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The specifics of chamber measurements of greenhouse gas emissions in coastal and marine ecosystems

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Abstract: The article presents the results of measuring CO2 fluxes on the beach in areas with and without marine macrophytes and at the water-atmosphere boundary in Kievka Bay. Such studies were conducted for Kievka Bay for the first time. A chamber dynamic method and a laser gas analyzer were used to measure CO2 fluxes at all plots. Higher values of CO2 fluxes were noted on the beach in areas with dry beach macrophytes compared to wet beach macrophytes. Areas with macrophytes had 23 times higher values of CO2 fluxes compared to areas without beach macrophytes. To identify patterns and intensity of CO2 gas exchange between the sea and the atmosphere, long-term monitoring measurements are necessary, since there are many variable factors. When measuring gas exchange between the sea and the atmosphere, sharp short-term increases or decreases in CO2 concentration were noted on the graphs of concentration versus measurement time. This was not associated with technical failures of the gas analyzer or features of the floating chamber. This introduces difficulties in interpreting the data, since the linearity of the graph is lost and the error in the flow value increases.
Keywords: *Algae, Beach, CO2 flows, CO2 in the sea, Marine macrophytes, Sea of Japan.*

1. Introduction

It is well known that the World Ocean plays a huge role in the global balance of energy, heat, and climatically active gases and is their global regulator. Methane and carbon dioxide are two of the most important and one of the strongest (after water vapor) greenhouse gases (GHGs) of the Earth's atmosphere. Both components are actively involved in the processes of climate change, the formation of the thermal balance of the atmosphere and chemical transformations of the atmospheric gas composition. One of the urgent ways to solve the problem under consideration is to take more complete account of the natural reservoirs of carbon runoff in the form of carbon dioxide and methane, including the coastal ecosystems of the northern and boreal seas – as essential elements of the country's natural capital.

In addition to the need to assess the contribution of the oceans to the global carbon stock, it is necessary to study carbon cycles in coastal terrestrial ecosystems. Over the past few years, research projects have begun to actively develop to assess the contribution of marching, mangrove and marine communities to carbon deposition. According to the estimates of the FAO UNESCO organization, 50 marine plots included in the UNESCO World Heritage List account for at least 21% of the global area of blue carbon ecosystems [1]. The protection of such ecocenoses plays an important role in the accumulation of carbon from the atmosphere, and their degradation can lead to the release of billions of tons of greenhouse gases. Most of the publications available in the literature are devoted to assessing the contribution of marine coastal ecosystems to the carbon balance formed in the tropical zone [2-5].

Seaweed (marine macrophytes) is one of the areas of research within the framework of the climate agenda. According to the UN Global Compact Report (2021), "Seaweed is arguably one of the most scalable nature-based solutions, offering opportunities for both decarbonization of the economy and carbon capture from the ocean surface" (p.9) [6,7]. Along with wetlands, mangroves and coastal plant

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ecosystems, algae thickets are recognized as important ecological sites, and the carbon contained within these ecosystems is called "blue carbon" [8,9]. Whether algae contribute to gas exchange at the water–ocean boundary is an open question. First of all, it depends on the design capabilities of the existing equipment.

The most accessible and widespread method of measuring the flow of greenhouse gases in real time is the chamber dynamic method. For terrestrial soils, there are a sufficient number of companies developing such equipment: Lacor, Picaro, Los Gatos, etc. There is no such industrial equipment for marine measurements, therefore, the purpose of our research was to assess greenhouse gas emissions from coastal soils with a standard terrestrial soil chamber and in marine areas using an author's floating camera.

2. Materials and Methods

The plots were located on the beach and coastal part of Kievka Bay, northwest coast of the Sea of Japan, Russian Federation. The main part of the coastline of Kievka Bay is low-lying and is occupied by a large sandy beach. The northwestern and southeastern shores of Kievka Bay are represented by high capes. The coastline of Kievka Bay is subject to active coastal abrasion. Kievka Bay has free water exchange and intensive coastal runoff: the flow of the Kievka river; water inflow from the open sea and neighboring bays; formation/destruction of seasonal stratification; autumn upwelling of waters.

Measurements were taken on the beach on August 3, 2023. On the beach, differences in CO_2 fluxes were looked for between areas with beach macrophytes and areas without beach macrophytes. In Kievka Bay, 14 macrophyte communities were noted (Galysheva and Kozhenkova 2023). In the marine zone near the measurement plots on the beach, the most developed communities are: Saccharina japonica, Phyllospadix iwatensis + Saccharina Intermedius + Costaria costata, Zostera marina (Galysheva and Kozhenkova 2023).

