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Assessment of carbon dioxide exchange processes between water bodies and the atmosphere

P.S. Korotkih[1], E.N. Neverov[2*], I.A. Korotkiy[1]

1. Department of Heat and Cooling Engineering, Kemerovo State University, Russia
2. Department of Technosphere Security, Kemerovo State University, Russia

** Corresponding author's E-mail: e.n.neverov@gmail.com*

ABSTRACT
Calculating the volume of carbon dioxide absorbed by the ocean is a challenging task because it depends on numerous factors, including depth, temperature, salinity, and others. Calculating the precise volume of CO2 absorbed by the ocean is even more difficult due to the complex and dynamic nature of these processes. Some studies and models provide only an approximate assessment of the annual carbon balance between the atmosphere and the ocean. The purpose of the present study was to examine the processes of CO2 exchange between water and the surrounding environment. For experimental testing, the authors developed a special apparatus used to conduct a series of studies to assess CO2 exchange processes between water and the environment. Studies were performed on distilled, fresh, and salt water. Dissolving CO2 in fresh and salt water is a complex process that plays a key part in the environment's biological, climatic, and geochemical aspects. The initial CO2 concentration in the operational volume of the experimental setup was 5,000 ppm (parts per million; 5%). The temperature inside the chamber amounted to 20 ± 2 ºC. The experiment lasted 10 days. Since the most important factor in the experiment was precision, the study employed the method of gas chromatography. Investigation of these features provided a better understanding of the importance of managing CO2 levels and its impact on Earth's ecosystem.

Keywords: Carbon dioxide, Disposal, Atmosphere, Ocean, Uptake, Dissolution, Water body.
Article type: Research Article.

INTRODUCTION
According to recent estimates, the oceans absorb about 25% of anthropogenic carbon dioxide emissions deposited in the atmosphere. This means that the ocean significantly reduces the concentration of CO_2 in the atmosphere, helping to slow global warming (Dubovik *et al.* 2022). Water bodies are critical absorbers of CO_2 from the atmosphere (Baideldynov *et al.* 2019). They uptake about 25% of the annual carbon emissions associated with human activities (Mustafayeva *et al.* 2019). This process occurs as a result of chemical reactions between CO_2 and water (Akbayeva *et al.* 2023). The oceans absorb CO_2 from the atmosphere in the upper surface and coastal regions. This carbon then travels to the deeper layers of the ocean through various processes such as vertical water circulation and biological processes. It is difficult to estimate the exact amount of CO_2 absorbed by the oceans because of the many factors that influence this process (Komarova *et al.* 2022). It is also important that the oceans release CO_2 back into the atmosphere through natural processes such as organic matter decomposition and volcanic activity (Hartmann *et al.* 2013; Yadav & Sen 2017; Keller *et al.* 2018; Gao *et al.* 2022). Calculating the amount of CO_2 absorbed by the oceans is a great challenge that demands consideration of many factors and variables. Through our literature review, we identified the main estimates and models that allow us to approximate CO_2 uptake by the ocean. One of the most widely used models for calculating ocean CO_2 uptake is the Bern Simple Climate Model. This model considers the ocean as a set of horizontal layers connected to each other vertically by water and gas flows.

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The calculation requires considering the following factors:

- Distribution of CO_2 concentration in the atmosphere at the Earth's surface;
- Distribution of CO_2 concentration in the ocean at different depths;
- The solubility level of CO_2 in ocean water, depending on temperature, salinity, and pressure;
- Physical processes such as ocean mixing, currents, and circulation;
- The interaction of CO_2 with marine biological systems, including phytoplankton and marine organisms.

Ocean carbon cycle model. This model describes the various processes that affect the uptake and release of CO_2 by the ocean. It accounts for the geographic distribution of ocean currents, temperature changes, changes in the physical chemistry of the ocean, and other factors.

Carbon balance model. This model uses data on carbon emissions from various sources, including fossil fuel combustion (Kulanov *et al.* 2020) and land-use change (Kulshikova *et al.* 2023), as well as data on ocean carbon uptake. The model helps to estimate the balance between carbon emissions and uptake (Komarova *et al.* 2023) as well as to quantify the extent to which the ocean contributes to carbon sequestration.

