

Original article

Investigation of the Relationship between Partial Pressure of Carbon Dioxide and Sea Surface Temperature in the Cyclic Seasonal Variations in the Black Sea

D. A. Sergeev^{1, 2, ✉}, Yu. I. Troitskaya¹, O. S. Ermakova¹,
N. A. Orekhova³

¹ Federal Research Center A. V. Gaponov-Grekhov Institute of Applied Physics of RAS,
Nizhny Novgorod, Russian Federation

² Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russian Federation

³ Marine Hydrophysical Institute of RAS, Sevastopol, Russian Federation

✉ danil@ipfran.ru

Abstract

Purpose. The purpose of the study consists in describing the parameterization based on the field data, which take into account the relationship between the variability of $p\text{CO}_2$ sw and the state of the surface water layer, depending on the sea surface temperature and allowing for geographical location and seasonality at the example of the Black Sea.

Methods and Results. The main seasonal trends of changes in $p\text{CO}_2$ related to the variations in sea surface temperature are proposed based on special processing of direct measurement data on $p\text{CO}_2$ of the surface layer obtained in the cruises of R/V *Professor Vodyanitsky* in 2015–2023 and at the stationary observation point of the Black Sea Hydrophysical Subsatellite Polygon (BSHSP), Katsiveli, in 2012–2022. The basic approach consists in describing the variations in $p\text{CO}_2$ sw distribution over the sea surface using the linear approximations (trends) for three fixed seasons represented by four months (January – April, May – August and September – December) in each of the grid cells. It is shown that both in the coastal zone and in the open sea, the hysteresis dependences of $p\text{CO}_2$ upon the sea surface temperature are manifested: the ratios of partial pressure and temperature during the periods of spring warming and autumn cooling are different. The reason for the observed hysteresis is related to a shift of the $p\text{CO}_2$ sw fluctuation phase and a temperature change of about 1.5–2 months.

Conclusions. The dependence of $p\text{CO}_2$ upon the sea surface temperature in an autumn-winter period turns out to be close to the dependences typical for the oceanic conditions in mid latitudes of the Northern Hemisphere (the Atlantic and Pacific oceans). This can indicate the universal mechanisms of influence of the sea surface temperature (SST) upon $p\text{CO}_2$ sw both for the local conditions in the Black Sea and for the open ocean during a certain seasonal period. Besides, such a similarity of dependences can mean that, most likely, SST directly conditions a value of $p\text{CO}_2$ sw, whereas biological activity is not a determining factor. The obtained results can be used for describing and studying the variations of the CO_2 sea – air fluxes in the Black Sea.

Keywords: $p\text{CO}_2$, sea surface temperature, Black Sea

Acknowledgements: The study was carried out with financial support from grant No. 169-15-2023-002 (dated 01.03.2023) provided by the Federal Service for Hydrometeorology and Environmental Monitoring and within the framework of state assignment of FSBSI FRC MHI FNNN-2022-0002 on the theme “Monitoring of the carbonate system, CO_2 content and fluxes in the marine environment of the Black and Azov seas”. The data were analyzed and compared to the open ocean data with the support of the RSF project No. 24-17-00299.

For citation: Sergeev, D.A., Troitskaya, Yu.I., Ermakova, O.S. and Orekhova, N.A., 2024. Investigation of the Relationship between Partial Pressure of Carbon Dioxide and Sea Surface Temperature in the Cyclic Seasonal Variations in the Black Sea. *Physical Oceanography*, 31(6), pp. 757-771.

© 2024, D. A. Sergeev, Yu. I. Troitskaya, O. S. Ermakova, N. A. Orekhova

© 2024, Physical Oceanography



Introduction

The development of methods and approaches for estimating the global carbon dioxide (CO₂) flux between the atmosphere and the hydrosphere of our planet, with a particular focus on the World Ocean, is a vital aspect of comprehensive studies of the Earth's carbon cycle.

A comparison of the estimated annual CO₂ emissions associated with anthropogenic activity, the estimated net CO₂ absorption by the land and the hydrosphere of our planet and the observed rate of CO₂ content increase reveals an imbalance in the atmosphere [1–3]. The magnitude of this imbalance, according to estimates by different authors, also varies and can be 10–50% [2, 3]. According to the authors of [3], the estimated imbalance for each year since 1960 fluctuates between +3 and –2 PgC/year (where 1 PgC = 10¹⁵ g of pure carbon). Such values are comparable with the approximate average estimates of the volume of annual CO₂ absorption by the ocean, which is approximately 2 PgC/year (for the period 1990–2020, according to the 5th and 6th reports of the Intergovernmental Panel on Climate Change^{1, 2}). The high error, estimated at ± 0.5 PgC/year (90% confidence interval), demonstrates the challenges in correct assessment of this very important component of the carbon cycle. At the same time, the results of studies [2] indicate that the discrepancy in CO₂ calculated for 2013–2022 decreased to –0.4 PgC/year by 2023, representing 10% of the total carbon budget. However, different approaches are applied to estimate the global CO₂ flux between the atmosphere and the ocean, which can result in discrepancies in the magnitude of the imbalance:

- calculations using 3D models of global biogeochemical ocean circulation, taking into account interactions with the atmosphere (Global Circulation Model – GCM) [4–9];

- 3D models of atmospheric CO₂ inversion based on indirect analysis of long-term observation data from ground-based sensor networks [10–13] and remote sensing methods [14];

- methods for calculating CO₂ flux [15, 16] based on the data on spatio-temporal dynamics of CO₂ partial pressure in the surface layer of the ocean ($p\text{CO}_2\text{ sw}$) and in the atmospheric surface layer ($p\text{CO}_2\text{ air}$) applied in the model of the gas exchange rate k across the water – atmosphere interface. This approach takes into account the dependence on hydrometeorological factors and the solubility coefficient α :

$$F = k\alpha\Delta p\text{CO}_2 = k\alpha(p\text{CO}_2\text{ sw} - p\text{CO}_2\text{ air}). \quad (1)$$

¹ Canadell, J.G. and Monteiro, P.M.S., 2023. Global Carbon and Other Biogeochemical Cycles and Feedbacks. In: V. P. Masson-Delmotte and P. Zhai, eds., 2023. *Climate Change 2021: The Physical Science Basis. Working Group I Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. New York, NY, USA; Cambridge, United Kingdom: Cambridge University Press, pp. 673-816. <https://doi.org/10.1017/9781009157896.007>

² Ciais, P. and Sabine, C., 2013. Carbon and Other Biogeochemical Cycles. In: T. F. Stoker, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley, eds., 2013. *Climate Change 2013: The Physical Science Basis. Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. New York, NY, USA; Cambridge, United Kingdom: Cambridge University Press, pp. 465-570. <https://doi.org/10.1017/CBO9781107415324.015>

The latter approach has the potential to yield the most accurate results; however, the results obtained using this method are highly dependent on the field data quality and the gas exchange rate model.

