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Study of greenhouse gases in the bottom-water-atmosphere system in coastal marine ecosystems of Kievka Bay, Sea of Japan

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Abstract: The paper presents for the first time the results of gas geochemical studies in the bottom-water-atmosphere system of coastal-marine ecosystems of Kievka Bay and the adjacent shelf. Regional estimates of methane and carbon dioxide content in bottom sediments, the water column and the near-water atmosphere were obtained. The maximum methane content up to 447 nmol/l was established in the bottom sediments of the central part of the bay, the place of accumulation of organic saturated fine-grained silt sediments, and the minimum in the open part of the sea. Methane concentrations in water varied from 2.6 to 17.5 nmol/l, with maxima in the surface horizons of the central part of the Kievka Bay water area. CO2 concentrations in the near-water layer of the atmosphere varied in the range from 422.10 to 477.37 ppm, averaging 426.56 ppm. The concentration of CH4 varied from 2.029 to 2.070 ppm, averaging 2.032 ppm. The methane flux at the water-atmosphere boundary varied from 0.01 to 18.10 mol/km2 day, averaging 2.7 mol/km2 day. The increased concentrations and fluxes of methane in the surface horizons of the shallow waters of Kievka Bay and the decreased salinity values indicate the influence of the river runoff of the Kievka River, as well as the potential influence of shelf bottom sediments. In general, the studies revealed methane emissions into the atmosphere of varying intensity (from weak to high), which characterizes Kievka Bay as a low-intensity source of methane entering the atmosphere during the autumn transition period of the year.

Keywords: *Flux, Greenhouse gases, Kievka Bay, Methane, Sea of Japan.*

1. Introduction

Currently, there are serious uncertainties in assessing the contribution of natural and anthropogenic sources of greenhouse gases. Direct measurements made during marine expeditions provide unique information on the actual content of climate-active gases in the bottom-water-atmosphere system, which is necessary for a detailed study of gas exchange processes at the boundary of these ecosystems. It is well known that the World Ocean plays a huge role in the global balance of energy, heat, and climate-active gases and is their global regulator. Methane and carbon dioxide are the two most important and among the strongest (after water vapor) greenhouse gases (GHG) in the Earth's atmosphere. The importance of the ocean in the processes of emission or absorption of carbon dioxide and methane, as well as taking into account all possible sources of these gases, is obvious to the global scientific community, which is creating international teams to study carbon balances and greenhouse gas fluxes in coastal and marine ecosystems [1-4]. Various studies have recognized that the waters of the World Ocean are an important source of methane entering the atmosphere, and its global marine emission can reach 25 million tons/year [5]. The contribution of the World Ocean to the methane entering the atmosphere remains incompletely defined and ranges from 0.005 to 3% of the global production of methane CH_4. Shelf areas are a more intense source of methane into the atmosphere compared to the

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open ocean and account for about 75% of the global marine methane flux [6]. Regional studies of the distribution of greenhouse gases in the bottom-water-atmosphere system expand our knowledge of the influence of greenhouse gases on the processes of change in the Earth's climate system, and also allow us to detail possible sources and scales of their migration.

2. Materials and Methods

The object of the research was the coastal marine ecosystems of Kievka Bay and the adjacent shelf waters of the Sea of Japan. Kievka Bay is located in the southeastern part of the coast of Primorsky Krai at a latitude of 42°50' N, and has a latitudinal extent. The main hydrological processes that determine the water regime of the bay are the runoff of the Kievka River, the inflow of waters from the open part of the sea and neighboring bays, the formation/destruction of seasonal stratification of water masses, and upwellings in autumn. The surface bottom sediments of the bay are represented by granulometric fractions from psammites to pelitic silts [7]. The main volume of research work was carried out from November 9 to 11, 2022, during the integrated expedition of the Pacific Oceanological Institute FEB RAS, with the support of the FEFU IMO, No. 83 on the research vessel «Professor Gagarinsky» [8]. A total of 12 oceanographic stations were set up in the study area, at sea depths from 12 to 309 m (Figure 1). At each station, samples of bottom sediments and water were collected and continuous measurements were taken in the atmospheric surface layer.

