Variability of the CO_2 Flux on the Water-Atmosphere Interface in the Black Sea Coastal Waters on Various Time Scales in 2010–2014

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Due to the present tendency to the increased carbon dioxide content in the atmosphere, one of the priorities in hydrochemical research consists in studying the gas exchange in the water-atmosphere system. At that, quantity assessment of the marine areas' role in the CO_2 transport requires taking into account water spatial heterogeneity based on its ability to invade or evacuate carbon dioxide. Represented are the results of estimating intensity and direction of the CO_2 flux between the sea and the atmosphere in the Black Sea coastal waters in 2010–2014 executed based on the *in situ* hydrochemical studies and reanalysis of meteorological data. The results of direct measurements of the CO_2 equilibrium partial pressure in the water surface layer and in the atmosphere near-surface layer were used for the first time for calculating the CO_2 flux in the Black Sea waters. The results of analysis of the CO_2 flux variability on different time scales are represented. The performed calculations show that the CO_2 evacuation prevails in a warm season, whereas its invasion – in a cold season. During the off-season transitions, the water area state is close to equilibrium. The timing limits of the seasons are not constant and vary practically each year. Probable reasons of a CO_2 flux seasonal variability are considered. Possible role of the abiogenic, biogenic and anthropogenic factors is assessed as a cause of the observed intensity fluctuations of the CO_2 exchange between the sea and the atmosphere. It is shown that on the synoptic time scale, the CO_2 flux is characterized by a narrower oscillations' amplitude as compared to its seasonal and inter-annual variability. It is noted that small-scale temporal variability of the CO_2 flux is more pronounced during the cold season. The features of the carbon cycle in the Black Sea coastal waters are considered. Possibility of using information on the CO_2 flux intensity and direction for assessing the water area ecological state is discussed.

Keywords: CO_2 flux, equilibrium partial CO_2 pressure, CO_2 evaporation, CO_2 invasion, seasonal variability of CO_2 flux, CO_2 flux daily variation, inter-daily variations of CO_2 flux, coastal waters, upwelling.

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Characteristics of the carbon cycle in marine areas are one of the most discussed topics in modern oceanological literature. Quantitative assessment of carbon dioxide (CO_2) fluxes between the ocean and the atmosphere is among the central objectives of carbon cycle research. Interest in studying the gas exchange between the atmosphere and the hydrosphere is due to the role of the oceans in the global carbon cycle. According to modern estimates, the total carbon sink in the ocean waters exceeds the same value for the atmosphere by 50 times and for land biocenoses – by 15 times. CO_2 sink in the water area is approximately seven times more than its absorption by the land biocenoses. Due to this, the World Ocean is the main factor influencing the carbon dioxide concentration the atmosphere [1–3].

The approach, in which the World Ocean is considered as a planetary-scale carbon dioxide absorber, is applicable when analyzing the global interaction between the ocean and the atmosphere but needs to be detailed to characterize particular water areas. Quantitative description of carbon cycle in the ocean can not be complete without studying the transformation of this element in the shelf waters. CO_2 sink into the coastal waters reaches 21 % and primary production formed in these areas makes up 15–30 % of the World Ocean corresponding values [4, 5].

Relatively small volume of waters and shallow depths, characteristic of coastal water areas, cause high variability of water environment physical characteristics under effect of the wind, upwellings, currents, etc. The named factors, combined with high intensity of biogeochemical processes at the sea, atmosphere and land interface, lead to the shift of equilibrium between the components of sea water carbonate system: [6, p. 310]:

$$CO_{2g} \rightleftarrows CO_{2water}, \quad (1)$$

$$CO_{2water} + H_2O \rightleftarrows CO_2 \cdot H_2O, \quad (2)$$

$$CO_2 \cdot H_2O \rightleftarrows HCO_3^- + H^+, \quad (3)$$

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+, \quad (4)$$

$$CO_3^{2-} + Ca(Mg)^{2+} \rightleftarrows Ca(Mg)CO_3. \quad (5)$$

The equilibrium shift in equations (1)–(5) reflects the changes in the carbon cycle functioning, accompanying the water area transition from CO_2 evasion to its invasion from the atmosphere.

