Variability of Equilibrium Partial Pressure of Carbon Dioxide ($p\text{CO}_2$) and Concentration of Dissolved Inorganic Carbon ($T\text{CO}_2$) in the Black Sea Coastal Waters in 2010–2014

D.S. Khoruzhii

Marine Hydrophysical Institute, Russian Academy of Sciences, Sevastopol, Russia
e-mail: khoruzhiy@mhi-ras.ru

Based on direct field measurements of $p\text{CO}_2$ and $T\text{CO}_2$ carried out in 2010–2014 in the Black Sea coastal waters, dynamics of inorganic carbon on different time scales is considered. It is shown that the highest variability of both parameters on a small time scale is observed during the seawater spring warming resulting from the upwelling impact. The diurnal variations of the $p\text{CO}_2$ and $T\text{CO}_2$ values (in course of the analogous period) demonstrate no pronounced tendencies; they are characterized by significant inter-annual variability. In course of summer and autumn-winter hydrological seasons, the diurnal variation of $p\text{CO}_2$ and $T\text{CO}_2$ is insignificant. The minimum values of $T\text{CO}_2$ are observed in summer and autumn-winter, whereas the maximum ones – in spring during upwelling. The $p\text{CO}_2$ value in seawater achieves its maximum in late spring and minimum – in late autumn–early winter hydrological season. The results of $p\text{CO}_2$ measurements in a warm season prove the previous notions on the Black Sea waters as a source of CO_2 emission to the atmosphere. Carbon dioxide is assumed to be more intensively bound and transformed into the other forms of inorganic carbon in a cold season. Possible reason of this phenomenon can consist in increase of the suspended matter inflow to the water area due to more frequent storms and growth of the terrigenous runoff volume. In cold season, the lower $p\text{CO}_2$ is characteristic of seawater and the higher one – of the atmosphere. Complex character of $p\text{CO}_2$ temporal variability testifies to heterogeneity and different intensity of the factors influencing this value in different seasons.

Keywords: equilibrium partial pressure of carbon dioxide ($p\text{CO}_2$), total dissolved inorganic carbon ($T\text{CO}_2$), diurnal variation of $p\text{CO}_2$ and $T\text{CO}_2$, inter-diurnal changes of $p\text{CO}_2$ and $T\text{CO}_2$, seasonal variations of $p\text{CO}_2$ and $T\text{CO}_2$, the Black Sea coastal waters, upwelling.

Sea areas are among the objects, considering within the framework of study of global carbon cycle in the terrestrial biosphere, which deserve special attention. For obtaining more accurate assessment of separated areas contribution to the transport and transformation processes of inorganic carbon compounds, we zone them basing on different criteria. This is carried out due to inhomogeneity of biochemical characteristics of the seas and oceans. Sea area structure includes relatively homogeneous zones. Within them biochemical and other water parameters change insignificantly, or their changes are defined by the known patterns which are characteristic of the considered zones only. Distinguishing of sea and ocean shelf areas is due to specificity of their biochemical characteristics. With a relatively small area (slightly more than 7 % of the entire ocean surface area), these zones significantly contribute to the process of carbon dioxide (CO_2) exchange between hydrosphere and atmosphere. According to existing assessments, more than 21 % of total CO_2 sink from the atmosphere to the ocean falls on shelf water areas [1, 2].

The role of coastal regions in CO_2 transport is conditioned by high intensity of biochemical processes in these zones. Inhomogeneity of shelf areas (in comparison with open water area parts) is their distinctive feature. The features of hydro-

chemical coastal water composition are affected by a number of factors: continental runoff, biogeochemical processes in the surf zone and anthropogenic activity. Vertical mixing of water, currents and biota impact [3] also make their contribution. Due to small volume of coastal waters (less than 1 % of the World Ocean overall volume [1]), the change of their chemical composition (including the equilibrium shift between the carbonate system components) is highly dynamic.

The Black Sea carbonate system features were previously considered by several authors [4 – 7]. The results, represented in these papers, were obtained by calculating carbonate system components using the pH value (pH) and total alkalinity (*Alk*) as the initial data. Measuring equipment improvement allowed us to shift to direct measurements of equilibrium carbon dioxide ($p\mathrm{CO_2}$) partial pressure and concentration of inorganic carbon ($T\mathrm{CO_2}$) dissolved in the seawater. As a result, the uncertainty, arising upon computational determination of these values, decreases. Features of $T\mathrm{CO_2}$ and $p\mathrm{CO_2}$ variation on a small time scale in surface waters in warm season were previously considered in [8 – 10].