The selection of gas exchange rate model is important for correct assessment of CO₂ fluxes. Gas exchange rate k depends on the physicochemical properties (solubility and diffusion capacity D) of the gas and conditions of the atmosphere and ocean. Studies have revealed that the rate of gas exchange is also determined by turbulence in the boundary microlayers of air and water, which occurs as a result of wind stress [17, 18]. Consequently, the parameter k is typically parameterized through the wind velocity at a height of 10 m (U_{10}), in addition to wave parameters. Since measuring waves in natural conditions is usually challenging, the simplest models do not include wave parameters. Instead, they implicitly take into account their relationship with wind velocity. Such models include, for example, the widely used empirical formula for the gas exchange rate proposed in [19]:

$$k = [2.5 (0.5246 + 1.6256 \cdot 10^{-2} t + 4.9946 \cdot 10^{-4} t^2) + 0.3U_{10}^2] \left(\frac{Sc}{660}\right)^{1/2},$$

where Sc is the Schmidt number equal to the ratio of water kinematic viscosity to the diffusion capacity of the gas; t is the water temperature in °C. This approach to estimating CO₂ fluxes is widely used for the Black Sea.

The homogeneity of $p\text{CO}_2$ distribution in the near-surface layer of the ocean in time and space (across the entire World Ocean) is of particular importance for the accurate assessment of gas fluxes. Despite a notable increase in the number of shipboard measurements over the past decade, the installation of new measuring systems on large stationary platforms and the centralized replenishment of the SOCAT atlas database of partial pressure distribution in the World Ocean upper layer (accessible via <https://socat.info/>), these data remain assessed as scarce^{1,2}. This is primarily due to the significant spatio-temporal heterogeneity of population.

To populate the database with data of given spatial and temporal resolution based on available measurement results with no “gaps”, various approaches, including both classical 2D transport models in the near-surface layer [1] and new methods based on the use of neural networks and machine learning methods, are applied [20–28]. However, due to the limited amount of initial data, the final resolution, primarily spatial one, remains insufficient to determine the balance of carbon sources and sinks in the earth system.

The development of satellite methods makes it possible to obtain CO₂ flux estimates for the entire World Ocean. Nevertheless, these methods are indirect, and direct observations for the purpose of validating satellite measurements, the availability of which is limited, are still required [29, 30]. In any case, in order to determine the gas flux from satellite data, it is necessary to know the CO₂ concentrations both at the ocean surface and in the atmospheric surface layer. Furthermore, the gas transfer coefficient is also required [30]. Unfortunately, none of these parameters are determined directly from satellite data. In this case, the parameterization of the relationship between $p\text{CO}_2$ and sea surface temperature (SST) may assist in addressing the issue of data availability.

The uncertainty of CO₂ fluxes is particularly pronounced in coastal zones and inland seas, which are more dynamic systems on the scale of the World Ocean.

In such ecosystems, the impact of water dynamics, temperature fluctuations and the intensity of production and destruction processes on the carbon balance is considerably more significant and rapid than in the open ocean [31, 32].

The most promising approaches for correct balance assessment are those that construct models based on field data, taking into account the relationship between the variability of $p\text{CO}_2_{\text{sw}}$ value and the state of the near-surface water layer in a wide range of changing conditions, including SST, with regard to geographic location, seasonality, etc. The model was initially proposed in [33], wherein a database of monthly average values of $p\text{CO}_2_{\text{sw}}$ distribution on a uniform grid covering the entire World Ocean surface (free of ice) [15] was employed to develop algorithms for constructing $p\text{CO}_2_{\text{sw}}$ empirical dependencies on T_{sw} (the ocean surface temperature). The main objective of this study was to describe fluctuations in the $p\text{CO}_2_{\text{sw}}$ distribution across the surface using linear approximations (trends) for three fixed seasons of four months each (January – April, May – August, September – December) within each grid cell.

In [34] this method was significantly modified: the authors abandoned the fixed number of seasons (it can vary within 1–4) and used a minimum season duration of three months. For this period, linear approximations of $p\text{CO}_2_{\text{sw}}$ dependence on T_{sw} were selected once more. In this case, the number of linear approximations applied and the duration of seasons were selected based on the criterion of obtaining the maximum correlation coefficient when approximating the data ($p\text{CO}_2_{\text{sw}}$ and T_{sw}). The modified method was then applied to the updated database containing information on $p\text{CO}_2_{\text{sw}}$ [16]. As demonstrated by [34], this relatively straightforward approach made it possible to describe up to 70% of the variations in the CO_2 flux between the atmosphere and the ocean, obtained from the results of GCM modeling [7] and long-term data collected from several marine platforms.

The objective of this study is to apply a similar approach to describe the seasonal variations of $p\text{CO}_2_{\text{sw}}$ in the Black Sea and to perform parameterization based on field data that accounts for the relationship between $p\text{CO}_2_{\text{sw}}$ variability and the state of near-surface water layer depending on the water surface temperature, taking into account the geographical location and seasonality.

Research materials and methods

This study used the data from two different types of field measurements. Firstly, the data were obtained from shipboard measurements of $p\text{CO}_2$ in the surface water layer, conducted on board the R/V *Professor Vodyanitsky* (cruises No. 81, 87, 89, 91, 94, 95, 98, 101, 102, 108, 114, 117, 119, 125, 126) between November 2015 and March 2023. These measurements covered all hydrological seasons, with the exception of the winter period (January, February). Secondly, the measurement data were obtained at a stationary point for the carbon dioxide flux observations located on the oceanographic platform of the Black Sea Hydrophysical Subsatellite Polygon (BSHSP, Katsiveli) from May 2012 to October 2022. Taking into account the fundamentally different conditions of measurements (including their frequencies on a spatio-temporal scale and the distance from the shore), the shipboard data and

the data obtained at the platform were processed separately. The area under study and the scheme of sampling points are illustrated in Fig. 1.