Four plots were selected on the beach, which differed in altitude, distance from the water's edge, and number of beach macrophytes: WM – wet coastal emissions of marine macrophytes; DM – dry coastal emissions of marine macrophytes; CR – section of the first coastal rampart; ST – section of the marine terrace (Figure 1c).

CO_2 fluxes on the beach were measured by a Picarro 4301 GasScouter analyzer in combination with a Picaro Mobile Soil Flux System, A0947 camera. The time range of one measurement was 5 minutes. Measurements were carried out three times for each plot.

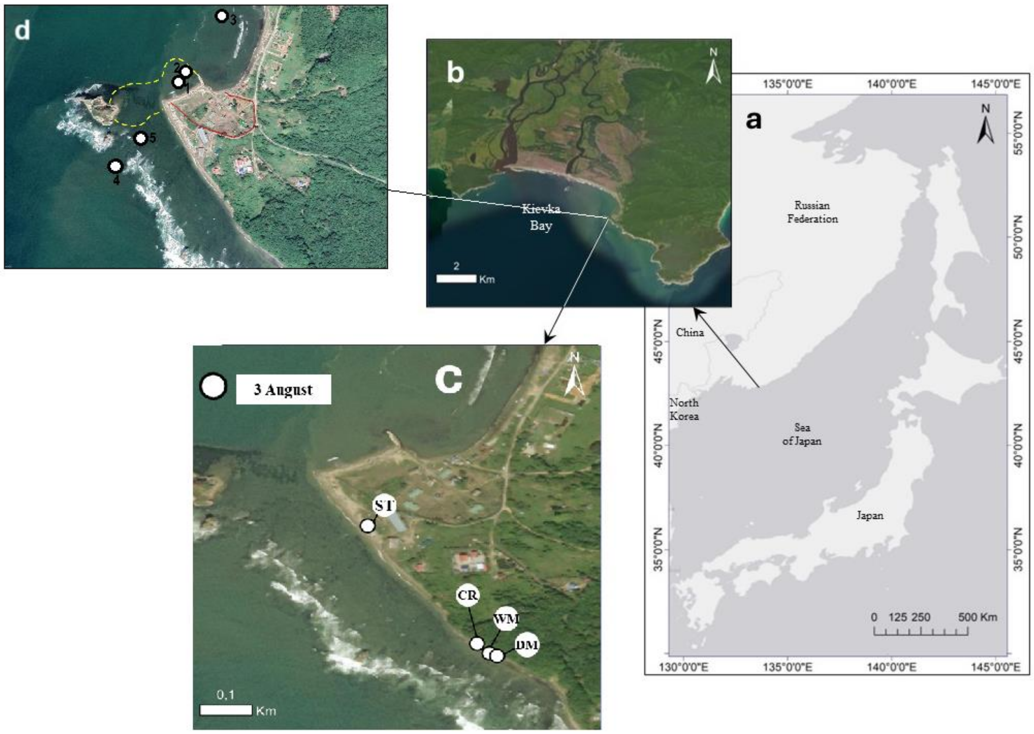

Figure 1.
(a) and (b) - Schematic map of the location of the study area; (c) - Schematic map of the location of the CO_2 flux measurement plots for August 3, 2023. Plots for August 3: WM - wet beach marine macrophytes; DM - dry beach marine macrophytes; CR - plots of the first coastal wall; ST - plots of the sea ter-race. (d) - the layout of the measuring points in the shallow part of Kievka Bay. The yellow line is the area of distribution of seagrasses.

The study of the respiration of the marine ecosystems of Kievka Bay was carried out in the summer period on August 1 and 2, 2023 in the areas of coastal marine ecosystems adjacent to the coast of Kievka Bay (Figure 1d).

The main purpose of the study was to assess the gas exchange of CO_2 in the water-atmosphere system in different areas of coastal marine ecosystems. The studied areas of coastal marine ecosystems were represented by five plots: No. 1 – field of Zostera on a sandy base that does not reach the water surface; No. 2 – field of Zostera on a sandy base that reaches the surface; No. 3 – sand without a plant ecosystem; No. 4 – fields of algae on pebbles; No. 5 – pebbles without algae. Measurements were made during the day and night periods. All variants of coastal marine ecosystems were measured during the daytime, and only variants No. 1, No. 2 and No. 3 were measured at night.