In the present paper the features of diurnal and interdiurnal variations of $p\mathrm{CO_2}$ and $T\mathrm{CO_2}$ in different seasons, as well as seasonal and interannual variability of the analyzed the values are discussed. The dependence of these values on hydrologic conditions is also considered.

Research area and techniques. $p\mathrm{CO_2}$ and $T\mathrm{CO_2}$ direct measurements have been carried out during the expeditionary investigations, regularly performed by staff members of the sea biogeochemistry department of Marine Hydrophysical Institute since 2009. The data obtained in 2012 – 2014 are of particular interest because two of nine expeditions performed at this time were carried out in late autumn – early winter hydrological seasons (late November – early December). As a result, an extensive experimental data array was collected. The analysis of these data allows us to consider $T\mathrm{CO_2}$ and $p\mathrm{CO_2}$ variability both at synoptic time scale and at the level of seasonal and interannual changes.

Equilibrium $p\mathrm{CO_2}$ and $T\mathrm{CO_2}$ concentration measurements were carried out at stationary oceanographic platform, situated near Katsiveli (the Southern Coast of the Crimea). The platform is located at 430 m distance from the shore, the depth in sampling point makes up 27 m.

Water for the study was collected by submersible vibration pump from three horizons: 0, 0.5 and 5 meters. A float was applied for the pump submersion depth fixation. The sampling was carried out three times a day: at 7:00, 12:00 and 18:00. Simultaneously with the sampling, a hydrologic probing (water temperature and salinity profiles were calculated by its results) was carried out.

For $p\mathrm{CO_2}$ and $T\mathrm{CO_2}$ measuring *AS-C*3 instrumental complex (based on 7000*DP* infra-red nonscattering analyzer) was applied. Measuring equipment calibration and $p\mathrm{CO_2}$ and $T\mathrm{CO_2}$ determination were performed according to manufacturer documentation [11, 12].

Measurement technique is described in detail in [13]. The water was pumped through the equilibrator connected with *LI*-7000*DP* analyzer measuring cell to measure $p\mathrm{CO_2}$. An air flow, circulating within closed-loop system between the equilibrator and measuring cell of the apparatus, was generated with built-in pump analyzer. When passing through the equilibrator, the air contacted with the water under analysis. As a result, $\mathrm{CO_2}$ partial pressure in the gaseous phase came to equilibrium with the liquid phase in a certain period of time (about 30 min). An occurrence of equilibrium was determined by the termination of $p\mathrm{CO_2}$ value

changes in the analyzer measuring cell. The same instrumental complex was applied for TCO_2 concentration measuring.

Water samples for TCO_2 concentration determination were collected into the bottles with ground-in stopper and they were analyzed immediately after sampling, without storage and conservation. An aliquot of 0.5 cm^3 of water was sampled into the apparatus reactor applying *KLOEHN* digital pump (which is a part of the instrumental complex) to measure TCO_2. Acidic reactant (ortho-phosphoric acid solution with mass fraction of 10 %) was injected into the reactor in the same manner. As a result of reaction with the acid, all inorganic forms of carbon were transformed into CO_2 which got into the analyzer measuring cell with the gas carrier current. CO_2 concentration in the aliquot was determined by the absorption peak area. It was calculated by the computer program supplied with the analyzer. On the basis of obtained peak area values, TCO_2 concentration in the water under analysis was calculated by the calibration graph (constructed using a standard solution of sodium carbonate). Measurement technique was previously described in detail in [13].

Results and their discussion. Low salinity of the Black Sea waters and high inorganic carbon concentration in their composition are the results of significant volume of continental runoff (which gets into the sea) and generation of great amounts of CO_2 in the deep part and at the bottom of the sea. In broad terms, the Black Sea water carbonate system is similar to the one of the ocean. At the same time, it is characterized by a number of specific features such as carbonate equilibrium "shift". Due to it free CO_2 percentage in the Black Sea surface waters is about 0.5 % of the total inorganic carbon concentration. For the ocean waters it makes up 1 %. Despite the equilibrium shift and CO_2 relative proportion decrease, the absolute value of its equilibrium partial pressure in the Black Sea waters appeared to be higher than in the ocean. This is due to high TCO_2 concentration. Previous calculations, carried out using pH and *Alk* measurement results, indicate that at the majority of the basin the Black Sea surface waters are oversaturated with free CO_2. Equilibrium pCO_2 value in the Black Sea surface layer was estimated at 400 – 500 µatm, and it exceeds the corresponding value for the atmosphere [7]. Thus, the Black Sea can be regarded as a source of CO_2 release into the atmosphere. The results of equilibrium pCO_2 direct measurements in the Black Sea surface waters (obtained during the expeditionary investigation in 2010 – 2014) proved, in many ways, the conclusions previously drawn on the basis of calculations.