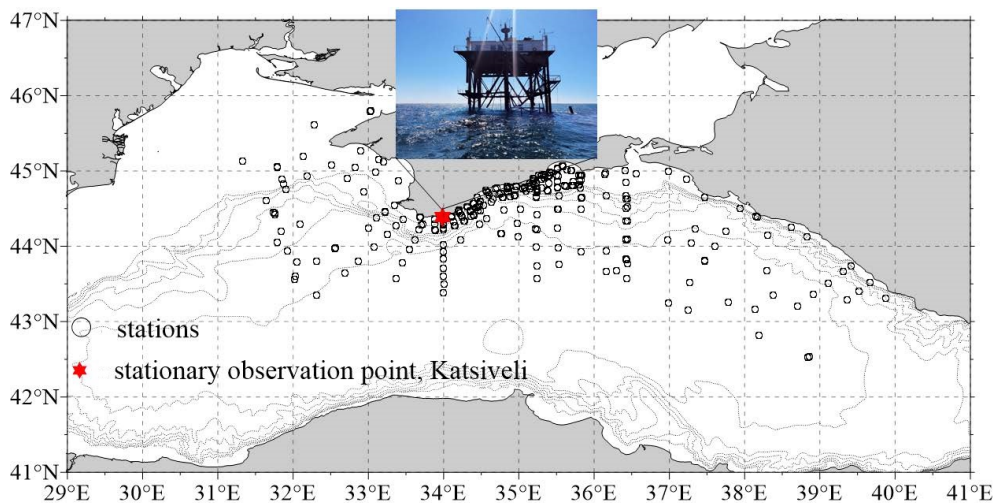


Fig. 1. Study area and sampling points for determining $p\text{CO}_2$ $_{\text{sw}}$ and the associated hydrometeorological conditions obtained at the R/V *Professor Vodyanitsky* and BSHSP stationary observation point

The hydrological characteristics (temperature and salinity of the surface water layer) were determined from the R/V *Professor Vodyanitsky* using the Sea-Bird 911 plus CTD or IDRONAUT OCEAN SEVEN 320PlusM probing systems. At stations with a depth of less than 50 m, a GAP AK-16 hydrological CTD probe was applied. The same characteristics at the BSHSP stationary observation point were obtained using a CTD48M hydrological probe (Sea & Sun Technology). In all cases, samples of the surface water layer (1.5–3.0 m) were collected using a submersible pump.

The volume concentration and $p\text{CO}_2$ were determined using LI-7000 infrared analyzer. The range of measured CO_2 concentrations is 0–3000 $\mu\text{mol/mol}$ with an error of 1% of the measured value [35]. The instrument was calibrated on a daily basis at two points: pure argon ($\text{CO}_2 = 0 \mu\text{mol/mol}$) and a certified calibration mixture with a volume fraction of CO_2 equal to 440 $\mu\text{mol/mol}$. Premium argon was used as the carrier gas. The conversion of CO_2 concentration ($\mu\text{mol/mol}$) to partial pressure of carbon dioxide (μatm) is performed using the following formula:

$$p\text{CO}_2 = x(\text{CO}_2) p_{\text{atm}}, \quad (2)$$

where $x(\text{CO}_2)$ is carbon dioxide concentration; p_{atm} is atmospheric pressure. A full description of the calculation is given in ³.

³ Dickson, A.G. and Goyet, C., 1994. *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water. Version 2*. Oak Ridge, TN: Oak Ridge National Laboratory (ORNL), 198 p. <https://doi.org/10.2172/10107773>

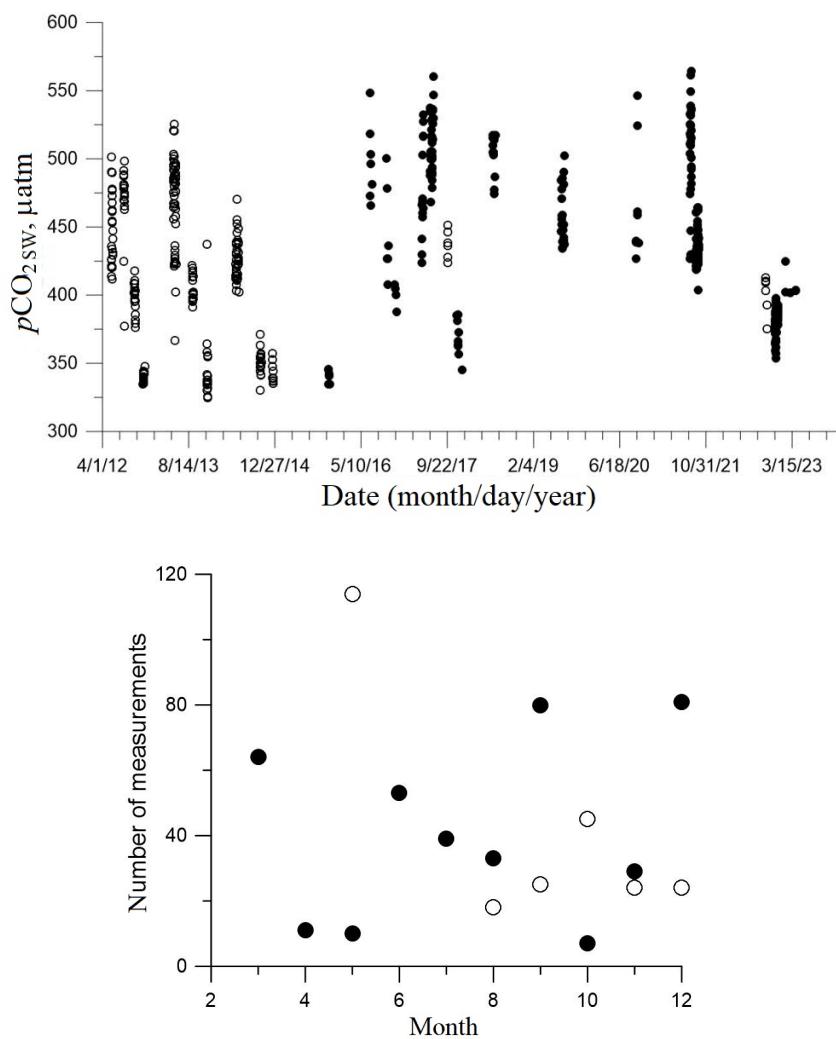


Fig. 2. Results of $p\text{CO}_{2\text{sw}}$ measurements: for the whole observation period (a) and a number of measurements by months (b). Dark circles denote the ship measurements, light ones – the measurements taken at the BSHSP stationary observation point

In conjunction with $p\text{CO}_{2\text{sw}}$, the accompanying meteorological parameters, namely wind velocity, atmospheric pressure and air temperature, were measured in the atmospheric surface layer using the recording equipment of the hydrometeorological data collection complex [36]. The data underwent quality control, with unreliable fragments being rejected, and were reduced to the standard observation height (10 m). According to the guidelines set forth by the World Meteorological Organization, the recorded data were averaged over a 10-minute period and further analysis was conducted on the averaged values [36].

Data were obtained on 395 measurements carried out from the vessel and 250 from the stationary observation point of the BSHSP. Figure 2 presents

a comprehensive overview of $p\text{CO}_2_{\text{sw}}$ measurements. These dependencies indicate that the data are distributed very unevenly with regard to both years and seasons.