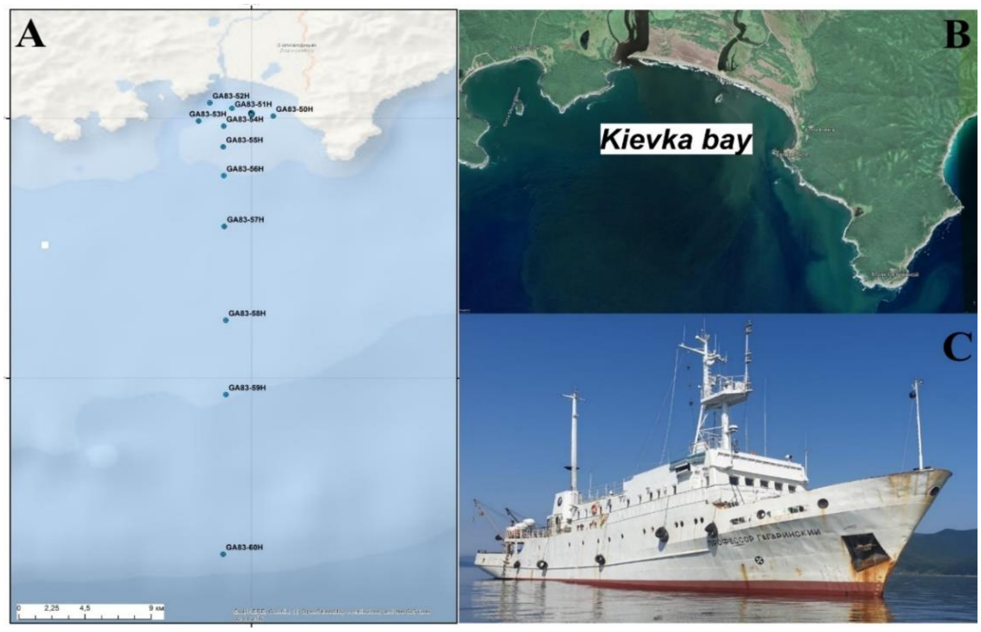

Figure 1.
Location of oceanographic stations along the Kievka Bay – shelf edge profile (A). Inner part of Kievka Bay (B). R/V Professor Gagarinsky with a complex of scientific equipment (C).

2.1. Bottom Sediments

Bottom sediments were collected using a box corer, which allows studying columns with a capacity of up to 30 cm. Sediment samples were collected using 12 ml syringes with cut-off nozzles in 43 ml containers filled with a saturated NaCl solution with the addition of a preservative (1 ml chlorhexidine bigluconate 0.05%). The sampling step was 5-10 cm. A total of 28 sediment samples were collected. Gas extraction was carried out using the Headspace method. Helium grade 6.0 was used as the gas phase, which was filled into the containers using a Tedlar Bag Dual Valve gas bag (USA) with two valves. The samples were vigorously shaken for at least 2 hours on a LS 110 mixing device (Russia), processed in a

FineSonicE05 ultrasonic bath, and then the gas phase was extracted with a syringe under equilibrium conditions. Gaseous components (CH_4 and CO_2) were determined using a CrystalLux-4000M gas chromatograph (MetaChrome, Russia). A gas sample is introduced into the chromatograph's dosing tap using a syringe. The chromatograph module has three detectors: two thermal conductivity detectors and one flame ionization detector, which makes it possible to analyze gas components in one go. The minimum volume of gas phase introduced into the device is 4 ml. The flame ionization detector (FID) is used for qualitative and quantitative processing of methane and other organic components with an accuracy of 10^{-6}%. Inorganic gases: nitrogen, oxygen, carbon dioxide, as well as methane with a concentration of more than 1%, are analyzed using a thermal conductivity detector (TCD), the sensitivity of which is 0.01%. Certified verification gas mixtures manufactured by PGS-Service were used to calibrate the device. The error of this method is no more than 3%.

2.2. Seawater

Underway flow system. Continuous water intake was carried out by a standard ship pump from the bow kingston (water intake depth 4 m from the sea surface) while the vessel was moving. The sampling resolution was 1 sample / 0.5 - 1 hour. A total of 23 water samples were collected. Continuous measurements of the temperature and salinity of the surface water layer were carried out using an SBE 45 thermosalinograph (USA). For each sample, the sampling time and navigation reference to the vessel's route were recorded. All measurements were integrated directly into the array of digital hydrological and meteorological data. Methane fluxes in the water-atmosphere interface were calculated according to Wanninkhof [9].