Summarized results of measurements, carried out in spring-summer (*a*) and autumn-winter (*b*) hydrologic seasons in 2010 – 2014, are represented in Fig. 1. As it was noticed in previous papers [8, 9], in spring and summer of 2010 – 2014 pCO_2 value in the surface waters exceeded the one for the atmosphere in most cases.

In 2012 – 2014 this trend continued: the highest pCO_2 values and maximum amplitude of their changes in the surface layer were observed during the survey performed in May. The increase of pCO_2 mean value in the water was observed in 2011 – 2013 during the spring warming. However, in 2014 this magnitude decreased to the values of 2010 – 2011. This may indicate the absence of a steady trend in its interannual variations.
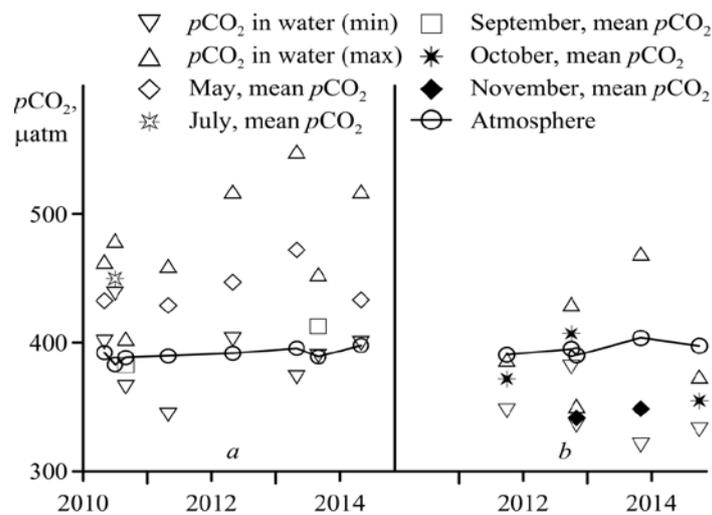
Fig. 1. Variability of pCO_2 in spring-summer (*a*) and autumnal-winter (*b*) hydrological seasons 2010 – 2014

The central month of spring hydrologic season (May) is characterized by the highest hydrologic characteristic variability due to intensive vertical mixing of waters. It is caused by seasonal warming and upwellings (the motion of cold deep waters, enriched with nutrients and inorganic carbon, towards the surface). Upwellings were observed during the survey carried out in May 2010, 2012 and 2013. Their duration was different: in 2010 the beginning of observations fell on the upwelling final phase, in 2012 upwelling lasted throughout most of the survey and in 2013 it lasted for several days in the middle of the survey. The range of pCO_2 values has increased due to the upwelling.

The pattern had been changing during the survey carried out in late summer – early autumn hydrologic seasons. On the basis of direct measurements it was determined that in this season Water-Atmosphere system reached equilibrium state, which is typical for autumn season. The decrease of pCO_2 in the water was observed at this time. Its value became lower than the corresponding value for the atmosphere. Temporal boundaries of equilibrium state are unstable. For instance, in September 2010 and 2013 (i. e. at the end of summer hydrologic season) pCO_2 values in the water were, in several cases, lower than mean values for the atmosphere during each survey. On the contrary, in October 2012 in most cases there were more pCO_2 in the water than in the atmosphere. In October 2014 it was observed a pattern typical for the cold season: during the entire survey pCO_2 content in the water was significantly lower than in the atmosphere. Such variability can be explained by delay or advance of hydrologic season onset due to meteorological features of some years.

Two surveys were carried out in late November – early December 2012 and 2013. The time of observations corresponded to the hydrologic autumn, but the results obtained during these expeditions differed from the values typical for the beginning of autumn season. During the entire time of observations in November – December 2012, pCO_2 content in the seawater was lower than the corresponding

figure in the atmosphere. Similar results were also obtained during the autumn observations in 2013. A feature of survey performed in 2013 was a transient pCO_2 increase after the storm, which resulted, simultaneously with pCO_2 rise, in change of other hydrochemical parameters: sharp increase of TCO_2 and pH decrease.