In order to assess the state of carbon cycle in the water area, a parameter, which can be founded on the basis of direct measurements with the minimal use of empiric values, is required. CO_2 flux between the sea and the atmosphere, occurring due to the gradient of pCO_2 values in the sea water and in the near-water layer of the atmosphere, meets these criteria. Research of CO_2 flux direction and intensity, as well as the temporal variation of these parameters, are carried out on regional level and global scale when studying the gas exchange between the World Ocean and the atmosphere [4, 5, 7].

pCO_2 value in the sea water is significantly determined by biota functioning and can serve as one of criteria for assessing the biological process intensity in the water biocenoses. Equally important is the possibility of using pCO_2 to assess the

anthropogenic load on the water area. This aspect is of particular interest in the study of shelf ecosystems that receive the main part of allochtonous organic matter, including the one of anthropogenic origin [4].

In the Black Sea carbon cycle has a number of features due to the specificity of the hydrochemical characteristics of the Black Sea waters: their salinity is almost twice lower and the concentration of dissolved inorganic carbon is about 1.5 times higher than in the oceans.

In the given paper the features of CO_2 exchange between the atmosphere and the Black Sea coastal waters based on the results of pCO_2 direct measurements in the atmosphere, the equilibrium partial pressure of CO2 in the surface layer of water and the sea water total alkalinity (*Alk*) are discussed. Field data were obtained during 13 expeditions carried out in 2010–2014 by the employees of the Marine Biogeochemistry Department of MHI [8, 9].

Region and methods of the study

Experimental part of the work was carried out within the framework of expeditionary research carried out at stationary oceanographic platform (SOP) located in the Goluboy Gulf, (the Southern Coast of Crimea, near Katsiveli urban-type settlement) 430 m off the shore (Fig. 1). Geographical coordinates of the platform are 44°23'34,86" N, 33°59'4,12" E, the depth at the sampling area – 27 m.

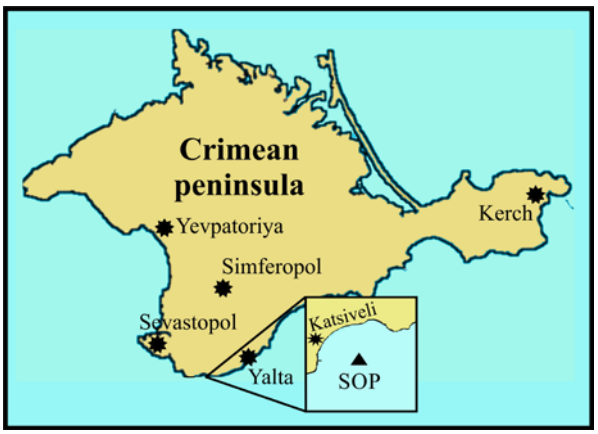

Fig. 1. Location of the stationary oceanographic platform

Formation of the water hydrochemical composition in the area under study occurs as a result of natural biogeochemical processes with minimal influence of anthropogenic factors: the absence of industrial organizations and large releases of household wastewater in the adjacent territory. Due to these features, the water area adjacent to the SOP was selected as the object of complex hydrologic-hydrochemical research carried out in 2012–2014 involving the capabilities of satellite sensing [10].

During the research, the sampling was performed from 0 to 0.5 m surface layer using a submersible vibration pump attached to the float. Fixation of the pump at a minimum distance from a float provided the sampling at a predetermined depth.

Equilibrium *p*CO2 measurements in the atmosphere and the water surface layer were carried out using *LI-*7000 *DP* infra-red non-scattering analyzer (manufacturer – *LI-COR Inc*., USA). Registration of measurement results was performed using proprietary software that allowed us to record the parameters with a scheduled frequency of 2 Hz.

For determining pCO_2 in the atmosphere, atmospheric air was pumped through the measuring cell of the analyzer, and argon – through the reference cell.

Measurement of equilibrium pCO_2 in the water was carried out during the water sampling. For this purpose, seawater was pumped through the equilibrator and the air was pumped in the opposite direction. After a certain time (up to 30 minutes) between the water and air circulating in a closed circuit between the working chamber of the equilibrator and the measuring cell of *LI-*7000 *DP* analyzer, equilibrium was established, and pCO_2 value ceased to change. Thereafter, the measurements continued for 3 minutes, and average value over this time was taken as a result.

