Carbonate System Characteristics of the Sevastopol Bay Waters in 2009–2015

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A 20% increase of the carbon dioxide concentration in the atmosphere during the last century and a dramatic increase in nutrient load to marine systems due to human activity have resulted in pronounced carbon cycle transformation in coastal areas. The results of the inorganic part of the carbon cycle and its transformation in the Sevastopol Bay (the Black Sea) are presented in this study. The bay is a semi-enclosed coastal area that has been under heavy anthropogenic pressure over the last century. Here we present data on dynamics of the inorganic part of the carbon cycle from 2009–2015. Values of pH and total alkalinity were obtained analytically, whereas CO₂, HCO₃⁻, CO₃²⁻ concentrations and pCO₂ values were calculated. Dissolved inorganic carbon and its partitioning into CO₂, HCO₃⁻, CO₃²⁻ demonstrate the state of the carbon cycle and its evolution. Our results show a negligible upward trend of dissolved inorganic carbon concentration (~1%), which may indicate the ability of the bay ecosystem to the "self-healing". However, carbon dioxide partial pressure significant growth in the bottom and surface layers of the bay (up to 23%) indicates negative changes, resulting to the carbon cycle transformation. Moreover, currently the Sevastopol bay waters are in a state of invasion, but, according to the calculations, there is a downward trend of the atmospheric carbon dioxide flow, and it is possible that the invasion can be replaced by evasion in 2018.

Keywords: carbon cycle, carbonate system, carbon dioxide partial pressure, ocean-atmosphere gas exchange, the Sevastopol Bay (the Black Sea).

DOI: 10.22449/1573-160X-2016-3-36-46

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Introduction. Coastal ecosystems are the points of keen interest for the investigations. First of all, this is due to the necessity of studying of their functioning and stability as well as dynamics and the mechanisms of possible changes under natural and anthropogenic influence, because they have a quite fast response to any changes in the ecosystem. The problems of natural resource safety, development of new approaches for ecosystem state monitoring and assessment, determination of their ecological capacity in the conditions of increasing anthropogenic pressure [1] becomes particularly actual.

Long-term observations reveal the fact that ecosystems, being under sufficient anthropogenic pressure, often continue to provide a stability of natural cycles, biomass production and utilization of substances which are harmful for the biota. This ability can be explained by buffer capacity of ecosystems that allows saving a lot of their initial characteristics, providing such properties as balance preservation, natural cycle locking in the system and its “self-recovery”. One of the most important marine buffer systems is the carbonate system as a component of biochemical carbon cycle which provides cycling of matter. The carbonate system mainly determines the pH. Any deviations of pH, e. g. toward the acidic environment (pH < 7) leads to the negative consequences for the ecosystems: an appearance of reduced forms of heavy metals and other toxic components in the water column (so-called secondary pollution of water), dissolution of coral reefs, carbonate sediments and mollusk shells with carbonate skeleton at their basis. Elements of carbonate system of waters (carbonate ions, bicarbonate ions, dissolved carbon dioxide, carbonic acid and hydrogen ions) are very sensitive to
any changes of biogeochemical and physical parameters taking place in coastal marine ecosystems [2]. Temperature, pressure and salinity changes affect redistribution of inorganic carbon forms. Organic carbon production, as well as its oxidation and exchanging processes at the bottom sediment and the “sea-atmosphere” boundaries determine the total inorganic carbon content in the water [2]. It is quite difficult to distinguish between the effect of biotic and abiotic processes, and therefore the change of carbonate system parameters is a consequence of a complex effect.

Climatic changes, increase of atmospheric carbon dioxide concentration over the past 200 years by more than 20 % [3], as well as a significant inflow of nutrients to the marine ecosystems due to human activities have resulted in carbon cycle transformation in coastal waters. Such changes as a decrease of pH, significant growth of dissolved carbon dioxide [4] and decrease of oxygen concentration in the bottom layer of the water column have been noticed. Thus, the assessment of carbonate system state has not only important scientific task, but also an applied one.