pCO_2 variation in different seasons of 2012 – 2014 is represented in Fig. 2. In each case time is expressed in days from the beginning of the survey. Expeditions performed in May were more durable, and this explains the asymmetry of the graphs.
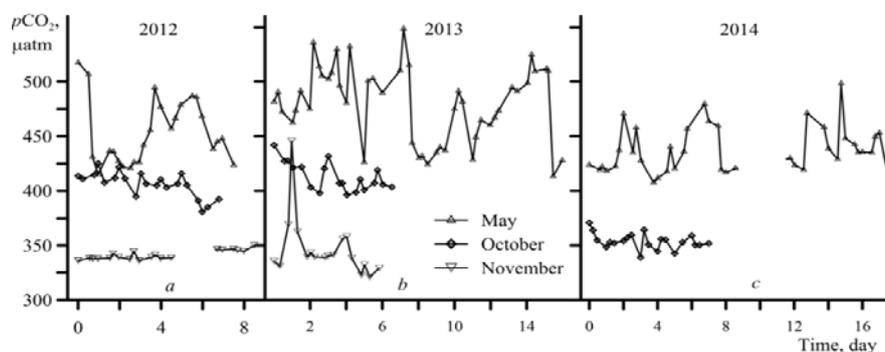

Fig. 2. Changes of pCO_2 in surface layer of the Black sea coastal waters near the South coast of the Crimea in different seasons 2010 – 2014

During the surveys carried out in warm season pCO_2 values in the water were higher than the corresponding value for the atmosphere. Decrease of CO_2 equilibrium pressure in the water was observed during upwellings, but even in these cases it remained higher than in the atmosphere [8].

In all cases maximum values of pCO_2 in the water were observed during the spring surveys and minimum ones – during the autumn surveys.

pCO_2 diurnal variation in different seasons is represented in Fig. 3. As is obvious from the graphs, most of autumn season surveys are characterized by narrow range of pCO_2 variations during the day, as well as the absence of pronounced regularities in the diurnal variations of this parameter. Meteorological and hydrological conditions changed from year to year, and due to this fact features of pCO_2 diurnal variation were also unstable.

pCO_2 value had the highest variability during the surveys carried out in May. During the autumn surveys, including the ones performed in late November, pCO_2 values were within a more narrow range.

In October 2012 the weather was fine during the entire period of observations and water temperature was above 20 °C. The highest pCO_2 value variability at this period was observed at day. This could be a result of both insolation, which leads to the warming of the surface layer of waters, and biota impact.

In November 2012 pCO_2 varied within the narrow range and remained significantly lower than the corresponding parameter for the atmosphere. Variations at daily scale were insignificant during this survey. A similar pattern was also observed in November 2013, but in this case a transient significant increase of $pCO2$ was noticed after the storm. Other hydrochemical parameters, pH and TCO_2 concentration, also changed due to the storm.
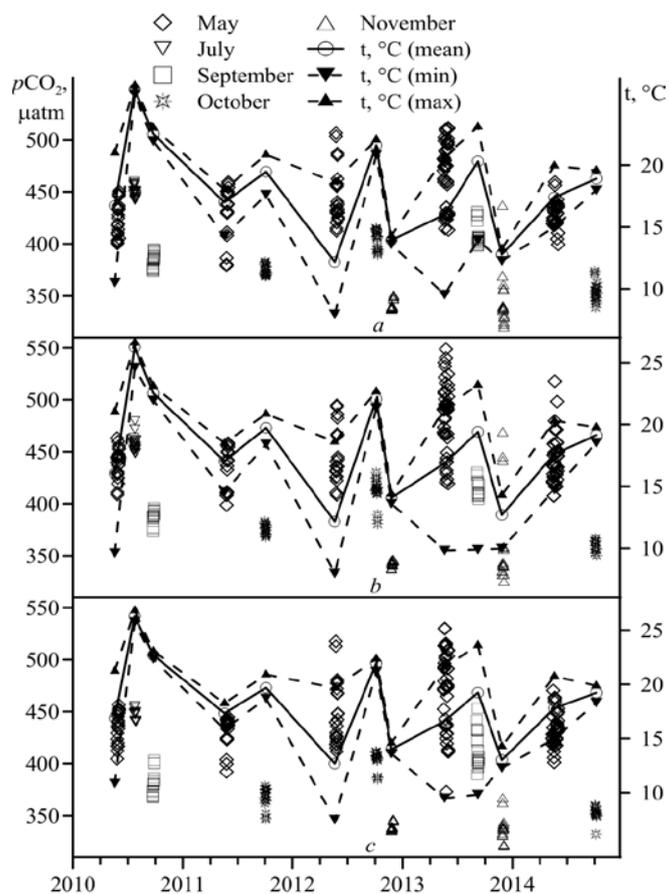
Fig. 3. Diurnal variation of pCO_2 and temperature of water near the shores of the Crimea in the morning (*a*), in the daytime (*b*), in the evening (*c*)

In October 2014, pCO_2 value in the surface layer of water was lower than in the atmosphere during the entire observational period. The widest pCO_2 value range was observed in the morning.