Measurements of gas exchange in the water-atmosphere system were carried out using a gas analyzer Picarro G4301, connected by air intake tubes with a light-permeable floating chamber of the author's design [10], the design of which is shown in Figure 2. The camera was installed on the water surface of coastal marine ecosystems at the points selected for the study. The camera was installed from the side of the boat, on which there was an operator with a gas analyzer. The time range of one measurement was from 15 to 30 minutes.

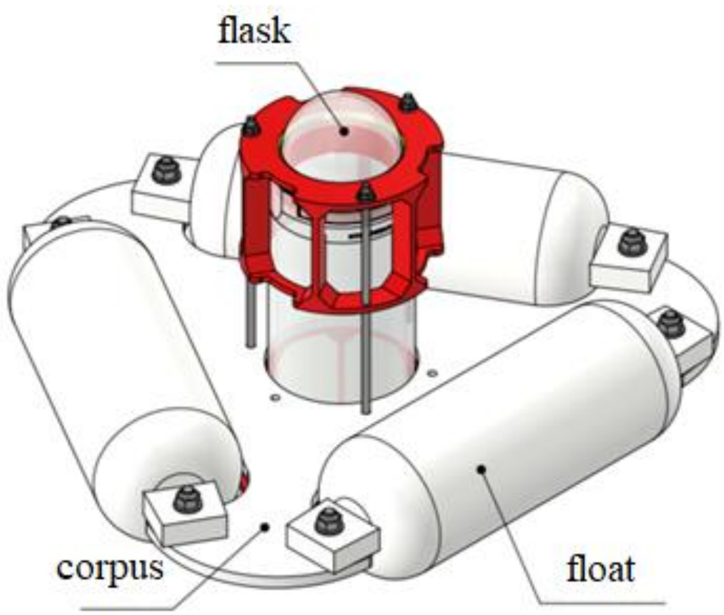

Figure 2.
Floating chamber for continuous measurement of greenhouse gas concentrations at the water-air interface.

Greenhouse gas fluxes were calculated using the formula (equation 1):

$$F_{gas} = \frac{\frac{\Delta[Gas]}{\Delta t} \cdot V \cdot \rho}{A} \quad (1)$$

where Fgas = linear flow of the test gas (CO_2) in μmol CO m^{-2} s^{-1}; Δ [Gas]/Δt—the number of gas particles at time t, expressed in μmol mol-1 s-1; V—the total volume of the chamber, m3; A—the area of the investigated surface, m^2; ρ—the molar density of air (mol m^{-3}), defined as P/RT, where P is the air pressure, Pa; R—the universal gas constant, equal to 8.31 Pa $m^3 \cdot mol^{-1} K^{-1}$; T— air temperature, K.. The determination coefficient R^2 was used to assess the reliability of the measured flow data.

The temperature and air pressure, necessary for calculating the gas flow, were measured using the Vaisala WXT520 weather sensor (Vaisala, Helsinki, Finland).

3. Results

As a result of the study of CO_2 gas exchange in the water-atmosphere system in the areas of coastal marine ecosystems, no patterns were found in the distribution of CO_2 fluxes between the studied areas both during the day and at night. The values of CO_2 fluxes differed significantly over the two days.

According to Table 1, negative values of the CO_2 flux were mainly obtained over two days, which indicates the absorption capacity of ecosystems for the measurement period. On August 2, negative values of CO_2 fluxes were noted in all sections, while the values of CO_2 fluxes in the sections decreased in a row № 4, № 3, № 1, № 5, № 2. It should be noted that on August 1, in addition to negative values of CO_2 fluxes, positive values were observed in sections No. 2 and No. 3, and the values of fluxes decreased in a row № 3, № 2, № 4, № 5, № 1, which, as you can see, does not coincide with the distribution on August 2.

Table 1.
The values of the CO_2 flux in the areas of the coastal marine ecosystems of Kievka Bay, measured in the daytime.

