

# Variation in the carbon cycle of the Sevastopol Bay (Black Sea)

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**Abstract.** Continuous increase in CO<sub>2</sub> inventory in the ocean results in dramatic changes in marine biogeochemistry, e.g. acidification. That is why temporal and spatial variabilities in atmospheric pCO<sub>2</sub> and dissolved inorganic carbon, including CO<sub>2</sub>, pH and alkalinity in water, as well as organic and inorganic carbon in bottom sediments have to be studied together making possible to resolve the key features of the carbon cycle transformation. A 30% increase of pCO<sub>2</sub> in the Sevastopol Bay for 2008 – 2016 evidences changes in the DIC components ratios and a significant decrease in the ability to absorb atmospheric CO<sub>2</sub> by surface waters. High organic carbon content in the bottom sediments and predominance of organic carbon production in the biological pump at inner parts of the bay reveal ongoing transformation of the carbon cycle. This has negative consequences for recreation, social and economic potentials of the Sevastopol region.

## 1. Introduction

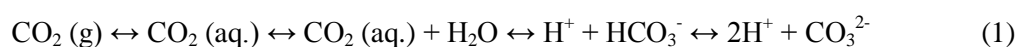
Increasing atmospheric CO<sub>2</sub> inventory, leading to climate changes and natural carbon cycle's transformations, has become the key scientific issue over the last decades. For last 120 years, the annual atmospheric CO<sub>2</sub> growth is about 0.4% due to global industrialization. Anthropogenic activities, such as cement production, fossil fuel burning, and forest slash, result in about 6·10<sup>15</sup> gC/year increase in the atmospheric CO<sub>2</sub> content. Nowadays, the global ocean CO<sub>2</sub> uptake from the atmosphere accounts for only ~ 30% of the annual production of CO<sub>2</sub>, while it was ~ 50% in 1800 – 1994 [1], revealing a lowering ocean capability to compensate for anthropogenic CO<sub>2</sub> production. As a part of the carbon cycle, the carbonate system serves as the ocean buffer capacity and secures its ability to uptake CO<sub>2</sub> from the atmosphere. Increasing CO<sub>2</sub> inventory in the ocean results in acidification. As a result, dramatic changes occur in marine biogeochemistry. This has irreversible consequences, such as degradation of biota's population and diversity, dissolution of coral reefs and shells with carbonate skeletons, etc. As a result, recreation, social and economic potentials of a region deteriorate. That is why temporal and spatial variabilities in atmospheric pCO<sub>2</sub> and dissolved inorganic carbon, including CO<sub>2</sub>, pH and alkalinity in water, as well as organic and inorganic carbon in bottom sediments have to be studied together making possible to resolve the key features of the carbon cycle transformation.

The carbon cycle includes atmosphere, hydrosphere and lithosphere compartments. Coastal areas account for only 7% of the World Ocean [2], but they are most valuable for all sorts of anthropogenic exercise and important for investigations. Coastal oceans are key locations, where terrestrial, oceanic and atmospheric parts of the global carbon cycle come together [3]. To make it more complicated, coastal ecosystems are under heavy anthropogenic pressures over the last century due to shipping and maritime activities, intensive land use, coast-based pollution, etc.



The Sevastopol Bay is a typical coastal marine system under heavy anthropogenic pressures. It is a maritime zone with seaports and docks. Domestic sewage are often loaded to the bay with limited treatment carrying nutrients and fresh organic matter. Protection piers between the outer part of the bay and open sea constructed in the middle 1970's restrict water exchange between the bay and sea by 40 – 70% [4]. The bay's ecosystem reveals oxygen deficit in the bottom waters and anaerobic/sulfidic conditions at and in bottom sediments, severe eutrophication, decline in biodiversity, dramatic changes in natural biogeochemical regimes and cycle's [5].

Dissolved inorganic carbon (DIC) is one of the most representative parameter of the ecosystem's stability and recoverability. For usual marine conditions,  $[\text{HCO}_3^-] : [\text{CO}_3^{2-}] : [\text{CO}_2]$  equals 100:10:1 [6, 7]. Variations in one of the DIC components result in repartitioning of all dissolved inorganic carbon forms. An increase in the  $\text{CO}_2$  flux, for example, results in acidification and increasing bicarbonate ion concentration (equation 1).