In warm season the lowest pCO_2 value variability was noted in June and September 2010. In both cases it was observed an insignificant variability of hydrological characteristics. In particular, water temperature varied within the narrow range. Wider range of pCO_2 values was characteristic of the daytime, and in September – of the evening hours.

In September 2013 water temperature variation amplitude was significantly higher due to transient upwelling observed during the survey. At this time pCO_2 values were in wider range and their maximum amplitude was observed in evening.

The highest pCO_2 variability is characteristic of the surveys carried out in May. Spring season is characterized by significant dynamics of hydrological conditions caused by both seasonal warming of water and repeatedly occurred upwellings. Water temperature sharply decreased and water hydrochemical characteristics changed due to these upwellings. Maximum pCO_2 variations were observed in the beginning and in the end of upwelling. Inhomogeneity of

conditions in different years does not allow us to distinguish an unambiguous trend in $p\text{CO}_2$ diurnal variability during the spring warming of waters.

In May 2010 and 2012 the width of range (within which $p\text{CO}_2$ values were) insignificantly changed during the day, but in 2012 variation amplitude was significantly greater and $p\text{CO}_2$ absolute values were higher than in 2010. In May 2013 the highest $p\text{CO}_2$ variability was observed at day and in evening.

$p\text{CO}_2$ diurnal variation also changed from year to year in the absence of upwellings. Thus, in May 2011 $p\text{CO}_2$ variability was higher in the morning and in May 2014 – at the day and in the evening.

Temporal inhomogeneity of $p\text{CO}_2$ diurnal variation (typical for the surveys performed in May) may be explained by unequal effect of some factors in different years. Particularly, variability of hydrological and meteorological conditions may be among these factors. Higher $p\text{CO}_2$ mean values in May 2013 (in comparison with May 2012) may have been caused by abnormally warm winter and early spring in 2013. The results of observations carried out in May 2012 and 2013 were similar in general terms. In both cases significant $p\text{CO}_2$ variations at synoptical scale were observed. This may take place due to upwellngs which occurred during the both surveys.

$T\text{CO}_2$ concentration is one of conservative parameters and its interannual variations were less pronounced than the ones of $p\text{CO}_2$. $T\text{CO}_2$ dynamics in spring – summer and autumn – winter seasons is represented in Fig. 4.
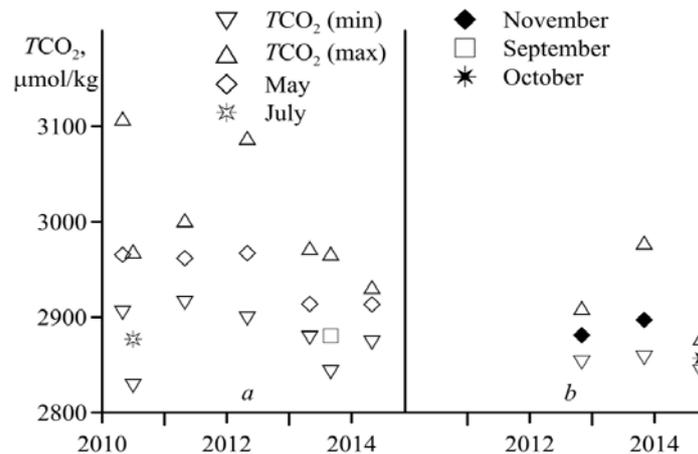

Fig. 4. Seasonal variation of $T\text{CO}_2$ in 2010 – 2014 (*a* – spring-summer, *b* – autumnal-winter hydrological seasons)

The maximum concentrations of $T\text{CO}_2$ were observed during spring warming of waters in 2010 and 2012. In both cases $T\text{CO}_2$ concentration increase and the maximum amplitudes of variation of this parameter were caused by upwellings. The sharpest $T\text{CO}_2$ concentration variations were observed at the beginning and in the end of upwellings, as well as for $p\text{CO}_2$ concentration. It should be noted that $T\text{CO}_2$ concentration increases were transient and did not affect mean value of this magnitude. In particular, in May 2010 – 2012 $T\text{CO}_2$ mean concentration varied within a narrow range, although in two cases an upwelling took place. In 2011 it was not observed.