№ plot	The value of the flow CO_2, mg CO_2 m^{-2} s^{-1}	
	1 august	2 august
№ 1	-15.10 ± 0,29	-3.16 ± 0.35
№ 2	0.65 ± 0.11	-25.55 ± 0.46
№ 3	5.41 ± 0.12	-3.12 ± 0.18
№ 4	-4.55 ± 0.20	-1.92 ± 1.16
№ 5	-7.93 ± 0.16	-4.17 ± 0.37

Over the course of two days, a spread of values was noted for each plot. The most stable values were found in plot No. 4 and No. 5 (kelp fields). A significant variation of values was noted in plots No. 1, No. 2 and No. 3 (fields of Zostera and sand). The maximum difference in CO_2 flux, which amounted to 26.2 mg CO_2 m^2 h^{-1}, was observed at the plot № 2.

During the night period, significant variation in CO_2 flux values was also noted in sections No. 1, No. 2 and No. 3 (Table 2). The maximum flow difference, which amounted to 133.45 mg CO_2 m^{-2} h^{-1}, was observed at plot No. 3.

Table 2.
CO_2 flux values in the areas of the coastal marine ecosystems of Kievka Bay, measured during the night period.

№ plot	The value of the stream CO_2, mg CO_2 m^{-2} s^{-1}	
	1 августа	2 августа
№ 1	-2.23 ± 0.13	0.38 ± 0.29
№ 2	-1.35 ± 0.38	-14.05 ± 0.48
№ 3	3.59 ± 0.17	137.04 ± 35.60

When considering correlations of CO_2 fluxes from offshore plots with values of solar radiation, air and water temperature, air pressure and oxygen content in the water column, correlations were noted only for the values of August 1. A positive correlation of the flow was noted with the values of solar radiation, air and water temperature, air pressure, and a negative correlation with the values of the oxygen content of the water column.

The values of CH_4 fluxes for two days (both during the daytime and at night) did not differ significantly from each other and were close to zero.

The lack of regularity in the distribution of flow values during the two days of measurements indicates, on the one hand, an insufficient time interval of measurements. Such measurements require longer monitoring studies during different seasons and different weather conditions. On the other hand, coastal marine ecosystems are influenced by many factors, such as weather characteristics, the hydrological regime of the territory, the depth of the measuring point, the diversity and number of living and plant ecosystems.

As a result of measurements at coastal plots, a significant difference in CO_2 fluxes between plots with and without marine macrophytes was obtained. The highest average CO_2 flux value of 1578.85 ± 13.79 mg CO_2 $m^{-2}h^{-1}$ was obtained at the DM plot (Figure 3). According to the results of the study [8], the highest values of CO_2 flux were obtained from algae samples with constant moisture. Samples with no moisture released 72% less CO_2 compared to samples with the least moisture [145]. As a result of this measurement, the CO_2 flux at the WM plots was on average 22% less than the flux at the DM plots and amounted to 1,296.27 ± 15.36 mg CO_2 $m^{-2}h^{-1}$. The results obtained do not correspond to the results of the study by Liu et. al [11], where wetter samples of marine macrophytes showed a greater result.

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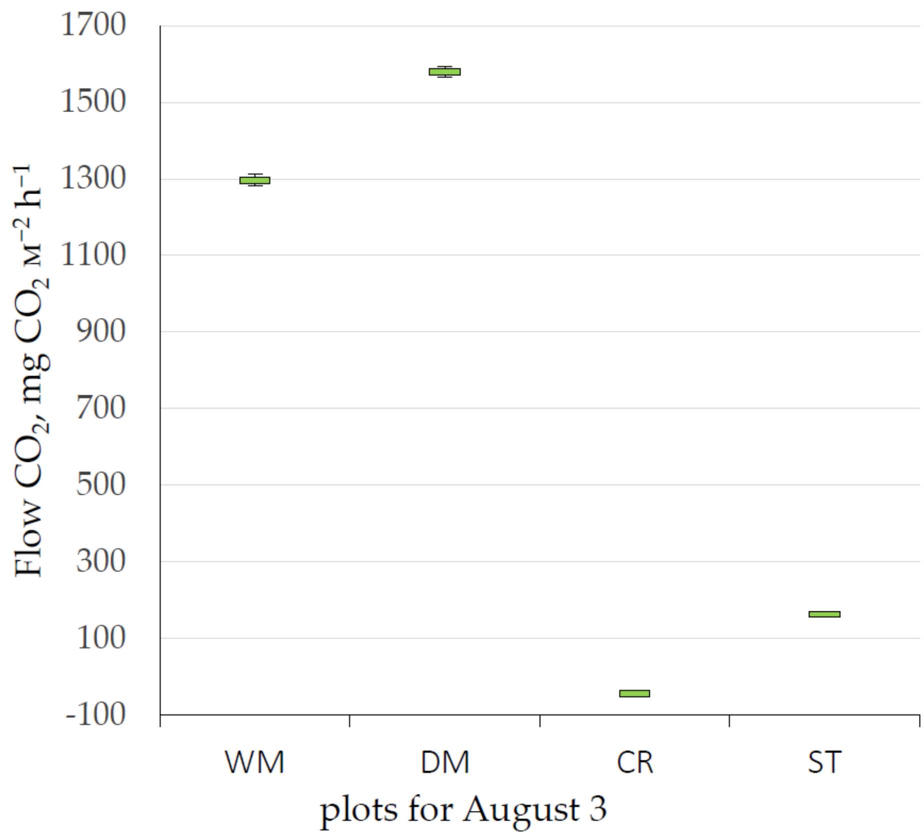