The data for January and February are unavailable, which is due to the difficulties of performing expeditionary research. Furthermore, the quantity of data in spring is limited. The largest quantity of data was obtained in summer and early autumn, which is due to favorable conditions for carrying out expeditionary work. Taking into account such strong heterogeneity in time due to the small amount of data, it was decided not to separate the shipboard measurements by space and to combine the data from different points in the Black Sea. In addition, as shown in [37], the $p\text{CO}_2$ data for the water surface layer, shelf and deep-water areas of the Black Sea do not differ statistically.

Results and discussion

Due to the insufficient amount of data, it is not possible to identify correlations between seasonal changes in $p\text{CO}_2_{\text{sw}}$ and T_{sw} based on the results of studies conducted in any particular year for the specified periods. In this regard, a parallel can be drawn with [16], whereby all data are recalculated for one of the selected (central) years. When processing data for both types of measurements, 2019 was selected as the central reference point. The data for this year were used without adjustments, whereas the data obtained in previous years were adjusted in consideration of the interannual trend in atmospheric CO_2 concentration. Correct assessment of the interannual trend in $p\text{CO}_2_{\text{sw}}$ is an important point. Small amount of data and their uneven distribution by seasons do not allow to obtain an accurate estimate. In the study [16], which analyzed the data for almost 50 years of observations, it was noted that when the data from the entire ocean area were averaged within confidence intervals ($\sim 30\%$), the global trends in the $p\text{CO}_2$ increase in the ocean and atmosphere coincided. On this basis, the authors of the study [34] proposed that the observed changes in $p\text{CO}_2$ can be described as a superposition of the global atmospheric trend and variations associated with changes in water temperature T_{sw} . Taking this into account, we applied a trend of $2.4 \mu\text{atm}/\text{year}$ for $p\text{CO}_2$ in the atmosphere obtained from the measurement data of the Mauna Loa Observatory (Hawaii) for the period 2012–2022. This estimate is also close to the one determined by NCEP reanalysis data for the Black Sea over the period 2015–2022.

Once all the data had been reduced to 2019, the mean values and standard deviations for the measured parameters ($p\text{CO}_2$ and surface water temperature) for each month were calculated.

A preliminary analysis identified three characteristic seasonal trends in the dependence of $p\text{CO}_2_{\text{sw}}$ on temperature, which form a cycle of seasonal changes in partial pressure (Fig. 3, *a*).

In Fig. 3, the following notations are used: black circles – according to measurements from the vessel, red ones – from the stationary observation point of the BSHSP; lines are results of linear approximation for the selected seasonal periods: green line for the end of winter – end of spring, red one – for the end of

spring – end of summer, blue – for the end of summer – autumn – beginning of winter; solid lines are for data from vessel measurements, dashed lines are for data from the platform; light circles are data for the Atlantic Ocean, triangles are for the Pacific Ocean (data for the oceans are taken from the study [34]) with the corresponding linear approximations.

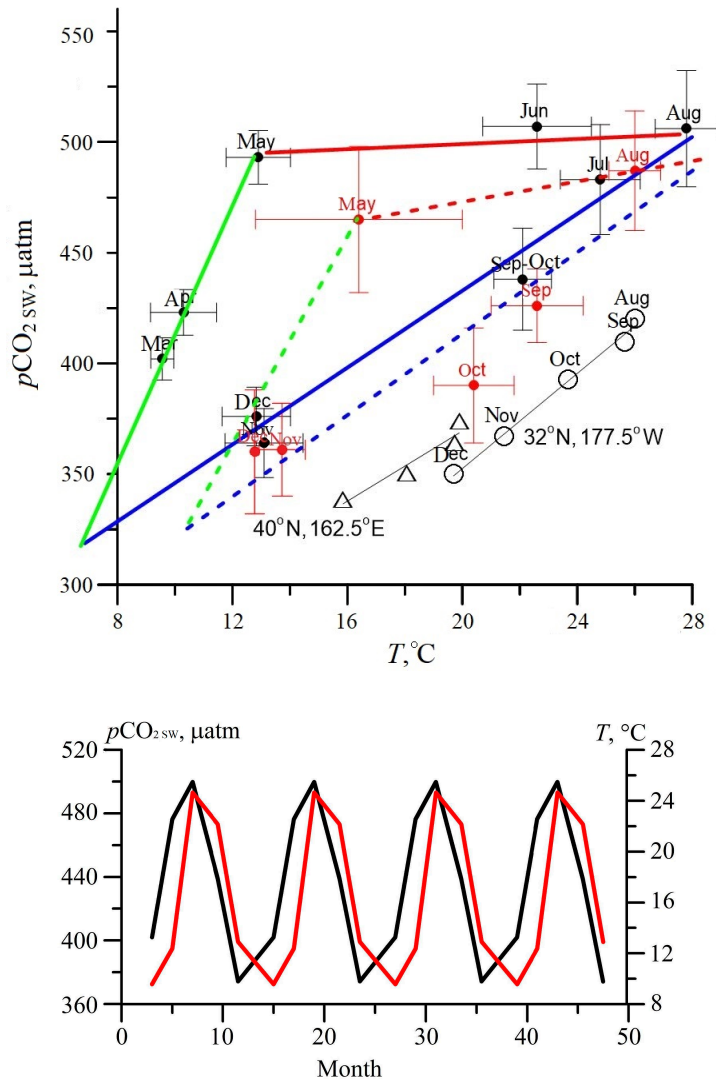


Fig. 3. Dependences of the monthly average $p\text{CO}_2 \text{ sw}$ on SST (all the data are reduced to 2019) (a), and periodically continued dependences of $p\text{CO}_2 \text{ sw}$ (black line) and SST (red line) upon time (b)

The first trend is a sharp increase in $p\text{CO}_2_{\text{sw}}$ levels with a temperature rise in the latter half of the spring season (late March – April – mid-May). Unfortunately, there is little data available for this time of year; however, the upward trend is evident. Subsequently, during the summer months (June – August), there is a gradual increase in $p\text{CO}_2_{\text{sw}}$ with a significant temperature rise. Furthermore, from September to December, there is a gradual decline (compared to spring) in CO_2 concentration with a temperature drop. Thus, the $p\text{CO}_2_{\text{sw}}$ dependence on water temperature is of hysteresis nature: the same value of water temperature corresponds to different $p\text{CO}_2_{\text{sw}}$ values during the spring and autumn periods. By plotting the $p\text{CO}_2$ and T_{sw} dependences on time and continuing the resulting periodic dependence with a 12-month period (Fig. 3, *b*), it becomes evident that the observed hysteresis is associated with a phase shift in $p\text{CO}_2_{\text{sw}}$ oscillations and a temperature variation by approximately 1.5–2 months.