Global climate models. These are complex models that incorporate various aspects of the climate system, including the ocean, atmosphere, glaciers, and other components (Martirosyan *et al.* 2022). They include parameters related to the carbon cycle and ocean carbon uptake and allow estimating the impact of various factors on global climate and CO_2 concentrations. Importantly, all these models and assessments rely on available data and approximations, so the precision of results varies. In addition, owing to climate change and other factors, carbon uptake by the ocean can change over time. For this reason, researchers continue to refine their models and calculation methods to obtain more accurate assessments of carbon uptake by the ocean and its role in global climate. Experiments on the uptake of CO_2 by water can be conducted to investigate the chemical and physical processes related to this phenomenon. Some experiments that can be performed for this purpose include:

1) **CO_2 solubility testing.** Such an experiment determines the amount of CO_2 that can be dissolved in a certain volume of water under different temperatures and pressures. This can be accomplished by using special apparatus, such as burettes or gas collectors, and measuring the volumes and concentrations of CO_2 before and after dissolution.

2) **Studying the effect of temperature on absorption**. This experiment allows the investigation of how temperature affects CO_2 absorption rates in water. To this end, a series of experiments can be carried out by changing water temperature and measuring the concentration of CO_2 at specific points in time. This can provide insight into how changes in climate and ocean temperatures can impact carbon uptake.

3) **Study of interaction with different reagents.** This experiment can establish how the addition of different reagents or substances can affect the uptake of CO_2 by water (Blodau 2002; Florides & Christodoulides 2009; Neverov *et al.* 2021). Thus, the purpose of our study was to assess CO_2 exchange processes between water and the environment.

MATERIALS AND METHODS

For the needs of similar experimental testing, we developed the apparatus presented in Fig. 1. This setup was also used in the present research to conduct a series of studies on CO_2 exchange processes between water and the surrounding environment. The starting concentration of CO_2 in the operating volume of the experimental installation was 5,000 ppm (parts per million; 5%). The temperature inside the chamber amounted to 20 ± 2 ºC. The experiment lasted 10 days. Studies were performed on distilled, fresh, and salt water.

In choosing the research methods, we proceeded from the fact that the concentration of CO_2 in water can be tested by various types of methods:

1. The potentiometric method is based on measuring the difference of potentials between two electrodes submerged in water with varying CO_2 concentrations.
2. Colorimetric analysis identifies CO_2 concentration by changing the color of the reagent that reacts with CO_2.

3. Photometry and spectrometry methods rely on measuring the absorption of light of a particular wavelength by CO_2 in water.

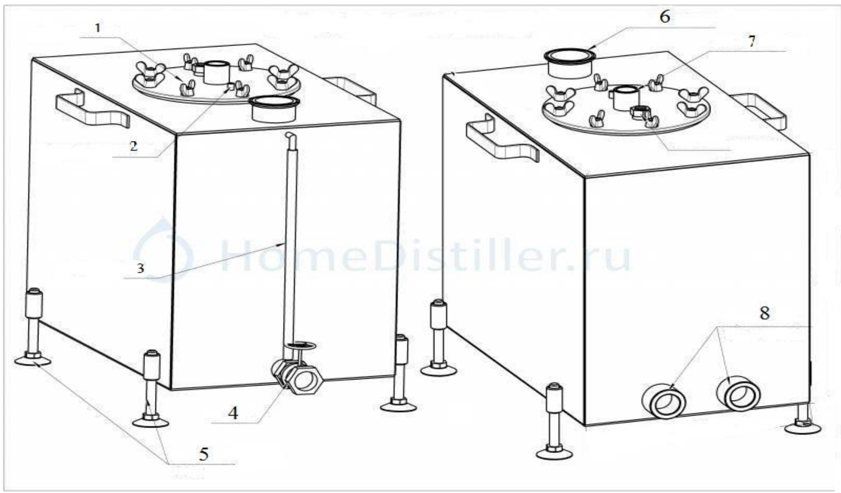

Fig. 1. Scheme of the experimental set-up; 1 – cover; 2 – valve to connect the CO_2 concentration meter; 3 – liquid level indicator; 4 – drain valve; 5 – legs; 6 – valve to connect the temperature and humidity meter; 7 – CO_2 feed valve; 8 – heating and cooling circuit couplings.

4. Gas chromatography (GC) is used to analyze gas samples, including CO_2 dissolved in water.
5. Infrared spectroscopy measures the spectral characteristics associated with CO_2 in water.

The choice of the research method was influenced by such factors as precision, sensitivity, and the accessibility of equipment for analysis. In this experimental study, the most important factor was precision; therefore, we employed the method of GC. This method is based on separating a mixture of gasses into its constituent components based on differences in their chemical activity and interactions with stationary and mobile phases. It presents a highly sensitive method of analysis that allows identifying even very low concentrations of CO_2 in water. The solubility of CO_2 in water is contingent on pressure and temperature. The mechanism of CO_2 dissolution in water is associated with the formation of a chemical bond between the molecules of CO_2 and water. This process proceeds in several steps:

1. Diffusion. CO_2 molecules diffuse through the gas phase and interact with the water surface.
2. Hydration. CO_2 molecules react with water molecules, forming carbonic acid (H_2CO_3) in solution:

$CO_2 + H_2O \rightarrow H_2CO_3$ (1)

3. Protolysis. Carbonic acid can dissociate into hydrogen ions (H^+) and hydroxide ions (OH^-):

$H_2CO_3 \rightarrow H^+ + HCO_3^-$ (2)

4. Further reactions. The ions generated can further react with water and form other chemical compounds such as carbonate ions (CO_3^{2-}) and extra hydrogen ions (H^+).