The titrimetric determination of alkalinity was carried out using *Metrohm Dosimat® Model 765* automatic burette, which provided determination of the titrant consumption with ± 0.001 cm^3 accuracy. 0.02 mol/dm^3 HCl solution, standardized in Na_2CO_3 one with 0.025 mol/dm^3 concentration was used as the titrant.

For calculating CO_2 flux at the ocean – atmosphere interface, a large number of equations derived from experiments in laboratory and field conditions were proposed by different researchers. L. Hasse identifies two main concepts developed to describe the gas transfer across the boundary between the sea and the atmosphere: the boundary layer model and the dynamic (updateable) surface model [11, p. 94]. The development of new calculation algorithms is due to the improvement of the measuring equipment, which made it possible to increase the number of parameters determined during the field experiments. As a result, the methodological approach to calculation of CO_2 flux changes: along with the previously used values (pCO_2 in the water and the atmosphere, *Alk*, sea water temperature and salinity, wind velocity), the new calculation equations include the data on the sea surface state, wave height and a number of other parameters. The values of empirical coefficients derived from the processing of data arrays, as well as the number of values used in the calculation, vary in the works of different authors, which complicates the correlation of the experimental data and indicates the absence of a single generally accepted approach to the solution of this problem [11–14].

The complexity of quantifying the intensity of gas exchange is explained by the multifactor nature of the dependence of the gas transfer rate at the phase interface. During the numerous model experiments, the nonlinear character of the dependence of one of the most important quantities determining the intensity of gas exchange – the root-mean-square steepness of the wave – on the wind speed was shown: at a certain moment an abrupt change in the graph angle occurs. Wind speed, at which the graph bends, can vary. This indicates the dependence of phase separation surface area on other factors.

The biota effect on CO_2 flux must be considered in several aspects. On one hand, carbon dioxide consumption by phytoplankton during the assimilation process results in the decrease of CO_2 partial pressure in the water surface layer. On

the other hand, the growth of microalgae amount leads to the increase of zooplankton amount and the intensification of CO_2 release.

In the present work, the calculation of the fluxes was performed using the equation of mass transfer, which includes the invasion and evasion coefficients proposed in [15, p. 201]:

$$F^{CO_2} = n_v \cdot \alpha'_{i,e} \cdot \Delta pCO_2. \quad (6)$$

In the equation (6) F^{CO_2} is CO_2 flux; n_v is an integral coefficient reflecting the sea surface state (wavers, foam, splashes) and showing how many times the gas exchange rate increases at different wind speeds above the sea surface compared to an ideal calm; α'_i and α'_e are the invasion and evasion coefficients, respectively, ΔpCO_2 is a difference between pCO_2 in the atmosphere and in the water.

The choice for invasion or evasion coefficient calculation is determined by the sign of ΔpCO_2 value: for the positive ΔpCO_2 values α'_i is applied, and for the negative ones $-\alpha'_e$. The both coefficients have (mol $CO_2 \cdot m^{-2} \cdot atm^{-1} \cdot day^{-1}$) dimension, and their calculation is performed according to the equations [16, p. 49]

$$\alpha_i = 3.6 + 0.201\,S + 10.205\,Alk, \quad (7)$$

$$\alpha_e = 3.6 + 0.46\,S + 4.793\,Alk. \quad (8)$$

In order to calculate n_v value expressed in $m^2 \cdot s^{-2}$ the following expressions are used:

$$n_v = 1 + 0.125v^2, \quad (9)$$

$$n_v = -4.0 + 0.175v^2. \quad (10)$$

Depending on the wind velocity (v), the formula (9) is applied for n_v calculation if $v \leq 10$ m/s, and the formula (10) if $v > 10$ m/s. Corresponding parameters, as well as the coefficients found by the equations (7) and (8) are used to calculate the fluxes according to the equation (6) [16, p. 201].