Extremely uneven data distribution across different seasons is also worth noting. For example, in April, little data was received and they correspond either to the beginning or the end of the month, i.e., they most likely refer to March or May, respectively. A similar situation is observed with the data for October, which can be combined with those obtained in September. The average SST recorded in August was found to be almost two degrees higher than the average SST for 2019. This discrepancy can be attributed to the limited number of measurements conducted at the beginning of the month, with the majority of data obtained in the daytime.

The linear approximations were determined for each of the three seasonal sections in accordance with the processing results. It should be noted that the spring (green line) and winter (blue) periods intersect at a point with a temperature of $7.6\text{ }^\circ\text{C}$, which is only $0.2\text{ }^\circ\text{C}$ less than the average SST for February 2019. This provides evidence that the constructed approximations are accurate. In other words, the corner points in Fig. 3 correspond to the “triangular” cycle of seasonal changes, and they can be attributed to February, late May – early June and August.

A comparable methodology was used in the analysis of the data obtained from the BSHSP stationary observation point. It is noteworthy that a limited amount of data was recorded during the summer months (specifically, in August) and the spring season (in May). At the same time, there was a significant amount of data in autumn and early winter. For comparison with the shipboard measurements, the data from the BSHSP observation point were adjusted for 2019 with the same coefficient of $p\text{CO}_2$ variation in the atmosphere and averaged for each month. The greatest difference by month between the measurements from R/V *Professor Vodyanitsky* during the expeditions and at the stationary observation point in Katsiveli was observed in the data for May, although a considerable variability in the data set should also be noted.

Based on the foregoing, we can assume that the most significant changes in the nature of the dependence occur during May – June. Since there are no available data for January – April for the stationary observation point, the spring approximation (green dashed line) was taken as a straight line connecting the point corresponding to May and the point on the blue dashed line where the water temperature is approximately equal to the average temperature for February 2019 for the area of the stationary observation point ($7.6\text{ }^\circ\text{C}$). The comparison demonstrated

that, despite the absence of data during the spring and summer periods and a considerable scatter in May, the general nature of the cyclical seasonal dependence of $p\text{CO}_2_{\text{sw}}$ on SST was preserved (Fig. 3, *a*).

Taking into account the obtained data, the “triangle” of seasonal changes for the data from the stationary observation point has shifted slightly downwards and sideways (almost parallel transport), which is associated, among other things, with a higher average water temperature in the coastal zone.

The revealed similarity in the behavior of $p\text{CO}_2_{\text{sw}}$ dependence on temperature for the measurements from the stationary observation point and numerous shipboard ones carried out over the past 10 years indicates that this dependence is universal for the entire Black Sea.

Furthermore, the constructed dependencies of monthly average $p\text{CO}_2_{\text{sw}}$ on surface water temperature were compared with similar dependencies obtained earlier for the open ocean using the data from [34]. The comparison demonstrated that, in the absence of similarities between the late winter to spring to mid-summer period and the late summer – autumn – early winter period in the subtropical and temperate zones of the Atlantic and Pacific Oceans of the Northern Hemisphere, the change trends were very close to each other (Fig. 3, *a*). In the Black Sea the trend was $\sim 8.8 \mu\text{atm/degree}$, in the Atlantic Ocean $10.1 \mu\text{atm/degree}$, in the Pacific Ocean $7.9 \mu\text{atm/degree}$. This may indicate universal mechanisms of the SST effect on $p\text{CO}_2_{\text{sw}}$ both for local conditions of the Black Sea and for the open ocean during this seasonal period.

Trends in the dependence of $p\text{CO}_2_{\text{sw}}$ on temperature determined based on monthly average data regarding to 2019

Month	Based on expedition data obtained at <i>Professor Vodyanitsky</i>	Based on data obtained at BSHSP stationary point
January	$p\text{CO}_2_{\text{sw}} = 8.85 \cdot T + 253.30$ (no data for January, it is an assumption)	$p\text{CO}_2_{\text{sw}} = 8.75 \cdot T + 237.76$ (no data for January, it is an assumption)
February	$p\text{CO}_2_{\text{sw}} = 8.85 \cdot T + 253.30$ (no data for February, it is an assumption)	?? (dependence is not defined)
March	$p\text{CO}_2_{\text{sw}} = 27.16 \cdot T + 142.73$?? (dependence is not defined)
April	$p\text{CO}_2_{\text{sw}} = 27.16 \cdot T + 142.73$?? (dependence is not defined)
May	$p\text{CO}_2_{\text{sw}} = 27.16 \cdot T + 142.73$ $p\text{CO}_2_{\text{sw}} = 0.44 \cdot T + 487.47$?? (dependence is not defined) $p\text{CO}_2_{\text{sw}} = 2.29 \cdot T + 427.42$
June	$p\text{CO}_2_{\text{sw}} = 0.44 \cdot T + 487.47$	$p\text{CO}_2_{\text{sw}} = 2.29 \cdot T + 427.42$
July	$p\text{CO}_2_{\text{sw}} = 0.44 \cdot T + 487.47$	$p\text{CO}_2_{\text{sw}} = 2.29 \cdot T + 427.42$
August	$p\text{CO}_2_{\text{sw}} = 0.44 \cdot T + 487.47$ $p\text{CO}_2_{\text{sw}} = 8.85 \cdot T + 253.30$	$p\text{CO}_2_{\text{sw}} = 2.29 \cdot T + 427.42$ $p\text{CO}_2_{\text{sw}} = 8.75 \cdot T + 237.76$
September	$p\text{CO}_2_{\text{sw}} = 8.85 \cdot T + 253.30$	$p\text{CO}_2_{\text{sw}} = 8.75 \cdot T + 237.76$
October	$p\text{CO}_2_{\text{sw}} = 8.85 \cdot T + 253.30$	$p\text{CO}_2_{\text{sw}} = 8.75 \cdot T + 237.76$
November	$p\text{CO}_2_{\text{sw}} = 8.85 \cdot T + 253.30$	$p\text{CO}_2_{\text{sw}} = 8.75 \cdot T + 237.76$
December	$p\text{CO}_2_{\text{sw}} = 8.85 \cdot T + 253.30$	$p\text{CO}_2_{\text{sw}} = 8.75 \cdot T + 237.76$

Note: The table cells corresponding to May and August are highlighted in gray since two approximations converge in them.