The Sevastopol Bay is a clear example of a coastal area that is under continual heavy anthropogenic pressure. Sewage waters and fuel remains (due to maritime activities) are an additional source of pollutants (including organic carbon and nutrients) for the waters of the bay. The effect of hydrodynamic factors and excavation of bottom sediments results in its disturbance and redeposition. This causes a secondary pollution of the water column. Moreover, a restricted water exchange with the open sea supports intensive organic carbon accumulation in the bay, and it also has negative consequences on its ecological state.

The components of carbonate system and carbon cycle in the Sevastopol Bay had been previously investigated by the authors of [4 – 7]. It was found that before 2008 mean annual total dissolved inorganic carbon $\text{T} \text{CO}_2$ had not significantly changed; carbon dioxide partial pressure in the water column had been increased till 2005, and during 2005 – 2008 period there had been no tendency to its increase or decrease. The coastal areas and estuaries are characterized by carbon dioxide emission to the atmosphere, but the waters of the bay absorbed $\text{CO}_2$ from the atmosphere and its flux increased [4].

The purpose of the paper is to continue the investigation of long-term dynamics of carbonate system components and the Sevastopol Bay carbon cycle on the basis of data obtained during the studies carried out in 2009 – 2014. These studies also include the forecast of coastal area carbon cycle stability.

**Materials and techniques.** Data were obtained in the Sevastopol Bay during 2009 – 2015 (Fig. 1). The dissolved oxygen concentration, salinity, pH and total alkalinity values were determined (according to the hydrochemical study techniques [8]) in the surface and bottom water samples with the Niskin bottles. Total alkalinity and pH were measured experimentally. Total alkalinity was determined by direct titration with potentiometric end point of 50 ml of seawater by 0.02 N hydrochloric acid solution [8] using the Dosimat 765 high-precision piston burette by Metrohm (Switzerland). When measuring 10 parallel samples, standard deviation did not exceed 0.005 µM. pH was determined with pH meter I-160 with NBS buffer solutions [9]. The standard deviation of 10 parallel probes did not exceed 0.02 pH units. Carbon dioxide concentration (CO$_2$), its partial pressure ($p\text{CO}_2$), concentrations of carbonate (CO$_3^{2-}$) and bicarbonate (HCO$_3^-$) ions were calculated. Carbonic acid constants, recommended by Marine Science Department of UNESCO [10], were used. It was assumed that boron is a conservative element.
and its concentration is proportional to the salinity. Therefore borate component of the total alkalinity was calculated as a function of salinity [11]. The effect of water, phosphoric, sulfuric, hydrofluoric and other acids presented in the seawater in low concentrations on the alkalinity value was not taken into account. Calculation methods of carbonate system components were described in detail in [3].

![Fig. 1. Sampling locations in the Sevastopol Bay in 2009 – 2015](image)

The amount of $\text{CO}_2$ flux at the sea surface was found using the technique, proposed in [12].

Data from station 1 were not taken into account for the calculation of average annual and seasonal values of carbonate system components. This is due to significant effect of Chernaya River fresh waters on hydrochemical characteristics, so the parameters were calculated with regard for the marine water of the Sevastopol Bay.

**Discussion of the study results.** Dissolved part of carbonate system components of the seawater can be represented as a system of reversible processes:

$$\text{CO}_2 \text{ (atm.)} \leftrightarrow \text{CO}_2 \text{ (diss.)} \leftrightarrow \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^- \leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+.$$

The study results concern the analysis of each component (of above mentioned processes for 2009 – 2015) in the Sevastopol Bay waters.

Total amount of dissolved $\text{CO}_2$, $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ forms is called the total dissolved inorganic carbon:

$$T\text{CO}_2 = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}].$$

This parameter is an integral characteristic which reflects the stability of carbonate equilibriums and relationships between all the components. Thus, it can be an indicator of carbon cycle transformation in the system [4].