Water column studies. Water was sampled using NISKIN bathometers (USA). Samples were collected taking into account the vertical distribution of temperature, salinity and other hydrological parameters during CTD probing using SBE 19 plus (USA). The concentration of gases (CH_4 and CO_2) in all collected water samples (49 samples) was determined using the Headspace method. Samples were collected in glass vials (68 ml) with rubber stoppers. Then they were kept for 2 hours to equalize the water temperature with the ambient temperature and shaken on a shaker. Gas samples were analyzed using a CrystalLux-4000M gas chromatograph (MetaChrome, Russia). The concentrations of methane dissolved in seawater were calculated according to the method of Yamamoto, et al. [10] as modified by Wiesenburg and Guinasso Jr [11] using the calculated methane solubility constants.

2.3. Atmospheric surface layer

The measurements were carried out using a Picarro G2311-f laser analyzer (Picarro, USA) [12]. The measurement rate was 10 Hz. The measurement range for CO_2 was 300–500 ppm, for CH_4 1–3 ppm, respectively [13]. The measurement accuracy (error) was 200 ppb for CO_2, 3 ppb for CH_4. Certified calibration gas mixtures manufactured by PGS-Service were used to calibrate the device. The gas analyzer was placed in the upper deck laboratory, equipped with a vacuum pump for continuous pumping of outside air, and equipped with air intake devices of our own design. The air intake chamber of the analyzer was located on an external rod in the front part of the vessel at an altitude of 10 meters above sea level. All primary data were filtered taking into account the influence of the vessel's exhaust gases, the vessel's course and the wind direction, which allows for effective data rejection. The data array was averaged over a 5-minute period.

3. Results and Discussion

3.1. Gas Geochemical Studies of Bottom Sediments

Most of Kievka Bay is occupied by soft soils - from psammites to pelitic silts. The maximum contents of organic carbon (up to 1.65%) are confined to the central waters of the bay, where the formation of silty fine-grained aquatic soils occurs [14]. As you move towards the edge of the shelf, the content of sandy fractions increases, which characterizes this area as a transit zone subject to active hydrodynamic processes.

According to research data from 2012-2018, the methane content in bottom sediments of a large area of Peter the Great Bay (Sea of Japan) was quite uniform in the surface layer (0-20 cm) of bottom sediments and did not exceed 50 nmol/l [6]. Data on the content of methane and other natural gases in the waters of Kievka Bay at the time of the study were not available. As a result of the chromatographic analysis carried out on board the vessel, the following were determined: methane, carbon dioxide (Figure 2). CH_4 was found in all samples (0-30 cm horizon) taken from bottom sediments in concentrations from 7 to 447 nmol/l. The highest methane concentrations were usually recorded within the upper interval of 0-15 cm. A general pattern for the work area is also a decrease in methane concentrations with sampling depth and with the distance of the stations from the coastline. The maximum methane content of up to 447 nmol/l was found at stations in the central part of the bay, the place of accumulation of organic saturated fine-grained silty aquatic soils (Figure 2).

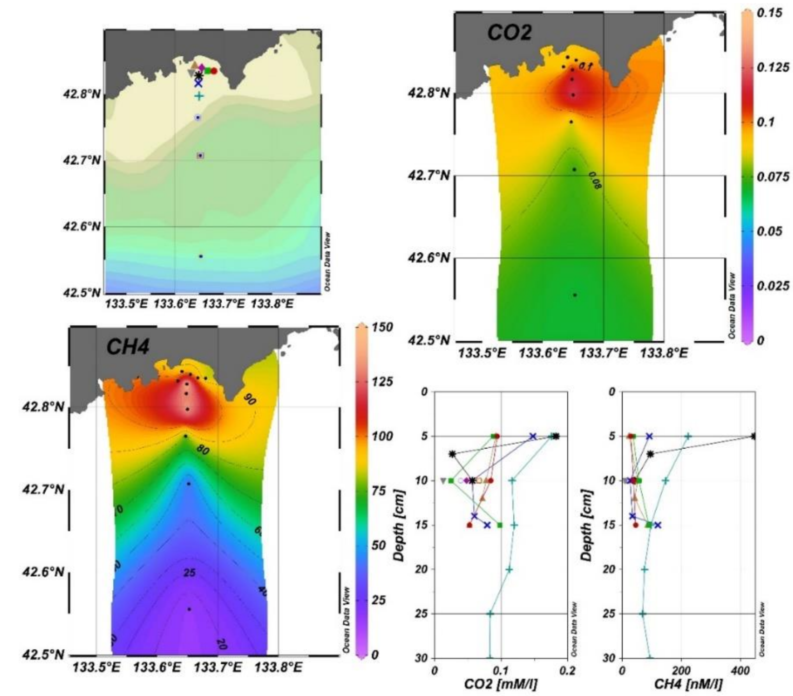

Figure 2.
Distribution of methane (nmol/l) and carbon dioxide (mmol/l) in the surface interval of aquatic soils (0-10 cm) of Kievka Bay and the adjacent shelf. The graphs show the distribution of methane and carbon dioxide by sampling depth.