The formulas for all linear approximations obtained during the data processing stage are presented in the Table. The basic formula represents the linear approximation of the dependence of partial pressure on water temperature with reference to the global trend of CO₂ concentration in the atmosphere. Using the obtained dependencies, it is possible to estimate the average monthly difference in $p\text{CO}_2$ at the interface between the water surface layer and the atmosphere for any given month of any given year as follows:

$$\Delta p\text{CO}_{2\ y,m} = \left[p\text{CO}_{2\ sw,2019\ m} + \left(\frac{\partial p\text{CO}_{2\ sw}}{\partial T^\circ} \right)_{2019\ m} \cdot \Delta T^\circ_{y,m-2019} \right] - p\text{CO}_{2\ air,2019\ m}, \quad (3)$$

in this case, the data on $p\text{CO}_2$ for the atmosphere can be obtained from reanalysis (similar to that presented in [38]) or by direct measurement.

In order to calculate the average monthly CO₂ flux through the sea surface, the $p\text{CO}_2$ gradient between the water surface layer and the atmospheric surface layer must be multiplied by the gas exchange rate and solubility, according to the equation (1) presented previously.

Conclusion

In this study, we proposed a model to describe the dependencies linking seasonal variations in $p\text{CO}_{2\ sw}$ with SST seasonal changes. These dependences are based on a special processing of direct $p\text{CO}_{2\ sw}$ measurements data carried out in expeditionary conditions from the R/V *Professor Vodyanitsky* (2015–2023) and at BSHSP stationary observation point (2012–2022). As a result, a cycle characterised by a rapid increase in $p\text{CO}_{2\ sw}$ in spring, an insignificant increase in summer and a smooth decrease in autumn–winter was obtained. The $p\text{CO}_{2\ sw}$ dependence upon water temperature is hysteresis in nature, whereby the same value of water temperature corresponds to different $p\text{CO}_{2\ sw}$ values in spring and autumn. This dependence is associated with a phase shift in $p\text{CO}_{2\ sw}$ oscillations and a temperature change of about 1.5–2 months.

A similar type of this cycle was independently demonstrated by processing measurements derived from both the vessel and the platform. It is noteworthy that the downward trend observed during the autumn-winter and winter periods was comparable to the trend observed in the open ocean conditions at Northern Hemisphere temperate and subtropical latitudes. It seems probable that the SST is the primary factor determining $p\text{CO}_{2\ sw}$, with biological activity having a lesser influence.

The sharp $p\text{CO}_{2\ sw}$ increase observed in spring requires further research to determine its underlying causes, primarily due to the limited amount of field data currently available. However, it can also be argued that at least biological processes associated with photosynthesis do not play a decisive role in this case. Otherwise, a negative trend would be expected rather than a positive one. Thus far, no negative trends have been identified when $p\text{CO}_{2\ sw}$ decreases with an increase in temperature, or vice versa, based on the available data set. In the future, it is necessary to continue research using accompanying data on ongoing biogeochemical processes.

The obtained result enables us to estimate interannual variations in the global CO₂ flux associated with corresponding temperature changes. It should be emphasized once again that the result was obtained on the basis of the assumption that the interannual trend in $p\text{CO}_2_{\text{sw}}$ is equivalent to that observed in the atmosphere of our planet. This assumption also requires further study, primarily to obtain more data, given that regional differences in $p\text{CO}_2_{\text{sw}}$ interannual trends can still be observed, particularly in coastal areas.

The $p\text{CO}_2_{\text{sw}}$ measurements were conducted at the Shared Use Center of the R/V *Professor Vodyanitsky* of FSBSI FRC “A.O. Kovalevsky Institute of Biology of Southern Seas” of RAS.

REFERENCES

1. Sarmiento, J.L. and Gruber, N., 2002. Sinks for Anthropogenic Carbon. *Physics Today*, 55(8), pp. 30-36. <https://doi.org/10.1063/1.1510279>
2. Friedlingstein, P., O’Sullivan, M., Jones, M.W., Andrew, R.M., Bakker, D.C.E., Hauck, J., Landschützer, P., Le Quéré, C., Luijckx, I.T. [et al.], 2023. Global Carbon Budget 2023. *Earth System Science Data*, 15(12), pp. 5301-5369. <https://doi.org/10.5194/essd-15-5301-2023>
3. Le Quéré, C., Raupach, M.R., Canadell, J.G., Marland, G., Bopp, L., Ciais, P., Conway, T.J., Doney, S.C., Feely, R.A. [et al.], 2009. Trends in the Sources and Sinks of Carbon Dioxide. *Nature Geoscience*, 2(12), pp. 831-836. <https://doi.org/10.1038/ngeo689>
4. Le Quéré, C., Aumont, O., Bopp, L., Bousquet, P., Ciais, P., Francey, R., Heimann, M., Keeling, C.D., Keeling, R.F. [et al.], 2003. Two Decades of Ocean CO₂ Sink and Variability. *Tellus B: Chemical and Physical Meteorology*, 55(2), pp. 649-656. <https://doi.org/10.3402/tellusb.v55i2.16719>
5. Obata, A. and Kitamura, Y., 2003. Interannual Variability of the Sea-Air Exchange of CO₂ from 1961 to 1998 Simulated with a Global Ocean Circulation-Biogeochemistry Model. *Journal of Geophysical Research: Oceans*, 108(C11), 3337. <https://doi.org/10.1029/2001JC001088>
6. McKinley, G.A., Rödenbeck, C., Gloor, M., Houweling, S. and Heimann, M., 2004. Pacific Dominance to Global Air-Sea CO₂ Flux Variability: A Novel Atmospheric Inversion Agrees with Ocean Models. *Geophysical Research Letters*, 31(22), L22308. <https://doi.org/10.1029/2004GL021069>
7. Doney, S.C., Lima, I., Feely, R.A., Glover, D.M., Lindsay, K., Mahowald, N., Moore, J.K. and Wanninkhof, R., 2009. Mechanisms Governing Interannual Variability in Upper-Ocean Inorganic Carbon System and Air-Sea CO₂ Fluxes: Physical Climate and Atmospheric Dust. *Deep Sea Research II*, 56(8-10), pp. 640-655. <https://doi.org/10.1016/j.dsr2.2008.12.006>
8. Law, R.M., Ziehn, T., Matear, R.J., Lenton, A., Chamberlain, M.A., Stevens, L.E., Wang, Y.-P., Srbnovsky, J., Bi, D. [et al.], 2017. The Carbon Cycle in the Australian Community Climate and Earth System Simulator (ACCESS-ESM1) – Part 1: Model Description and Pre-Industrial Simulation. *Geoscientific Model Development*, 10(7), pp. 2567-2590. <https://doi.org/10.5194/gmd-10-2567-2017>
9. Hauck, J., Köhler, P., Wolf-Gladrow, D. and Völker, C., 2016. Iron Fertilisation and Century-Scale Effects of Open Ocean Dissolution of Olivine in a Simulated CO₂ Removal Experiment. *Environmental Research Letters*, 11(2), 024007. <https://doi.org/10.1088/1748-9326/11/2/024007>
10. Bousquet, P., Peylin, P., Ciais, P., Le Quéré, C., Friedlingstein, P. and Tans, P.P., 2000. Regional Changes in Carbon Dioxide Fluxes of Land and Oceans since 1980. *Science*, 290(5495), pp. 1342-1346. <https://doi.org/10.1126/science.290.5495.1342>
11. Rödenbeck, C., Houweling, S., Gloor, M. and Heimann, M., 2003. CO₂ Flux History 1982–2001 Inferred from Atmospheric Data Using a Global Inversion of Atmospheric Transport. *Atmospheric Chemistry and Physics*, 3(6), pp. 1919-1964. <https://doi.org/10.5194/acp-3-1919-2003>