$T\text{CO}_2$ in the bottom waters was insignificantly higher than in the surface one (by ~1 %), except for the winter time when $T\text{CO}_2$ in the surface layer was higher (Fig. 2). Its maximum concentrations in the surface waters were observed in winter (Fig. 2, a), and in the bottom waters in winter and spring (Fig. 2, b). The minimum concentrations were in the surface and bottom layers of the bay in summer-fall
Such changes of total dissolved inorganic carbon correspond to natural seasonal variations: to the growth of gas solubility with the temperature decrease. However, a significant exceedance of $\mathrm{TCO}_2$ concentration in the bottom layer (in comparison to its concentration in the surface one) is quite expected in summer and fall periods. This is due to the gas solubility decreasing in the surface layer and more intensive organic carbon oxidation in the upper layer of bottom sediments. Our data indicate that the difference between the $\mathrm{TCO}_2$ concentrations in the bottom and surface layers during this period is less than 1 %. This is related to the fact that the oxygen consumption, which limits the process of organic matter aerobic oxidation, did not exceed 25 μmol/l. According to the equation of biochemical oxidation, ~20 μmol/l of CO₂ is formed. It makes up ~1 % from the concentration of total dissolved inorganic carbon. For providing a significant difference between $\mathrm{TCO}_2$ of bottom and surface layers it can be assumed that currently the oxidation of organic matter proceeds not so actively.

**Fig. 2.** Seasonal changes in the total dissolved inorganic carbon $\mathrm{TCO}_2$ in (a) surface and (b) bottom layers (+, – – – winter; ●, ---- spring; ■, ---- summer; ● fall; ––– average annual linear trend)
At the same time, from 2009 to 2015 a trend to $\text{TCO}_2$ increase (Fig. 2) had been observed. $\text{TCO}_2$ decrease in fall (Fig. 2) was caused by temperature factor and the time of the survey: in 2011 (when the maximum $\text{TCO}_2$ was observed) the sampling was carried out in late fall at 9 °C temperature. This corresponds to the average temperature of winter period in the Sevastopol region [13]. In 2013 and 2014 the sampling was carried out at 14°C temperature, the trend change in this period was not statistically significant. The most essential concentration increase was observed in winter period in the surface layer (Fig. 2, a). In general, the changes of average annual $\text{TCO}_2$ in the water column in 2009 – 2015 did not reveal its significant increase or decrease. It may indicate the stability of the Sevastopol Bay carbonate system component ratio and its ability for “self-recovery”.

Bicarbonate ion makes the main contribution to the total content of dissolved carbon dioxide forms (~90 %). Thus, bicarbonate ion concentration change should be similar to $\text{TCO}_2$ dynamics. The increase of its concentration was observed in 2009 – 2015 (Fig. 3).

![Graph a](image1)

**Fig. 3.** Seasonal changes in bicarbonate ion concentrations $\text{HCO}_3^-$ in (a) surface and (b) bottom layers (+, −−−−− winter; ⋄, −−−−− spring; ■, −−−−− summer; ●, − fall; average annual linear trend)
When the carbon dioxide content in the water column (related to its inflow with the river run-off and/or from the anthropogenic sources) increases, the growth in bicarbonate ion concentration is accompanied with the hydrogen ion concentration increase and pH decrease. Average annual pH dropped from 8.37 to 8.29 in the surface layer and from 8.35 to 8.28 in the bottom one. Smaller pH value in the bottom layer of waters indicates active organic matter oxidation processes in the bottom sediments, which result in CO$_2$ production and accumulation in the water column:

$$\text{CH}_3\text{O} + \text{O}_2 \leftrightarrow \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-.$$  \hspace{1cm} (1)

This is also evidenced by high (over 4 %) organic carbon content in bottom sediments [3] and lowering in oxygen concentration in the bottom waters at this period up to its complete absence [14].

CO$_2$ accumulation in the bottom waters is accompanied by partial pressure increase:

$$\rho \text{CO}_2 = \frac{[\text{CO}_2]}{K_0},$$  \hspace{1cm} (2)

where $[\text{CO}_2]$ is an equilibrium carbon dioxide concentration, $\mu$mol/kg; $K_0$ is Henry’s constant for carbon dioxide, $\mu$mol/(l·atm).