This method of calculation was selected based on the following considerations. Firstly, its use does not require the involvement of additional data that are inaccessible for surveying during past years. Secondly, the use of the transport equation assumes that the gas exchange rate depends on the pCO_2 values in the atmosphere and water, as well as on the wind velocity, but does not depend on the water temperature. Such approach to the analysis of CO_2 flux between the atmosphere and the ocean makes it possible not to be limited by a surface film at the interface, but to consider the gas exchange as a process of substance transfer between the gas phase and the entire water column, which reflects the physical meaning of gas exchange between the sea and the atmosphere more accurately.

The disadvantages of this method include the semi-empirical estimated nature of the obtained results. In particular, to assess the kinetic forces involved in the formation of CO_2 flow at the interface, it is necessary to take into account both the meteorological conditions and the water surface state: steepness and fetch of the waves, foaming and the presence of microbubbles [12]. Consideration of these factors in this calculation method is limited by the use of empirical coefficients. As

in this paper a framework assessment of trends in CO_2 flux changes at different time scales is carried out, the use of a semi-quantitative method of calculation seems to be acceptable.

In the most common alternative methods, the consideration of gas exchange is limited to studying the interaction between the atmosphere and the surface film on the aqueous phase surface [12, 14]. With this approach, the film thickness is a critical quantity, and the ambiguity in its assessment leads to significant discrepancies in the results of calculations. Some researchers point out that it is impossible to estimate accurately the thickness of a surface film by extrapolating the results of laboratory experiments to the field conditions [11]. Due to this, in each case the calculation result contains uncertainty, the value of which remains the subject of discussions [17].

Results and their discussion

The calculation of CO_2 fluxes was carried out using the values of CO_2 equilibrium partial pressure in the surface layer sea water and in the atmosphere, total alkalinity and seawater salinity determined during the field studies at the SOP. The wind velocity required for CO_2 calculation in six cases was measured during the work at SOP and in other cases the reanalysis data were used.

The results of CO_2 flux in warm and cold seasons, as well as average values for each survey, are shown in Fig. 2. Seasonal features of CO_2 flux direction can be seen on the diagram: CO_2 evasion into the atmosphere (positive flux direction) prevailed in the warm season, and invasion (negative flux direction) prevailed during the cold season.

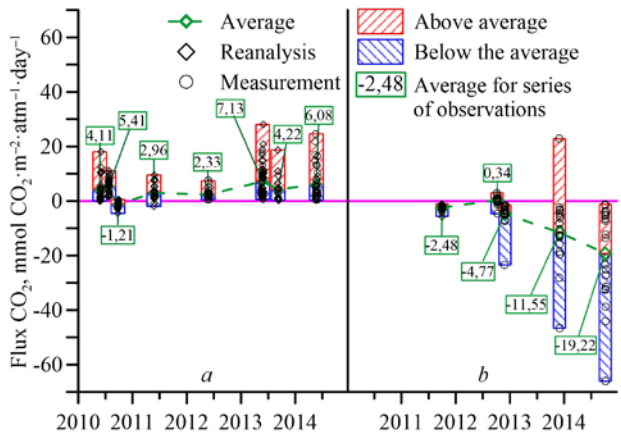

Fig. 2. CO_2 fluxes between the sea and the atmosphere during the warm (*a*) and cold (*b*) seasons in 2010–2014

For each survey average intensity of CO_2 flux was calculated. In warm season this value varied within the interval from –1.21 to 7.13 mmol $CO_2 \cdot m^{-2} \cdot atm^{-1} \cdot day^{-1}$. Invasive flow direction prevailed only during the survey performed in September 2010. Another distinctive feature of this survey was the minimum amplitude – the difference between the maximum and the minimum values of CO_2 flux intensity. Relatively low CO_2 flux intensity in warm season was observed in May 2012

against the background of prolonged upwelling which caused an abrupt decrease of water temperature. During the other surveys performed in warm season the values of the flux average intensity were higher.

The maximum amplitude of CO_2 flux intensity values was observed during the spring heating of waters in 2010, 2013 and 2014. In May 2013 average intensity of CO_2 flux increased more than threefold compared to the one observed in May 2012. One of the causes for the fluctuations in the values of this quantity can be upwellings – rises of colder deep waters to the surface, most often observed in May. The duration and intensity of upwellings during the survey carried out in May varied in different years. In 2010, the beginning of the observations fell at the final stage of upwelling, in 2012 a powerful upwelling continued for the most of the survey and in 2013 it lasted several days in the middle of the survey.