In May 2013 and 2014 TCO_2 mean concentrations were close but in both cases they were lower than in previous years. TCO_2 concentration range in 2013 was narrower than in the previous year, despite the fact that upwellings were observed in both cases.

In May 2014 it took place a gradual water temperature increase without sudden drops. As a result, TCO_2 concentration varied within narrower interval.

The minimum TCO_2 mean concentrations were typical for summer and autumn – winter seasons, but in warm season TCO_2 variation amplitude was higher than in late autumn.

TCO_2 diurnal variation is represented in Fig. 5. In most cases TCO_2 concentration variations are poorly pronounced during the day. This may be explained by the fact that significant TCO_2 fluctuations are observed only under the conditions of water hydrological characteristic change.

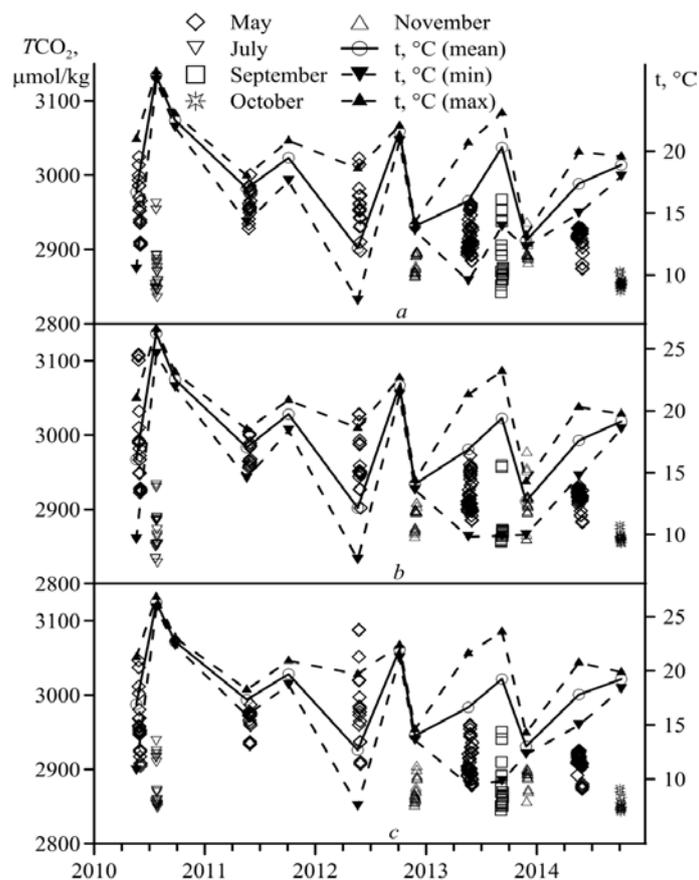**Fig. 5.** Diurnal variation of TCO_2 and temperature of water near the shores of the Crimea in the morning (*a*), in the daytime (*b*), in the evening (*c*)

Owing to the great number of parameters affecting pCO_2 and TCO_2 values in surface waters, it is difficult to determine the contribution of separate factors. As a rule, identification and quantification of feedback scale, caused by individual

impact of each factor, is impossible due to inhomogeneity of affecting parameters. This is why an empirical criterion – Pearson correlation coefficient (r) was applied to evaluate the bonding force between the parameter under study and affecting factor.

Initially, temperature was considered as the main parameter affecting the equilibrium between the carbonate system components and determining the value of equilibrium $p\text{CO}_2$ [8]. Such choice was based on temperature dependence of carbon dioxide and calcium carbonate (CaCO_3) solubility in the water. In the form of CaCO_3 inorganic carbon is inclusive of hydrobionts exoskeleton as well as deposits and buries in bottom sediments. Water temperature increase results in solubility decrease of both CO_2 and CaCO_3 [14, 15].

Temperature effect on CO_2 solubility is described by Henry's law [14]:

$$\left[\text{CO}_2\right] = K_0 f\text{CO}_2, \tag{1}$$

where [CO_2] is dissolved carbon dioxide concentration; K_0 is Henry's constant, its value depends on temperature and salinity; $f\text{CO}_2$ is carbon dioxide fugacity (the value which is close to equilibrium partial pressure, but it takes into account CO_2 difference from the perfect gas).