12. Saeki, T. and Patra, P.K., 2017. Implications of Overestimated Anthropogenic CO₂ Emissions on East Asian and Global Land CO₂ Flux Inversion. *Geoscience Letters*, 4(1), 9. <https://doi.org/10.1186/s40562-017-0074-7>
13. Van der Laan-Luijkx, I.T., Van der Velde, I.R., Van der Veen, E., Tsuruta, A., Stanislawski, K., Babenhauserheide, A., Zhang, H.F., Liu, Y., He, W. [et al.], 2017. The Carbon Tracker Data Assimilation Shell (CTDAS) v1.0: Implementation and Global Carbon Balance 2001–2015. *Geoscientific Model Development*, 10(7), pp. 2785-2800. <https://doi.org/10.5194/gmd-10-2785-2017>
14. Chevallier, F., Fisher, M., Peylin, P., Serrar, S., Bousquet, P., Bréon, F.-M., Chédin, A. and Ciais, P., 2005. Inferring CO₂ Sources and Sinks from Satellite Observations: Method and Application to TOVS Data. *Journal of Geophysical Research: Atmospheres*, 110(D24), D24309. <https://doi.org/10.1029/2005jd006390>
15. Takahashi, T., Feely, R.A., Weiss, R.F., Wanninkhof, R.H., Chipman, D.W., Sutherland, S.C. and Takahashi, T.T., 1997. Global Air-Sea Flux of CO₂: An Estimate Based on Measurements of Sea-Air pCO₂ Difference. *Proceedings of the National Academy of Sciences of the USA*, 94(16), pp. 8292-8299. <https://doi.org/10.1073/pnas.94.16.8292>
16. Takahashi, T., Sutherland, S.C., Wanninkhof, R., Sweeney, C., Feely, R.A., Chipman, D.W., Hales, B., Friederich, G., Chavez, F. [et al.], 2009. Climatological Mean and Decadal Change in Surface Ocean pCO₂, and Net Sea-Air CO₂ Flux over the Global Oceans. *Deep Sea Research Part II: Topical Studies in Oceanography*, 56(8–10), pp. 554-577. <https://doi.org/10.1016/j.dsr2.2008.12.009>
17. Jähne, B., Münnich, K.O., Börsinger, R., Dutzi, A., Huber, W.A. and Libner, P., 1987. On the Parameters Influencing Air-Water Gas Exchange. *Journal of Geophysical Research: Oceans*, 92(C2), pp. 1937-1949. <https://doi.org/10.1029/JC092iC02p01937>
18. Komori, S., Nagaosa, R. and Murakami, Y., 1993. Turbulence Structure and Mass Transfer across a Sheared Air-Water Interface in Wind-Driven Turbulence. *Journal of Fluid Mechanics*, 249, pp.161-183. <https://doi.org/10.1017/S0022112093001120>
19. Wanninkhof, R., 1992. Relationship between Wind Speed and Gas Exchange over the Ocean. *Journal of Geophysical Research*, 97(C5), pp. 7373-7382. <https://doi.org/10.1029/92JC00188>
20. Zeng, J., Nojiri, Y., Landschützer, P., Telszewski, M. and Nakaoka, S., 2014. A Global Surface Ocean fCO₂ Climatology Based on a Feed-Forward Neural Network. *Journal of Atmospheric and Oceanic Technology*, 31(8), pp. 1838-1849. <https://doi.org/10.1175/jtech-d-13-00137.1>
21. Rödenbeck, C., Bakker, D.C.E., Gruber, N., Iida, Y., Jacobson, A.R., Jones, S., Landschützer, P., Metz, N., Nakaoka, S. [et al.], 2015. Data-Based Estimates of the Ocean Carbon Sink Variability – First Results of the Surface Ocean pCO₂ Mapping Intercomparison (SOCOM). *Biogeosciences*, 12(23), pp. 7251-7278. <https://doi.org/10.5194/bg-12-7251-2015>
22. Bakker, D.C.E., Pfeil, B., Landa, C.S., Metz, N., O'Brien, K.M., Olsen, A., Smith, K., Cosca, C., Harasawa, S. [et al.], 2016. A Multi-Decade Record of High-Quality fCO₂ Data in Version 3 of the Surface Ocean CO₂ Atlas (SOCAT). *Earth System Science Data Discussions*, 8(2), pp. 383-413. <https://doi.org/10.5194/essd-2016-15>
23. Landschützer, P., Gruber, N. and Bakker, D.C.E., 2016. Decadal Variations and Trends of the Global Ocean Carbon Sink. *Global Biogeochemical Cycles*, 30(10), pp. 1396-1417. <https://doi.org/10.1002/2015gb005359>
24. McKinley, G.A., Fay, A.R., Lovenduski, N.S. and Pilcher, D.J., 2017. Natural Variability and Anthropogenic Trends in the Ocean Carbon Sink. *Annual Review of Marine Science*, 9(1), pp. 125-150. <https://doi.org/10.1146/annurevmarine-010816-060529>
25. Gregor, L., Lebehot, A.D., Kok, S. and Scheel Monteiro, P.M., 2019. A Comparative Assessment of the Uncertainties of Global Surface Ocean CO₂ Estimates Using a Machine-Learning Ensemble (CSIR-ML6 Version 2019a) – Have we Hit the Wall? *Geoscientific Model Development*, 12(12), pp. 5113-5136. <https://doi.org/10.5194/gmd-12-5113-2019>
26. Gruber, N., Clement, D., Carter, B.R., Feely, R.A., van Heuven, S., Hoppema, M., Ishii, M., Key, R.M., Kozyr, A. [et al.], 2019. The Oceanic Sink for Anthropogenic CO₂ from 1994 to 2007. *Science*, 363(6432), pp. 1193-1199. <https://doi.org/10.1126/science.aau5153>