Deep waters are characterized by higher concentrations of inorganic carbon and compounds of nutrients in comparison with the surface layer waters. Due to the rise of deep waters, primary production processes are intensified and pCO_2 in the surface layer of waters decreases. Upwellings are rare phenomena, therefore their impact on the equilibrium between the carbonate system components in the coastal zone caused by water temperature decrease is of short-time and irregular nature.

Carbon dioxide exchange between the sea and the atmosphere is also affected by inter-annual variability of temporal boundaries of seasonal transitions. In particular, upwellings were not observed both in May 2011 and May 2014, but due to the early spring in 2014 the ranges of water temperature and CO_2 flux intensity variation were wider than in 2011.

In July 2010 a steady CO_2 evasion was observed, CO_2 flux average intensity was higher and the range of its variations was narrower than in May of the same year.

Just like in previous years, during the surveys carried out in May of 2013 and 2014, CO_2 evasion average intensity of which increased in comparison with the similar periods of previous years was observed.

According to observation data, at the end of the summer and early autumn hydrological season in 2010–2012 the state was close to the equilibrium one, average intensity of CO_2 flux between the sea and the atmosphere was significantly lower than in other seasons. At this time, the water area transition to a state characteristic of the cold season takes place. Temporal boundaries of such transition vary due to inter-annual variation of the water area hydrologic regime and meteorological conditions.

In 2010–2012 the range of CO_2 flux average intensity variation was relatively narrow: from –2.48 mmol $CO_2 \cdot m^{-2} \cdot atm^{-1} \cdot day^{-1}$ in October 2011 to 0.34 mmol $CO_2 \cdot m^{-2} \cdot atm^{-1} \cdot day^{-1}$ in October 2012. In September 2010 and in October 2011 CO_2 invasion from the atmosphere prevailed.

In September 2013, during most of the observations, the water temperature remained above 20 ºC, the evasion prevailed, and average value of CO_2 flux rate increased to 4.2 mmol $CO_2 \cdot m^{-2} \cdot atm^{-1} \cdot day^{-1}$.

In October 2014, persistent CO_2 invasion from the atmosphere was observed throughout the survey. Its average intensity exceeded the values recorded during the previous observations in the cold season. As a possible cause of such a change in CO_2 flux nature, one can consider high wind activity and intense sea waves during observations.

In November 2013 and in October 2014 the maximum amplitudes of CO_2 flux intensity variation were recorded. This could be due to intensive wind activity during these surveys.

Thus, in the cold season a steady CO_2 invasion from the atmosphere was characteristic of the study area. Its intensity increased from November 2012 and reached the maximum in October 2014. The exceptions were the separated observations in November 2013 when the storm caused an intensive mixing of coastal waters, resulting in a shift of equilibrium between the components of the carbonate system and a sharp increase in pCO_2 in the surface layer waters.

At the inter-annual scale, the amplitude of average flux intensity variations in warm and cold seasons reached 8.3 and 19.6 mmol $CO_2 \cdot m^{-2} \cdot atm^{-1} \cdot day^{-1}$, respectively.

Analysis of CO_2 flux diurnal variation in the coastal waters of the Black Sea revealed its features in different seasons. Diurnal variations of CO_2 flux average intensity are shown in Fig. 3. In the most of cases, at the small time scale CO_2 variation was poorly pronounced. Average parameters of morning, afternoon and evening observations carried out within one survey differed insignificantly: the difference between the maximum and the minimum values of CO_2 flux intensity was 0.3–2.6 mmol $CO_2\, m^{-2} \cdot atm^{-1} \cdot day^{-1}$.

In the cold season the range of the flux average intensity during the day was wider: from 0.3 to 16.7 mmol $CO_2\, m^{-2} \cdot atm^{-1} \cdot day^{-1}$. The maximum fluctuations were observed in November 2013 and in October 2014, which is due to the maximum amplitude of wind velocity values during these surveys.