The process of CO_2 analysis consisted of several stages:
1. The water sample was extracted and gasified.
2. Gasses from the sample were passed through a column where the components were separated.
3. Each component reached a detector that recorded its presence and quantity.
4. CO_2 concentration was determined by the delay time of its passage through the column and the intensity of the signal on the detector.

RESULTS

The graph of CO_2 dissolution in water usually represents the dependence of the concentration of dissolved CO_2 on time or on another variable, such as pressure or temperature. This graph provides a visualization of how the solubility of CO_2 in water changes under different conditions. The pattern of the graph may depend on temperature, pressure, and initial CO_2 concentration and take the form of a curve, linear relationship, or exponential function. The higher the pressure or lower the temperature, the more CO_2 can dissolve in water. Fig. 2 shows a graph of changes in the concentration of CO_2 in the air.

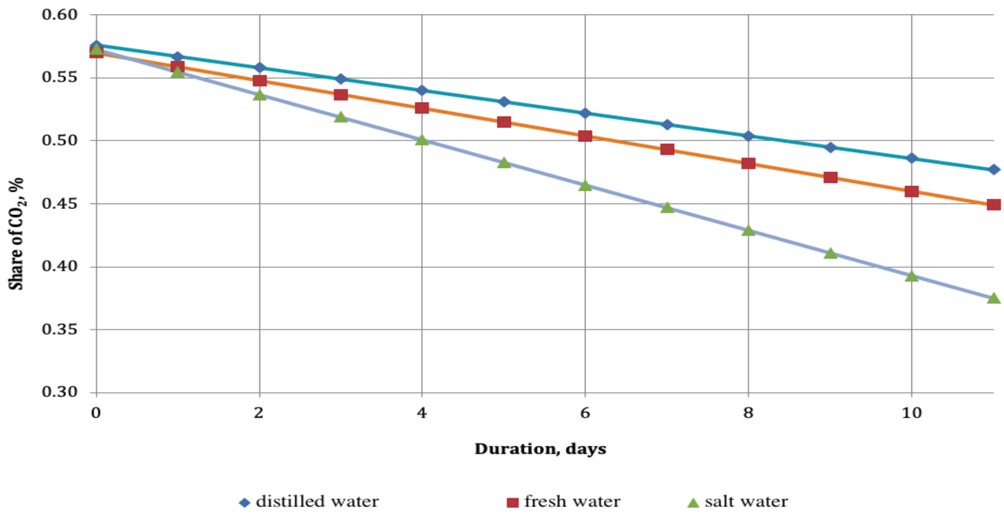

Fig. 2. Graph of changes in CO_2 concentration in the air.

The initial concentration of CO_2 in distilled water is very low. Water that passes through the distillation process regularly contains very little dissolved gasses, including CO_2. Water stored in closed containers virtually always has a concentration of CO_2 close to equilibrium with the atmospheric concentration of CO_2, which currently amounts to around 400 ppm. This suggests that distilled water contains less than 1 ppm of CO_2. The concentration of CO_2 in fresh and salt water can vary greatly depending on the source of that water and other factors. Water typically dissolves CO_2 from the atmosphere, which causes it to saturate. Overall, typical concentrations of CO_2 in fresh water can range between 2 and 4 mg L^{-1}, which corresponds to approximately 2,000 to 4,000 ppm. The concentration of CO_2 in salt water also varies depending on different factors, such as water salinity, temperature, pressure, and other chemical processes. The data obtained through GC are given in Table 1.

Table 1. GC results.