Carbon dioxide was detected in all bottom sediment samples. Carbon dioxide concentrations varied from 0.01 to 0.18 mmol/l. Its maximum contents were confined either to the uppermost sampling horizon 0-5 cm (oxidized layer) or at some stations to the lowest horizons.

Analysis of the distribution of gas components in bottom sediments in the Kievka Bay area allows us to draw the following conclusions:

- Increased concentrations of methane and carbon dioxide are confined to the surface intervals and the central part of Kievka Bay, in the area of distribution of organic saturated silt sediments;
- Analysis of the distribution of natural gases and component composition allows us to speak about the predominantly biochemical and microbial genesis of the formation of gas anomalies and the favorable ecological state of bottom sediments in the study area.

3.2 Gas geochemical studies of the marine water

According to data from 1996-2012, background concentrations for the Peter the Great Bay (PGB) water area did not exceed 3.5-5.3 nmol/l [6]. As a result of studies from 2012-2014, it was also established that most of the PGB area had background methane concentrations (3.5-4.7 nmol/l) in the surface water layer [15]. High methane concentrations (8.9-26.7 nmol/l) were found only in the coastal part and closed bays of the PGB [15]. At the same time, for open deep-water areas of the Sea of Japan, methane concentrations in the surface layer are characterized by minimum values of 1.6-2.2 nmol/l [6]. As a result of the studies in 2022, methane concentrations along the Kievka Bay - shelf edge profile varied from 2.6 to 13.2 nmol/l, in the surface layer - from 3.6 to 13.2 nmol/l, in the bottom layer - from 2.6 to 5.4 nmol/l. The salinity value in surface waters varied from 33.0 to 33.7‰, temperatures from 6.4 to 7.4°C, in the bottom horizons from 33.8 to 34.0‰, temperatures from 0.9 to 6.2°C, respectively. Elevated methane concentrations in the surface horizons of the shallow waters of Kievka Bay and lower salinity values indicate the influence of river runoff from the Kievka River, as well as the potential influence of shelf bottom sediments. In the seaward part of the section, the distribution of methane takes on a typical form for the open part of the Sea of Japan with minimal concentrations of methane (Figure 3), which indicates the predominance of coastal sources of its supply. The active removal of methane to the surface can also be prevented by the stable stratification of water masses recorded on the general profile (Figure 3).