Depending on the intensity of water vertical mixing, $\rho \text{CO}_2$ in the bottom waters reflects variation in carbon dioxide partial pressure in the surface layer. In its turn, it also depends on temperature and salinity, as well as on photosynthesis process [15] due to CO$_2$ utilization:

$$6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow 6\text{H}^+ + 6\text{HCO}_3^- \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2.$$  \hspace{1cm} (3)

Photosynthesis results in carbon dioxide consumption, $\Delta \text{CO}_2$ and $\rho \text{CO}_2$ decrease and pH value rise. This is accompanied by the equilibrium shift in carbonate system towards HCO$_3^-$ decrease. In the Sevastopol Bay surface waters pH lowering, $\Delta \text{CO}_2$ and $\rho \text{CO}_2$ increase were observed (Fig. 2, 4). It may be indicative of the fact that photosynthesis is not a limiting process for this layer in the formation of carbonate system characteristics. The main contribution to the change in characteristics is made by hydrogen ion-enriched bottom waters which were formed as a result of organic matter oxidation (Equation (1)). Thus, the photosynthesis and the organic matter oxidation are the main biological-and-chemical processes affecting the carbonate system component ratio in the surface layer of waters [3].

As expected, carbon dioxide partial pressure in the bottom is higher than in the surface waters (Fig. 4). This is due to the intensive oxidation of organic matter (Equation (1)) producing in the waters of the bay and/or fluxing with anthropogenic sources. The photosynthesis (Equation (3)) here is absent or less significant in comparison with organic matter oxidation.

In the seasonal change in $\rho \text{CO}_2$ curves (Fig. 4) for the surface and bottom layers, a steady trend to its increase in winter and summer periods is observed. For the surface layer an increase of partial pressure average values from 2009 to 2015 made up 83 $\mu$atm, for the bottom layer it were 59 $\mu$atm. This is equal to 22 and 15 %, respectively.
In winter and spring $p\text{CO}_2$ in surface layer was higher than in the bottom one. In addition, the maximum $p\text{CO}_2$ were observed in spring period in spite of spring phytoplankton bloom, which should result in CO$_2$ consumption and, correspondingly, in $p\text{CO}_2$ decrease. This is likely to be caused by the effect of Chernaya River (which flows into the bay) flood run-off. Fresh waters of the river are the additional CO$_2$ source. In summer and fall period $p\text{CO}_2$ is, on the contrary, higher in the bottom layer than in the surface one. In summer the maximum $p\text{CO}_2$ values in the bottom layer are observed. Temperature increase in summer season and gas solubility decrease, limited diffusion flux of oxygen and fine-size of sediments enriched with organic matter contribute to intensive organic matter oxidation and CO$_2$ production (Equation (1)).

**Fig. 4.** Seasonal changes in the carbon dioxide partial pressure $p\text{CO}_2$ in (a) surface and (b) bottom layers (+, – – winter; ●, – – spring; ■, – – summer; ●, – – fall; – – average annual linear trend; – – the carbon dioxide concentration in the atmosphere)
A sharp difference of $pCO_2$ in spring 2009 (Fig. 4, a) is explained by the temperature effect: the sampling was performed in late spring at 23 °C, and this corresponds to the summer period temperature.

Moreover, $pCO_2$ change in the surface layer specifies the intensity of CO$_2$ flux at the water-atmosphere boundary determines their direction and characterizes the water column as carbon dioxide source or sink.

It was previously determined that atmospheric carbon dioxide partial pressure constantly increases and currently it is $\sim$400 μatm [16]. Thus, it may be assumed that during the investigated period the Sevastopol Bay waters mainly were a sink for carbon dioxide from the atmosphere (Fig. 4, a), except for the summer 2014 when $pCO_2$ in the surface layer reached 426 μatm. This characterizes the surface layer of waters as a gas source for the atmosphere. This situation is typical for such water ponds in the summer period [17].