Wind activity is an important but not the only factor affecting the intensity of gas exchange between the sea and the atmosphere. According to modern concepts, there are two main mechanisms in the CO_2 exchange between the water and the atmosphere – physical and biochemical. Due to this, seasonal variations of water hydrological parameters and the processes of vertical mixing (upwelling, in particular) affect the physical component. The effect of the physical mechanism is traced on small time scales, as it is determined by the displacement of equilibrium between the carbonate system components [6].

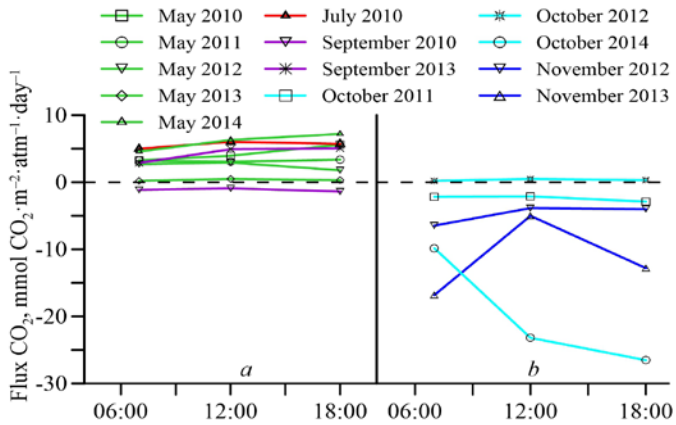

Fig. 3. Daily variation of CO_2 fluxes during warm (*a*) and cold (*b*) seasons in 2010–2014

In the functioning of biochemical mechanism two components are usually distinguished. The first one is a carbonate "pump", the functioning of which leads to the formation and sedimentation of calcium carbonate with the simultaneous release carbon dioxide with its evasion into the atmosphere:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + H_2O + CO_2. \quad (11)$$

The second component is a biological "pump", the functioning of which is due to primary production activity of hydrobionts:

$$CO_2 + H_2O \leftrightarrow CH_2O + O_2. \quad (12)$$

Coastal ecosystems are characterized by high intensity of biogeochemical processes. The prevalence of the biogenic or abiogenic component at a given point of time leads to the equilibrium shift in the systems (11) and (12). As a result, the coastal water area can rapidly move from carbon dioxide invasion from the atmosphere to its evasion.

In the warm season, the main source of CO_2 intake may be the destruction of autochthonous organic matter in the water area. The oxidative reactions ensures the formation of sufficient amounts of carbon dioxide to meet the needs of autotrophic organisms, as a result of which CO_2 is not a limiting factor for primary production processes. The decrease of oxidative process rate in the cold season leads to the fact that free CO_2 content in the surface layer declines. This forms the conditions for its invasion from the atmosphere.

Variability of the coastal runoff during the year can be attributed to the factors contributing to the seasonal variability of CO_2 flux. The maximum of precipitation falls on the cold season, and this leads to the increase in the volume of terrigenous runoff. The release of additional quantities of the nutrient compounds and suspended matter into the coastal waters affects the functioning of biota, particularly, it promotes the primary production processes.

Similar effect can be caused by anthropogenic factor in the area of research. There are no major sources of pollution, but agricultural activity is carried out in the adjacent territory and construction is underway. As a result, soil erosion which leads to the formation of fine particles is intensified, and compounds of nutrients are washed out from agricultural land. Their inflow into the coastal water area increases in autumn-winter period and it also affects the natural course of biogeochemical processes.

Conclusions

The analysis of CO_2 flux seasonal variability revealed that evasive direction prevails in a warm season and invasive one – in a cold season. Temporal boundaries of inter-seasonal transitions of the water area regime vary from year to year.

CO_2 flux variability on a small time scale is characterized by a narrower range in comparison to the inter-seasonal and inter-annual variability. In order to interpret the variability of gas exchange between the sea and the atmosphere on different time scales, it is necessary to analyze a number of factors of different nature.

CO_2 flux direction change can serve as an indirect criterion for assessing the anthropogenic impact on the functioning of the carbon cycle in the water area.

Determining the causes of the revealed features of CO_2 fluxes temporal variability require further comprehensive studies.

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