	Starting concentration of CO_2 (ppm ± 5)	Final concentration of CO_2, (ppm ± 5)	Mass fraction of impurities (% ± 0.005)
Distilled water	100	4,100	0.01
Fresh water	1,000	5,050	0.1
Salt water	1,750	5,900	0.5

DISCUSSION

The dissolution of CO_2 in water results in an equilibrium state, where some of the CO_2 remains as ionic molecules and some is converted into chemical compounds that play an important role in maintaining the pH of the aquatic environment and other aspects of chemical equilibrium. CO_2 dissolution also generates carbonic acid, which makes the water slightly acidic (Jahad *et al.* 2022). This affects water quality and can impact marine organisms, as the change in acidity can affect their vital functions. Furthermore, dissolved CO_2 can oxidize various substances in water, thus affecting the chemical processes occurring in water systems (Bostubayeva *et al.* 2023; Motamedi *et al.* 2023). Fresh water, especially when cold, promotes better oxygenation (saturation with oxygen) compared to seawater. This factor is essential for sustaining the life of various aquatic organisms (Różkowski & Rzętała 2021). The dissolution of CO_2 in fresh water can also vary across regions since it is influenced by climatic conditions, the degree of contamination (Kuderina *et al.* 2021), and geological features. The solubility of CO_2 in seawater, in turn, can differ across oceans and seas due to varying salinity and temperatures. In freshwater bodies, CO_2 dissolution can occur at different depths (Khayyatnezhad & Keynoos 2022). Cold layers of fresh water tend to have higher CO_2 solubility than warmer ones. CO_2 dissolution in fresh water can cause reactions with dissolved minerals, leading to the formation of various chemical compounds and thereby affecting the chemical composition of water. The dissolution of CO_2 in water is a critical factor in many spheres of human life, affecting natural processes and industrial applications, as well as global climate and biodiversity (Aipeisova *et al.* 2022; Alhendi 2022). CO_2 dissolution in fresh and salt water has some differences associated with the chemical properties and structure of water.

Fresh water

1. Fresh water contains small amounts of dissolved salts and minerals, making it less alkaline than seawater.
2. As CO_2 dissolves, fresh water becomes slightly acidic due to the formation of carbonic acid (H_2CO_3).
3. Fresh water regularly has lower concentrations of dissolved ions, which can influence the speed of the CO_2 dissolution reaction.

Sea (salt) water

1. Contains considerable amounts of dissolved salts, including sodium, magnesium, calcium, etc., which makes it more alkaline compared to fresh water.
2. The CO_2 dissolved in seawater interacts with bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}), creating buffer systems that support a relatively stable pH.
3. Due to the large amounts of ions in seawater, the concentration of dissolved CO_2 can be higher compared to fresh water in the same conditions.

The concentration of CO_2 in seawater is usually about 2-3 mmol L^{-1} (millimoles per liter), which equals approximately 58-87 mg L^{-1}, or 58,000-87,000 ppm. There are many other gasses dissolved in seawater, such as oxygen and nitrogen, which affect the solubility of CO_2. Salinity can also influence various chemical equilibriums that condition CO_2 concentrations in water.

Determining the concentration of CO_2 in salt water precisely requires the use of analytical methods, such as GC, spectrophotometry, and other methods for analyzing gasses in liquids. This testing determines the current concentration of CO_2 in the analyzed salt water and enables more precise conclusions on its composition. Salt concentration in seawater approximates 3.5% by mass, meaning that there are approximately 35 g salt per kg of seawater. This value can fluctuate in different parts of the oceans and is dependent on various factors, such as climate, evaporation rates, and river inflows. The primary components of salt in seawater are chlorides, sulfates, carbonates, sodium, magnesium, and potassium. The salinity of seawater also affects its density and temperature properties, which in turn impacts sea currents and climate. The total salt concentration in seawater makes it unsuitable for humans to drink without extra treatment. However, seawater contains many minerals and elements, which makes it a vital source for marine life. However, CO_2 concentration can be several times higher in some sources of water, especially if it goes through natural or anthropogenic processes (Bekezhanov *et al.* 2021), such as soil outgassing, biological activity, or atmospheric pollution (Narozhnykh *et al.* 2018).

CONCLUSION

The general specific feature of CO_2 dissolution in both types of water is its dependence on pressure, temperature, and access to the surface for contact between water and the atmosphere. These processes are influential factors in the global carbon cycle, climate change, and ecosystems of both freshwater and marine ecosystems. A large share of the CO_2 emitted into the atmosphere due to human activity is dissolved in the ocean. This facilitates the formation of carbonic acid and thus causes ocean acidification, which impacts marine life and ecosystems. The dissolution of CO_2 in fresh and salt water is a multifaceted process that has a tremendous impact on the environment and the global climate system. This complex interaction has far-reaching implications for biodiversity, geology, climate, and life on Earth altogether. The dissolution of CO_2 in the ocean also influences climatic processes. Oceans serve as a massive reservoir of CO_2, uptaking a major part of its anthropogenic emissions. This decreases the concentration of CO_2 in the atmosphere, thus helping to ease global warming. The dissolution of CO_2 in fresh and salt water is a complex and dynamic process that is critical for understanding changes in the natural environment and the impact of CO_2 on various aspects of nature and human activity.

Investigation of these features advances our knowledge about global processes and contributes to the development of sustainable solutions to preserve the environment.

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