Figure 3.
CO_2 fluxes measured on August 3, 2023. DM – dry coastal emissions of marine macrophytes; CR – section of the first coastal shaft; ST – section of the marine terrace. An error limit equal to the standard error of the flow is specified for the flow values.

The lowest average CO_2 flux value -42.29 = 5.69 mg CO_2 m^2 h^{-1} was obtained at the CR plot. The CR plots were composed of pebbles with almost complete or partial absence of beached marine macrophytes. During periods of storms, these areas are flooded with water, which, together with the constituent material, makes it impossible to form a stable microbiological community that would contribute to the production of CO_2.

In the ST plots, the average flow value was CO_2 163.95 ± 1.97 mg CO_2 m^2 h^{-1}. These plots, compared with the CR plots, were composed of a sandy fraction and had sparse thickets of herbaceous and shrubby vegetation, which indicates greater stability of the ecosystem and the presence of permanent nutrients for plant growth and development. Consequently, microbiological processes occur in these areas, which lead to the release of CO_2.

On average, the flow in areas with the presence of marine macrophytes (both wet and dry) was 23 times greater than in areas with the absence of marine macrophytes.

Despite the significant difference in the received flows, we cannot project them over long time periods. This is because the measurements were carried out during one day under certain conditions, which is not representative even for the summer period. It should be noted that during the measurement period on August 3, the air temperature ranged from 23.4 to 25.4 °C, the air pressure ranged from 999.2 to 999.7 mbar.

August is the peak of the growing season for most plants in the Primorsky Territory. Thus, to understand the dynamics of the CO_2 flux during the spring-autumn or year-round period, it is necessary to conduct appropriate monitoring studies.

4. Conclusion

This study was the initial stage of evaluating the potential possibility of creating a climate project using coastal macrophyte emissions in the Primorsky Territory (Far East) of the Russian Federation. We understand that regular measurements in seasonal dynamics are necessary for a complete quantitative and qualitative assessment. It is also necessary to estimate the amount of marine macrophyte emissions in the study area.

For the Kievka Bay, greenhouse gas emissions were assessed for the first time. During the measurements, it was revealed that predominantly negative values of the CO_2 flux were recorded in the marine areas, which indicate the absorption capacity of the studied ecosystems for the measurement period.

According to the results obtained in coastal areas, areas with the absence of marine macrophytes had lower values of CO_2 fluxes compared with areas with the presence of macrophytes. This effect was noted both with the natural distribution of macrophytes on the coast, and after their manual collection. On average, the CO_2 fluxes measured by us in August in areas with natural deposition of marine macrophytes (both wet and dry) were 23 times higher than in areas with no marine macrophytes.

When performing measurements and processing the results, some specifics of measuring greenhouse gas fluxes in coastal and marine ecosystems were noted. When calculating greenhouse gas fluxes from offshore plots, the graphs of concentration dependence on the measurement time showed moments of sharp changes in concentrations like instantaneous emissions or gas uptake. These fluctuations in the graphs made data processing difficult, since they violated the linearity of the graphs and reduced the values of the coefficient of determination R^2, which was used in the calculation of $\Delta[Gas]/\Delta t$ to assess the reliability of flow data.

It is noted that it is difficult to fix the linearity of the flow when measuring greenhouse gas fluxes in coastal areas without vegetation cover. At the time of measurements, an active air exchange of the upper soil layer of the measured area with the atmosphere was observed. To solve the problem, an additional device is needed for a tighter adhesion of the chamber surface to the soil due to a deeply immersed mortise ring.

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