The following equation [14] is used to calculate fugacity of dissolved CO_2 in seawater:

$$f\text{CO}_2 = p\text{CO}_2 \exp\left(p\frac{B + 2\delta}{RT} \right), \tag{2}$$

where p is the total pressure in the system; R is the universal gas constant; T is the absolute temperature; B and δ are the coefficients calculated by the following equations [14]

$$B = (-1636.75 + 12.0408T - 3.27957 \cdot 10^{-2}T^2 + 3.16528 \cdot 10^{-5}T^3)10^{-6}, \tag{3}$$

$$\delta = (57.7 - 0.118T)10^{-6}. \tag{4}$$

Henry's constant is calculated by the equation proposed in 1974 by Weiss (*R.F. Weiss*) [14]:

$$\ln K_0 = \frac{9345.17}{T} - 60.2409 + 23.3585\ln\left(\frac{T}{100}\right) +$$

$$S\left[0.023517 - 0.00023656T + 0.0047036\left(\frac{T}{100}\right)^2 \right], \tag{5}$$

where S is the salinity.

Time variation of coastal surface water temperature is complex: the changes of this quantity are caused by the processes occurring on a small time scale, along with the seasonal trends. In particular, intensive insolation leads to surface layer temperature increase, resulting in CO_2 solubility decrease. Upwellings cause a sharp surface water temperature decrease and CO_2 solubility increase. The contribution of these phenomena at different time scales is non-constant and it significantly varies in different seasons.

The results from previous studies [8] indicated the essential role of temperature as a factor affecting $p\text{CO}_2$ value during the spring warming of water.

Correlation analysis of data arrays obtained during different surveys was applied to evaluate the bonding force between the temperature and $p\mathrm{CO}_2$. The results of the analysis revealed that water temperature effect on $p\mathrm{CO}_2$ is non-constant and it significantly changes on both inter-seasonal and inter-annual time scales. To evaluate the bonding force between the temperature and $p\mathrm{CO}_2$, the determination coefficient (squared Pearson correlation coefficient (r^2)) was also applied. According to the results of such evaluation, the strongest bonding force between the temperature and $p\mathrm{CO}_2$ was observed in 2012 and 2013 during the spring warming of waters: r^2 value made up 0.807 and 0.847, respectively. In other cases the force was weaker: 0.630 in 2011, 0.477 in 2010 and 0.239 in 2014.

Thus, under conditions of spring warming of waters, high bonding force between the temperature and $p\mathrm{CO}_2$ was observed only in two of five cases, in other cases it appeared to be moderate or weak. Noticeable relation was observed in October 2012 ($r^2 = 0.68$), whereas during other surveys it was weak or absent.

Therefore, water temperature can not be considered as the main factor affecting $p\mathrm{CO}_2$ value in the coastal waters. Above described relationship between the temperature and CO_2 solubility may be distorted or masked under effect of other factors.

Upwellings significantly affect $p\mathrm{CO}_2$ value in the coastal waters. Due to them not only sharp surface water temperature decrease takes place, but also a change of water hydrochemical characteristics. Deep waters are characterized by high concentrations of dissolved inorganic carbon and nutrient compounds. Upwelling causes vertical mixing of coastal waters and these compounds get into the surface layer. This results in primary production process intensification accompanied by CO_2 uptake in the coastal waters.

According to contemporary conceptions, equilibrium $p\mathrm{CO}_2$ value in the surface waters (and, as a consequence, the direction of CO_2 fluxes between the sea and the atmosphere) are caused by the functioning of two mechanisms: physical and biochemical. Functioning of the first mechanism is determined by the seawater physicochemical properties (in particular, by temperature and chemical composition peculiarities). As it was mentioned above, in most cases the role of temperature can not be regarded as a primary one.

Action of the second mechanism (the biochemical one) is due to functioning of coastal water ecosystem biotic component. Hydrobionts vital activity has a dual effect on free CO_2 concentration and thus the biochemical mechanism is usually divided into two components [2, 16]. The first one is a carbonate "pump", which provides calcium carbonate formation and sedimentation with simultaneous carbon dioxide release and its evasion into the atmosphere:

$$\mathrm{Ca}^{2+} + 2\mathrm{HCO}_3^- \rightleftarrows \mathrm{CaCO}_3{\downarrow} + \mathrm{H}_2\mathrm{O} + \mathrm{CO}_2{\uparrow}. \tag{6}$$

Carbonate "pump" functioning results in $p\mathrm{CO}_2$ increase in the seawater. Calcium carbonate is produced by a number of hydrobionts, and primarily by coccolithophorides (microalgae) which generate about 50 % of total CaCO_3 in the ocean [17, 18].