Fig. 5. Change in the average value of the flux $F_{CO_2}$ in the surface waters of the Sevastopol bay in 2009 - 2015 (solid and dashed line represents the linear trend of long-term changes in average values of carbon dioxide flux and its forecast)

Quantitative assessment of gas exchange intensity at the water-atmosphere boundary is given by the semi-empirical equation of “simple mass transfer” with regard for the calculation of mass transfer coefficient and its dependence on wind velocity. The equation was proposed by Yu. I. Lyahin [12]. The calculated values of $F_{CO_2}$ carbon dioxide fluxes reveals the fact that the bay waters in summer season were in evasion indeed (Fig. 5), i. e. they were a carbon dioxide source for the atmosphere. In the other periods the bay waters were in invasion, i. e. they absorbed CO$_2$ from the atmosphere (Fig. 5). The maximum values occurred mainly in winter period at that. This can be explained by physics and chemical processes (gas solubility increase) and the effect of hydrodynamic factors. The value of CO$_2$ fluxes in 2009 winter and spring periods had been conditioned mainly by physical oceanography no.3 (2016)
temperature. Positive value of flux in winter 2009 corresponds to its values in cold period, when active CO\(_2\) absorption by water from the atmosphere should take place. Negative value of flux (i.e. the process of CO\(_2\) emission to the atmosphere by the surface waters) in spring 2009, which is typical for the warm period, is explained by the effect of seawater temperature, which corresponds to the summer season temperature (23°C). It should be noticed that the maximum value of flux (21.6 mol/(m\(^2\)d), Fig. 5), being observed in September 2009, was conditioned by the wind (when its daily average velocity made up 6.6 m/s).

It is likely that carbon dioxide (being absorbed from the atmosphere by the bay waters) is eventually involved into the processes related to the organic matter production. This results in intensive organic matter accumulation in the upper layer of bottom sediments as confirmed by our previous studies [4, 14]. Despite the fact that the bay waters still absorb carbon dioxide from the atmosphere, a pronounced downturn of its flux intensity is observed (Fig. 5). We have determined the following fact: if current conditions (climate and anthropogenic factors) remain the same, \(F_{CO_2}\) intensity will continue to decline. Therefore, CO\(_2\) invasion will be replaced with the evasion by the beginning of 2018. If we take into account the fact that carbon dioxide flux values at water-atmosphere boundary were obtained in 2009 under extreme conditions, the consideration of the period under study indicates more intensive partial pressure increase and evasion appears by 2015 – 2016. This is confirmed by our latest data (Fig. 5). Such state is unusual for the coastal ecosystems and it will lead to significant transformation of carbon cycle and the ratio of carbonate system components in the Sevastopol Bay.

**Conclusions.** Obtained results suggest that in the cold period (winter, spring) the Sevastopol Bay carbonate system component ratio is highly affected by Chernaya River riverine waters in the surface layer. In warm period (summer, fall) the ratio is affected mostly by the organic matter oxidation in the bottom waters and photosynthesis in the surface one. The bay waters still remain the sink for carbon dioxide from the atmosphere.

There is an obvious upward trend in \(T\)CO\(_2\) changes in 2009 – 2015 but they are not statistically significant and make up \(\sim 1\) %. This may mean that by the present time the ecosystem of the bay is still capable for “self-recovery”. However, an \(T\)CO\(_2\) upward trend, and, which is more important, a significant increase in \(p\)CO\(_2\) in the bottom and surface layers of the bay (up to 23 %) over the investigated period indicate the presence of negative changes. They result in the transformation of carbon cycle natural of coastal ecosystem. Moreover, at present the Sevastopol Bay waters are in the invasion, and it is typical of coastal ecosystems. However, the calculated values of CO\(_2\) fluxes at the water-atmosphere boundary indicate a pronounced tendency to their decrease in 2009 – 2015 and probability of replacing invasion by evasion (carbon dioxide emission to the atmosphere) by 2018. Evasion is a typical feature of estuarine systems, lakes and other hydrologic systems with high organic matter content.

Thus, if environmental measures for reduction of anthropogenic load at the Sevastopol Bay waters are not taken, it will lead to irreversible consequences with catastrophic changes in its ecosystem in the nearest future.
Acknowledgements. The research is carried out within the framework of Russian Foundation for Basic Research project no. 16-35-60006 “Long-term Changes in the Carbon Cycle Characteristics of the Sevastopol Bay”.

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