The initial buffer capacity supports and varies due to absorption of atmospheric  $\text{CO}_2$ , but it compensates and limits variations in pH and  $\text{CO}_2$  inventory in seawater. A doubling  $\text{CO}_2$  concentration results in the DIC increase by only 10% [8]. Yet, any shift in DIC evidence changes in production and degradation processes, as well as in  $\text{CO}_2$  fluxes. Variations in DIC,  $\text{CO}_2$ , pH, and alkalinity make possible to assess the ecosystem's stability.

The main purpose of our study is the investigation of the present state of the Sevastopol Bay's ecosystem and assessment of the carbon cycle transformation due to intensive anthropogenic pressures.

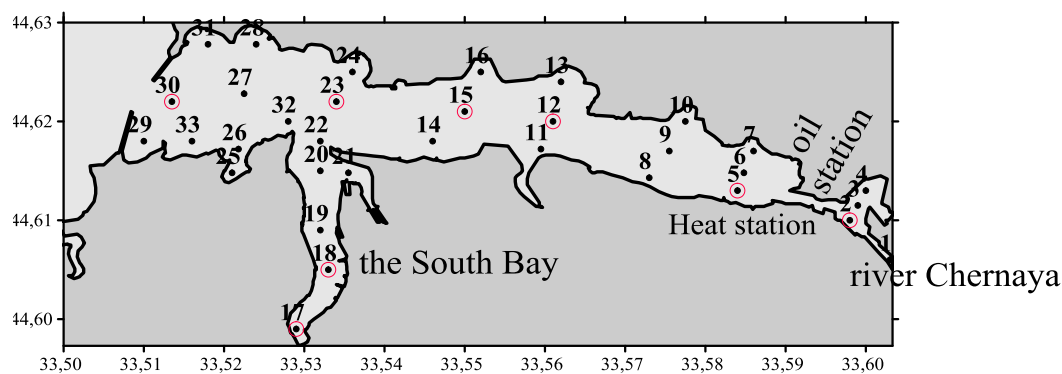
## 2. Material and methods

Monitoring of the Sevastopol Bay has been performed at Marine Hydrophysical Institute since 1998 [4]. Samples are taken from the surface and bottom waters with Niskin bottles at locations/stations presented at figure 1. Sediment columns are collected in plexiglass tubes by scuba diver.

Salinity and temperature are measured with a CTD probe, whereas pH and alkalinity are determined in a shore laboratory following standard analytical procedures [9]. DIC and  $\text{pCO}_2$  values, as well as other carbonate system's parameters, are calculated as suggested in [9]. The dissociation constants of carbonic acid, recommended by the Department of Marine Sciences of UNESCO, have been used [9]. The boron content has been calculated from the salinity, as boron was assumed a conservative part of salinity [8]. The effect of dissociation of water, phosphoric acid, sulfuric acid, hydrofluoric acid and other acids have not been taken into account.

Data from the 1<sup>st</sup> station have not been taken into account (figure 1) for calculation of mean values, because fresh waters of the river Chernaya, rather than marine waters of the bay, have been usually traced there.

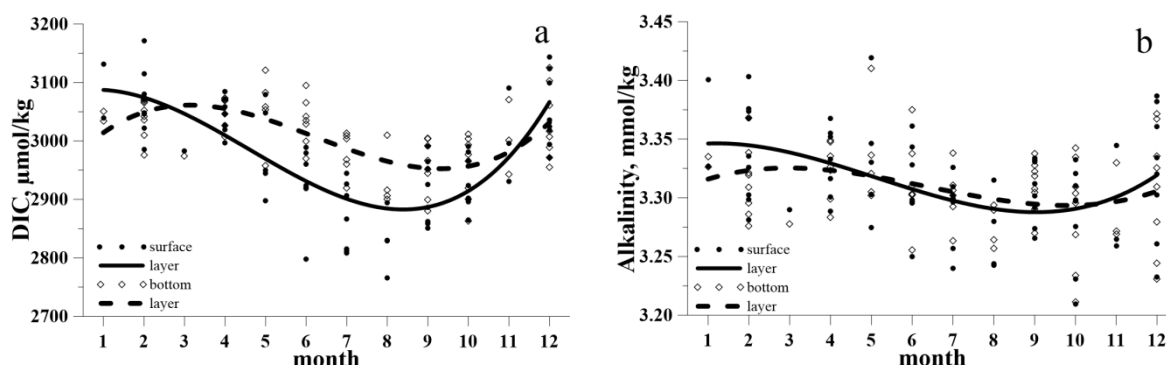
Organic and inorganic content have been analyzed in bottom sediments according to [10]. Voltammetric profiling with a glass Au-Hg microelectrode has been applied [11] to detect key redox species (oxygen, sulfides, Mn (II), Fe (II, III),  $\text{FeS}_{\text{aq}}$ ) in porewaters.