According to equation (6), Ca^{2+} ion concentration increase and CaCO_3 solubility decrease promotes the rise of free CO_2 concentration. Dissolution and dissociation of calcium salts from the bottom sediments, as well as and terrigenous

runoff into the sea, are sources of Ca^{2+} ions. Runoff volume and its composition change throughout the year, complicating the assessment of its effect on coastal water condition. CO_2 and $CaCO_3$ solubility decrease, due to water temperature rise, results in increase of equilibrium pCO_2 in the water and intensification of CO_2 evasion into the atmosphere [15, 19].

The second component of biochemical mechanism is represented by biological "pump":

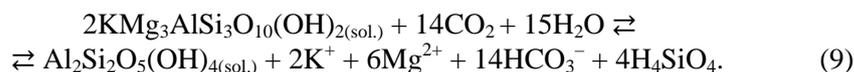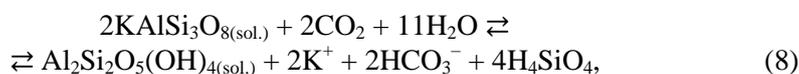$$CO_2 + H_2O \rightleftarrows CH_2O + O_2. \tag{7}$$

Photosynthetic organisms, which perform carbon dioxide assimilation during the organic substance formation, provide the shift of equilibrium to the right. CO_2 release and the shift of equilibrium to the left are the results of biological oxidation.

The complexity of unambiguous interpretation of living organisms effect on pCO_2 value can be seen on the example of coccolithophorides, which currently are one of dominant phytoplankton species in the Black Sea. As photosynthetic organisms, these microalgae consume free CO_2 from the seawater, thereby reducing its equilibrium partial pressure. At the same time, when microalgae fission and grow they produce $CaCO_3$ which forms the basis of external skeleton of their cells. As a result, pCO_2 in the water increases according to the equation (6).

The dominance of certain processes of both biogenic and abiogenous nature (causing the equilibrium shift in the systems (6) and (7)) in the ecosystem at the given time period may results in either increase or decrease of equilibrium pCO_2 in the surface waters.

pCO_2 increase is observed when carbonate "pump" provides $CaCO_3$ formation and biological one provides organic matter oxidation.

One more source of uncertainty in assessing the expected CO_2 concentration is the fact that equilibrium shift between the carbonate system components is affected, along with $CaCO_3$, by other minerals presenting in the composition of bottom sediment and suspended matter (which comes with terrigenous runoff). In particular, the interaction with clay materials is described by the following equations [19]:

$$2KAlSi_3O_{8(sol.)} + 2CO_2 + 11H_2O \rightleftarrows$$
$$\rightleftarrows Al_2Si_2O_5(OH)_{4(sol.)} + 2K^+ + 2HCO_3^- + 4H_4SiO_4, \tag{8}$$

$$2KMg_3AlSi_3O_{10}(OH)_{2(sol.)} + 14CO_2 + 15H_2O \rightleftarrows$$
$$\rightleftarrows Al_2Si_2O_5(OH)_{4(sol.)} + 2K^+ + 6Mg^{2+} + 14HCO_3^- + 4H_4SiO_4. \tag{9}$$

As a result of direct reaction (8), kaolin is formed from the feldspar and in reaction (9) kaolin is formed from the biotite. In both cases direct reaction is accompanied by CO_2 consumption which leads to decrease of its concentration in the water. The decrease of free CO_2 equilibrium partial pressure in the surface waters takes place due to its sequestration.

The dependence of coastal water hydrochemical composition formation on the mentioned processes is more pronounced than for open water areas. Firstly, small depth and intensive vertical mixing in the area under investigation heighten the bottom sediment effect not only on the composition of bottom layer, but also on the entire water column. Secondly, equilibrium between the carbonate system components affects the suspended matter intake caused by both terrigenous runoff and surf.

Conclusions. The results of $p\text{CO}_2$ and $T\text{CO}_2$ direct measurements proved previously existed concept of the Black Sea waters as a source of CO_2 emission into the atmosphere.

The data of observations, carried out in autumn, indicate that in a cold season CO_2 equilibrium partial pressure in the Black Sea coastal waters is lower than in the atmosphere. Due to this fact CO_2 invasion from the atmosphere into the water is observed.

One may assume that in a cold season more intensive bonding of carbon dioxide and its transformation into other forms of inorganic carbon take place. This could be caused by the increase of suspended matter inflow into the water area due to more frequent storms and of terrigenous runoff volume increase.

In most cases water temperature can not be considered as the main factor affecting $p\text{CO}_2$ value in the coastal waters.

Quantitative estimation of biota effect on $p\text{CO}_2$ and $T\text{CO}_2$ variation requires further comprehensive study of this problem.

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