuation of the bloom by the end of June (average number of coccoliths $112 \cdot 10^9$ pcs/m^3) followed by carbonate decomposition (Fig. 2, 3).

We attempted to describe the dynamics of pCO_2 in terms of processes involving inorganic carbon and its transformation, as well as changes in the parameters of the carbonate system (equations (1), (2), (5), (6)). However, the lack of a statistically significant correlation between the number of coccolithophore cells (and the number of coccoliths) and either pCO_2 (correlation coefficients of −0.22 and −0.06 for cruises 127 and 131, respectively) or alkalinity (correlation coefficients of 0.05 and 0.09 for cruises 127 and 131, respectively), along with their moderate correlation with pH (correlation coefficients of 0.30 and 0.40 for 127th and 131st cruises, respectively), indicates that coccolithophores do not play a key role in the state of the carbonate system and its parameters.

The lack of correlation between coccolithophore concentration and alkalinity suggests that changes in alkalinity are not related to biological processes but are primarily determined by an abiotic factor – changes in salinity (correlation coefficients of 0.86 and 0.88 for 127th and 131st cruises, respectively). It should be noted that the ranges of alkalinity variation during the voyages were small – approximately 4% (statistically significant changes are greater than 2%) of the average value.

As expected, in accordance with equations (1)–(5), the change in pH was opposite to the change in pCO_2: an increase in pCO_2 was accompanied by a decrease in pH. This relationship was most clearly expressed in the 131st cruise. In the first period (May 28, 2024–June 7, 2024), the increase in pCO_2 was 10%, and the decrease in pH was less pronounced in percentage terms, but the concentration of hydrogen ions (equation (3)) increased by ~7%. After that (June 11–17, 2024), there was an 8% decrease in pCO_2 and a 7% decrease in hydrogen ion concentration. The correlation coefficient between pH and pCO_2 was −0.53 and −0.57 for 127th and 131st cruises, respectively, indicating a moderate relationship and the contribution of the abiotic component to CO_2 dynamics (equation (1), carbonate equilibrium system).

Nevertheless, the contribution of the temperature to the dynamics of pCO_2 was most pronounced, with correlation coefficients of 0.52 and 0.71 for 127th and 131st cruises, respectively. At the same time, an increase in temperature contributes to both the intensification of biological processes and a shift in the equilibrium in the carbonate system towards CO_2 accumulation.



F i g . 4 . Spatial distribution of pCO_2 (*a*), temperature (*b*) and coccoliths (*c*) in the surface water layer based on data from the 131st cruise (1st stage, 28.05–07.06.2024)

The influence of sea surface temperature on pCO_2 is also evident in the spatial distribution of these parameters. This is exemplified by data from the 131st cruise (Figure 4), which shows that areas of maximum pCO_2 coincide with regions of elevated surface water temperature.

Furthermore, the spatial distribution of coccoliths did not correspond with the pCO_2 pattern (Fig. 4, *a*, *c*), which also confirms the assumption about the minor contribution of the biotic factor to the pCO_2 value of the surface water layer.

Based on the calculated data (Fig. 4, *c*) and satellite imagery data (for example, URL: http://dvs.net.ru/mp/data/modis/2406/24062955.gif), it is assumed that fields of suspended matter, consisting mainly of coccoliths, are formed under the influence of a hydrodynamic factor: water, enriched with coccolithophore cells and the suspended matter they produce, is carried along with the Main Black Sea Current from the southern regions of the sea. As a result, a field of suspended matter concentrations is formed, where clearer water is pressed against the shore and more turbid water is observed in the open sea part of the polygon.

Conclusions

During the study periods (May–July), coccolithophore blooms (more than 100 million cells/L) were observed in the surface waters, and the proportion of suspended matter of coccolithic origin was 50% or more. The spatial distribution of the concentration of suspended matter represented by coccolithophores was determined by the dynamics of the water and the structure of currents in the Black Sea.

The waters were oversaturated with CO_2 compared to the atmosphere, with an average pCO_2 of 486 ± 18 μatm, which is ~ 20% higher than the average annual pCO_2 value for this region.

Analysis of coccolith dynamics in late spring allowed us to identify three periods: the beginning of blooming and gradual accumulation of coccolithophores (late May – early June; average number of coccoliths $83 \cdot 10^9$ pcs/m^3), their accumulation and bloom outbreak during June (average number of coccoliths $131 \cdot 10^9$ pcs/m^3), and then the attenuation of the bloom by the end of June (average number of coccoliths $112 \cdot 10^9$ pcs/m^3) followed by carbonate decomposition.

No statistically significant correlation was found between the number of coccolithophore cells (and the number of coccoliths) and either pCO_2 (correlation coefficient −0.22 and −0.06 for 127th and 131st cruises, respectively) or alkalinity (correlation coefficients of 0.05 and 0.09 for the 127th and 131st cruises, respectively), as well as a moderate correlation with pH (correlation coefficients of 0.30 and 0.40 for the 127th and 131st cruises, respectively). The absence of a pronounced relationship between coccolith concentrations and pCO_2, pH, and alkalinity values suggests that, despite the contribution of coccolithophore blooms to maintaining high CO_2 concentrations in the sea surface, this factor is not the main one.

The temperature factor contributes most significantly to the dynamics of pCO_2, with correlation coefficients of 0.52 and 0.71 for 127th and 131st cruises, respectively. This is primarily due to the fact that an increase in temperature contributes to both the intensification of biological processes and a shift in the equilibrium in the carbonate system towards CO_2 accumulation. Thus, even during the coccolithophore bloom period, temperature is the key factor determining the pCO_2 value of the surface water layer.

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