**Figure 1.** Sampling locations in the Sevastopol Bay (Red rings are for stations of bottom sediments sampling).

### 3. Results and discussion

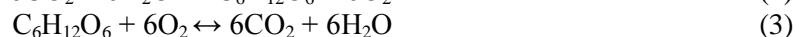
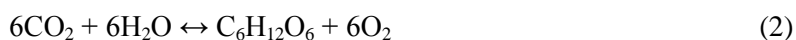
The most important natural drivers of the ecosystem of the Sevastopol Bay include water exchange with the adjacent marine area, wind, seasonal variations in temperature, and fresh water load by the river Chernaya. Morphometry features support eddy dynamic structures in the bay [4]. All these and human activities result in specific hydrochemical water column features, including the carbonate systems' components.



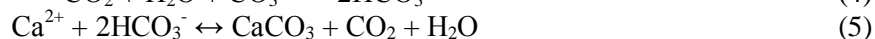
**Figure 2.** Monthly dynamics of DIC (a) and Alkalinity (b) in the surface and bottom waters of the Sevastopol bay (data for 1998 – 2016).

In cold time (from November to March), waters of the bay are vertically well mixed supporting equal values of DIC,  $p\text{CO}_2$  and pH from surface to bottom (figure 2a). In warm months (from April to October) values of DIC decline from spring to summer and increase in fall. Yet, values of DIC in the surface layer decrease faster, as compared to those in the bottom layer, resulting in significantly different values of DIC. Unlike DIC, alkalinity reveals similar mean values in the surface and bottom layers of water throughout the year. Yet, intra-annual variations in alkalinity are similar to those for DIC: maximum values appear on wintertime and minimum values appear in summer. Intra-annual variability of these parameters depends on water dynamics and  $\text{CO}_2$  fluxes, which is governed by physical, chemical and biological processes [6, 8].

Atmospheric  $\text{CO}_2$  dissolves in seawater and supports photosynthetic (equation 2) organic carbon production in the surface layer. In the bottom layer, organic matter respiration (equation 3) results in oxygen utilization and  $\text{CO}_2$  production.



Other reactions governing the carbonate system are presented by equations 4 and 5. However, the contribution of these reactions to DIC concentration does not exceed 3% [12]. In the Sevastopol Bay, these reactions occur mainly in the bottom layer.



Spring phytoplankton blooming results in decreasing DIC concentrations. The lowest values of DIC and a maximal difference between the surface and bottom layers are detected in August-September (2990 and 3014  $\mu\text{mol}\cdot\text{kg}^{-1}$  surface and bottom layers respectively). This is a result of several reasons; an increase in the photosynthetic activity, a decrease in gases solubility, and a strong summer water stratification, preventing  $\text{CO}_2$  supply from bottom waters.

Intensive organic carbon accumulation in bottom sediments also results in depletion of DIC in waters. Currently, high organic carbon concentration ( $\geq 4\%$ ) is observed in the bottom sediments of the Sevastopol Bay [5].

When the temperature decreases from summer to fall, solubility of gases increases (particularly oxygen) and bottom sediments serve as a source of  $\text{CO}_2$  for bottom waters, while water mixing in late fall and winter results in equal DIC concentrations from surface to bottom.

Alkalinity does not depend on the  $\text{CO}_2$  flux, but its value is determined by the presence of bicarbonates and carbonates. Thus, only a combination of water exchange in the bay and freshwater discharge explains intra-annual oscillations in the value of alkalinity (figure 2b).