27. Denvil-Sommer, A., Gehlen, M., Vrac, M. and Mejia, C., 2019. LSCE-FFNN-v1: A Two-Step Neural Network Model for the Reconstruction of Surface Ocean pCO₂ over the Global Ocean. *Geoscientific Model Development*, 12(5), pp. 2091-2105. <https://doi.org/10.5194/gmd-12-2091-2019>
28. Iida, Y., Takatani, Y., Kojima, A. and Ishii, M., 2020. Global Trends of Ocean CO₂ Sink and Ocean Acidification: An Observation-Based Reconstruction of Surface Ocean Inorganic Carbon Variables. *Journal of Oceanography*, 77(2), pp. 323-358. <https://doi.org/10.1007/s10872-020-00571-5>
29. Gulev, S.K., 2023. Global Climate Change and the Oceans. *Studies on Russian Economic Development*, 34(6), pp. 738-745. <https://doi.org/10.1134/S1075700723060060>
30. Pipko, I.I., Pugach, S.P., Repina, I.A., Dudarev, O.V., Charkin, A.N. and Semiletov, I.P., 2015. Distribution and Air-Sea Fluxes of Carbon Dioxide on the Chukchi Sea Shelf. *Izvestiya, Atmospheric and Oceanic Physics*, 51, pp. 1088-1102. <https://doi.org/10.1134/S0001433815090133>
31. Bates, N.R., 2018. Seawater Carbonate Chemistry Distributions across the Eastern South Pacific Ocean Sampled as Part of the GEOTRACES Project and Changes in Marine Carbonate Chemistry over the Past 20 Years. *Frontiers in Marine Science*, 5, 398. <https://doi.org/10.3389/fmars.2018.00398>
32. Bauer, J.E., Cai, W.-J., Raymond, P.A., Bianchi, T.S., Hopkinson, C.S. and Régnier, P.A.G., 2013. The Changing Carbon Cycle of the Coastal Ocean. *Nature*, 504, pp. 61-70. <https://doi.org/10.1038/nature12857>
33. Lee, K., Wanninkhof, R., Takahashi, T., Doney, S.C. and Feely, R.A., 1998. Low Interannual Variability in Recent Oceanic Uptake of Atmospheric Carbon Dioxide. *Nature*, 396, pp. 155-159. <https://doi.org/10.1038/24139>
34. Park, G.-H., Wanninkhof, R., Doney, S.C., Takahashi, T., Lee, K., Feely, R.A., Sabine, C.L., Triñanes, J. and Lima, I.D., 2010. Variability of Global Net Sea-Air CO₂ Fluxes over the Last Three Decades Using Empirical Relationships. *Tellus B: Chemical and Physical Meteorology*, 62(5), pp. 352-368. <https://doi.org/10.1111/j.1600-0889.2010.00498.x>
35. Khoruzhiy, D.S., 2010. Usage of Device Complex AS-C3 for Detection of Carbon Dioxide Partial Pressure and Inorganic Carbon Concentration in Sea Environment. MHI, 2010. *Ekologicheskaya Bezopasnost' Pribrezhnoy i Shel'fovoy Zon i Kompleksnoe Ispol'zovanie Resursov Shel'fa* [Ecological Safety of Coastal and Shelf Zones and Comprehensive Use of Shelf Resources]. Sevastopol: MHI. Iss. 23, pp. 260-272 (in Russian).
36. Garmashov, A., 2020. Hydrometeorological Monitoring on the Stationary Oceanographic Platform in the Black Sea. In: SGEM, 2020. *20th International Multidisciplinary Scientific GeoConference SGEM 2020: Proceedings*. Sofia, Bulgaria. Vol. 20, Book 3.1, pp. 171-176. <https://doi.org/10.5593/sgem2020/3.1/s12.023>
37. Konovalov, S.K. and Orekhova, N.A., 2024. New View of the CO₂ Content in Surface Waters of the Black Sea Based on Direct Measurements. *Doklady Earth Science*, 518, pp. 1737-1742. <https://doi.org/10.1134/S1028334X24602943>
38. Watson, A.J., Schuster, U., Bakker, D.C.E., Bates, N.R., Corbière, A., González-Dávila, M., Friedrich, T., Hauck, J., Heinze, C. [et al.], 2009. Tracking the Variable North Atlantic Sink for Atmospheric CO₂. *Science*, 326, pp. 1391-1393. <https://doi.org/10.1126/science.1177394>

Submitted 14.06.2024; approved after review 09.07.2024;

accepted for publication 12.09.2024.

About the authors:

Daniil A. Sergeev, Head of Laboratory of Experimental Methods in Geophysical and Technical Hydrodynamics, Federal Research Center A.V. Gaponov-Grekhov Institute of Applied Physics of RAS (46 Ulyanova Str., Nizhny Novgorod, 603950, Russian Federation), CSc (Phys.-Math.), **ORCID ID: 0000-0003-4910-3935**, **ResearcherID: L-4569-2016**, **Scopus Author ID: 660388734**, daniil@ipfran.ru

Yulia I. Troitskaya, Head of the Department of Nonlinear Geophysical Processes, Federal Research Center A.V. Gaponov-Grekhov Institute of Applied Physics of RAS (46 Ulyanova Str., Nizhny Novgorod, 603950, Russian Federation), DSc (Phys.-Math.), **ORCID ID: 0000-0002-1387-970X**, **ResearcherID: F-1352-2015**, **Scopus Author ID: 35784884700**, yuliya@ipfran.ru

Olga S. Ermakova, Senior Researcher, Laboratory of Nonlinear Physics of Natural Processes, Federal Research Center A.V. Gaponov-Grekhov Institute of Applied Physics of RAS (46 Ulyanova Str., Nizhny Novgorod, 603950, Russian Federation), CSc (Phys.-Math.), **ORCID ID: 0000-0003-0687-4000**, **ResearcherID: D-3643-2015**, **Scopus Author ID: 16051997000**, o.s.ermakova@mail.ru

Natalia A. Orekhova, Head of Laboratory for Monitoring and Research of Greenhouse Gases and Oxygen in the Marine Environment, Marine Hydrophysical Institute of RAS (2 Kapitanskaya Str., Sevastopol, 299011, Russian Federation), CSc (Geogr.), **ORCID ID: 0000-0002-1387-970X**, **ResearcherID: I-1755-2017**, **Scopus Author ID: 35784884700**, natalia.orekhova@mhi-ras.ru

Contribution of the co-authors:

Daniil A. Sergeev – literary review, selection of data processing method

Yulia I. Troitskaya – data processing, preparation of illustrations

Olga S. Ermakova – data analysis

Natalia A. Orekhova – literary review, data analysis of $p\text{CO}_2$

The authors have read and approved the final manuscript.

The authors declare that they have no conflict of interest.