Unlike DIC and alkalinity,  $\text{pCO}_2$  is highly dynamic and rapidly reacting to any changes occurring in a system. It depends on temperature,  $\text{CO}_2$  concentration and pH (6).

$$\text{pCO}_2 = \frac{[\text{CO}_2]}{K_0} \quad (6)$$

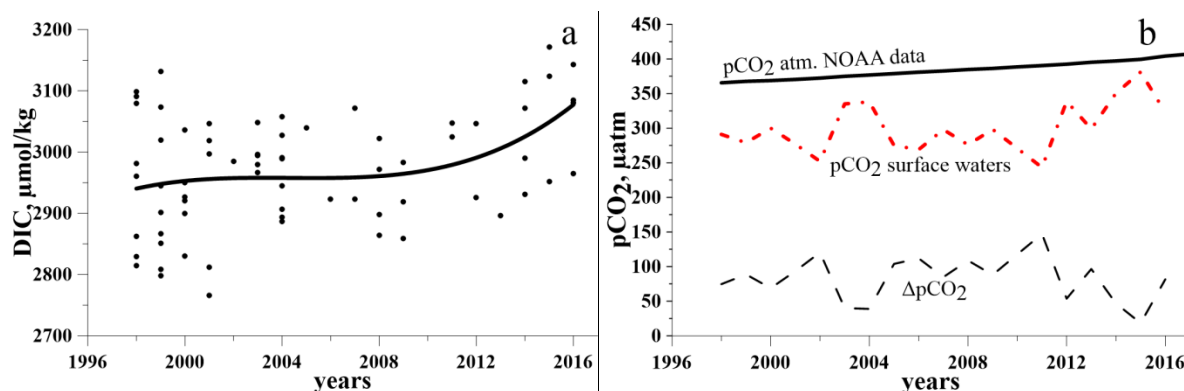
where  $[\text{CO}_2]$  – equal concentration of  $\text{CO}_2$   $\mu\text{mol}/\text{kg}$ ;  $K_0$  – Henry's constant of carbon dioxide,  $\mu\text{mol}/(\text{l atm})$ .

Knowing the surface  $\text{pCO}_2$  one could identify an ecosystem as a source of  $\text{CO}_2$  to or sink from the atmosphere. When the value of  $\text{pCO}_2$  in seawater is greater than its value in the atmosphere (currently it is about 405  $\mu\text{atm}$  [1]), the water column is a source of  $\text{CO}_2$ . The Sevastopol Bay's waters absorb  $\text{CO}_2$  from the atmosphere because  $\text{pCO}_2$  is from 225 – 388  $\mu\text{atm}$ , except for summer time, when it reaches 426  $\mu\text{atm}$ . Such situation is typical for coastal organic carbon saturated marine environments [2, 3].

Our data show noticeable seasonal variations in surface  $\text{pCO}_2$ , because of variations in temperature, hydrodynamics, biological and chemical processes. Since the components of the carbonate systems are in equilibrium, an increase of the  $\text{CO}_2$  flux results in lower values of pH. Seasonal variations in pH are as much as 0.09 pH units in the bottom layer, but they do not exceed 0.03 pH units for the surface layer. The surface layer is in contact with the atmosphere, supporting active exchange of  $\text{CO}_2$ , seasonal variations in pH are mostly the result of better dissociation of carbonic acid and increased solubility of  $\text{CO}_2$  at higher summer temperatures. Unlike the surface layer, the bottom layer is isolated by the presence of a strong pycnocline and respiration of organic carbon results in active production of  $\text{CO}_2$  and decrease in pH. Thus, the seasonal dynamic of the carbonate systems' components in the Sevastopol Bay indicates its dependence on biological and chemical processes of photosynthesis and organic matter degradation in summer. In cold time, the load of the river Chernaya and intensive water mixing are two major factors to control on the carbonate system.

Inter-annual dynamic of the carbonate systems' components for the last 20 years, from 1998 to 2016, reveals an increase in DIC,  $\text{pCO}_2$ , and acidification, especially in the surface waters (figure 3). Most significant changes take place for  $\text{pCO}_2$  (up to 17%). According to NOAA data  $\text{pCO}_2$  continuously increases in the atmosphere [1]. For this period, the atmospheric  $\text{pCO}_2$  has increased by

up to 11% providing an additional CO<sub>2</sub> source. Yet, pCO<sub>2</sub> has increased at a higher rate since 2008, as compared to pCO<sub>2</sub> in the atmosphere (figure 3b). From 2008 DIC concentration has increased by up to 5% and pCO<sub>2</sub> has increased by up to 30%. These considerable values indicate negatives changes, occurring in the ecosystem of the Sevastopol Bay.



**Figure 3.** Inter-annual variations in DIC concentration surface waters (a) and pCO<sub>2</sub> and the difference between pCO<sub>2</sub> in the atmosphere and surface water (b) of the Sevastopol Bay

There are inter-annual oscillations in pCO<sub>2</sub> in the surface waters of the Sevastopol Bay, but the tendency suggests an uprising trend in excess of the trend of CO<sub>2</sub> in the atmosphere (figure 3b). Using annual pCO<sub>2</sub> data variation, we have estimated a pCO<sub>2</sub> difference between the atmosphere and the bay's surface water that reflects an ability of the Sevastopol Bay to absorb CO<sub>2</sub> from the atmosphere. This ability has dropped from 1998. Data from 2011 to 2015 suggested that the ecosystem of the Sevastopol Bay would exhaust its sorption ability by 2018 and would be a source of CO<sub>2</sub> for the atmosphere. But in 2016, pCO<sub>2</sub> dropped down suggesting that the Sevastopol Bay would remain a sink of CO<sub>2</sub> from the atmosphere.

Studies of the bottom sediments geochemistry and porewater chemistry in 2003 – 2016 reveal pronounced changes in the carbon cycle also. Bottom sediments are a steady system and any changes in this system occur at a longer time-scale comparing to the water column. Organic and inorganic carbon is main constitutions of the carbon cycle in the sediments. Currently, the organic carbon content in the sediments is ~3.3% with variations from 1.9 – 7.2%, over the bay's area. In the areas under heavy anthropogenic pressure (for example, the South Bay, where shipping docks are located, figure 1) the content of organic carbon exceeds 4%. The CaCO<sub>3</sub> content in bottom sediments is on average 31%. There are two types of the carbon pump: biological and physical [13]. In the biological carbon pump, main processes are production organic carbon or its respiration to CO<sub>2</sub>. One of these processes can dominate in the ecosystem or they can be equal. A rain ratio parameter ( $\gamma$ ) is used to identify the dominate process of carbon production in the sediments (7):

$$\gamma = \frac{CaCO_3}{(C_{org} + CaCO_3)}, \quad (7)$$

where CaCO<sub>3</sub> и C<sub>org</sub> is molality of inorganic and organic carbon, respectively.

The rain ratio parameter can vary from zero to one. If this parameter is zero, than only organic carbon is produced.

The rain ratio parameter is on average 0.55 in the Sevastopol Bay for 2016 and it is 0.63 in the outer part of the bay. Thus, the inorganic pump is prevailed. But spatial variations in  $\gamma$ -parameter have revealed areas with prevailing organic carbon pump (0.39 – 0.44). These are areas under high anthropogenic pressure.

Organic carbon production and accumulation in sediments favor oxygen consumption and CO<sub>2</sub> production (equation 3). Voltammetric studies have revealed that the depth of penetration of oxygen in bottom sediments does not exceed 2 mm, but oxygen is often absent even at the surface of sediments. Thus, organic carbon rich sediments are a source of CO<sub>2</sub> for the water column.

#### 4. Conclusion

The most important natural drivers of the ecosystem of the Sevastopol Bay include water exchange with the adjacent marine area, wind, seasonal variations in temperature, and fresh water load by the river Chernaya. Eutrophication in the form of organic carbon and nutrients load is the most prominent anthropogenic influence of the carbon cycle in the bay.

A 30% increase of pCO<sub>2</sub> for the period of 2008 – 2016 evidences changes in the DIC components ratios and a significant decrease in the ability to absorb atmospheric CO<sub>2</sub> by surface waters. High organic carbon content in the bottom sediments and predominance of organic carbon production in the biological pump ( $\gamma$ -parameter ~0.4) at inner parts of the bay reveal ongoing transformation of the carbon cycle. All these changes evidence negative shifts in the bay ecosystem lowering its self-recover possibility.

#### Acknowledgement

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