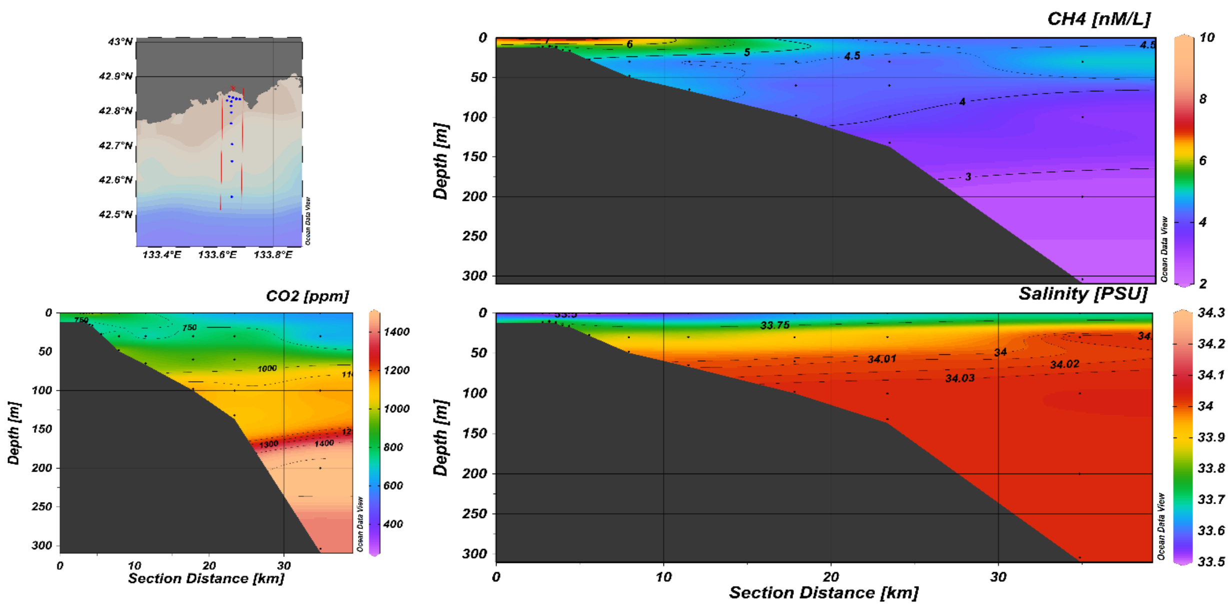

Figure 3.
Distribution of methane (nmol/l), carbon dioxide (ppm) and salinity (PSU) in the section between Kievka Bay and the shelf edge.

3.3. Gas Geochemical Studies of Surface Waters

The process of greenhouse gas exchange in the water-atmosphere system is a very dynamic phenomenon sensitive to the influence of various factors. Of great importance is not only the direct quantitative content of gases in water and the surface atmosphere, but also a complex of hydrometeorological factors. Thus, temperature, salinity and depth (pressure) of sea waters are the main parameters affecting the solubility of gaseous compounds in aquatic ecosystems. Wind force is the main driver of the intensity of the gas exchange process itself, and the pressure and temperature of the surface atmosphere also have a lesser influence. To quantitatively calculate the flow at the water-atmosphere boundary, discrete studies of the surface water layer, the surface layer of the atmosphere and the collection of meteorological information were organized on the vessel. As a result of complex processing of the obtained data using formula [9] the methane flux in the water-atmosphere interface, equilibrium concentrations of methane in the surface water layer (C_{eq}) and the value of water saturation with methane SR (%) were calculated. The calculation of the methane flux included 42 measurement points of the studied parameters (23 "Underway" samples, 7 samples from the daily climatic station and 12 samples from stations of the Kievka Bay - shelf edge profile). To assess the intensity of methane flows, the classification developed for the seas of the Far East was used [16]. The temperature of surface waters in the study area, according to the SBE 45 flow-through thermosalinograph, varied from 6.8 to 7.7°C, which is close to the CTD sounding data. A small difference (no more than 0.4°C) in the values shows the convergence of the obtained results. The minimum temperature values were confined to the surface horizons of the open sea area, the maximum – to the inner waters of Kievka Bay.

The salinity of surface waters according to the flow-through thermosalinograph SBE 45 varied from 32.9 to 33.7 ‰. The maximum salinity was confined to the open sea area, the minimum – to the coastal areas of Kievka Bay.

The measured wind speed in the atmospheric surface layer varied from 0.4 to 6.3 m/s.

The equilibrium concentrations of methane in the surface water layer varied in a narrow range of 3.3-3.5 nmol/l, on average 3.4 nmol/l. The SR value varied from 3 to 414%, from almost equilibrium values to supersaturation.

Methane concentrations in the surface layer varied from 3.5 to 17.5 nmol/l. The maximum peak concentrations were recorded during the daily station and in the central part of the Kievka Bay water area. The methane flux at the water-atmosphere boundary was recorded in the range from 0.01 to 18.10 mol/km^2 day, with an average of 2.7; median of 1.1 mol/km^2 day. Minimum low-intensity methane fluxes within 0.1-0.3 mol/km^2 day are typical for the open water area, and the maximum (14.1-18.1 mol/km^2 day) are typical for the inner water area of Kievka Bay. The detected flux values fall within the range of 1 to 23 mol/km^2 day obtained for the spring season in the northeastern Sea of Japan [17] and the average values are close to those established for the deep waters of the Sea of Japan (2.6 mol/km^2 day) and the pelagic waters of the Pacific Ocean (2.9 mol/km^2 day) [17]. At the same time, the established average flux values for the autumn period are lower than for the spring period in the northeastern Sea of Japan (3.4-3.8 mol/km^2 day).

In general, methane emissions into the atmosphere of varying intensity (from weak to high) were detected at almost all measurement points, which characterizes Kievka Bay as a low-intensity source of methane entering the atmosphere during the autumn transition period of the year. High concentrations of methane in the surface layer and high rates of methane emissions into the atmosphere usually correlate with each other and with local increases in wind conditions.

3.4. Gas Geochemical Studies of the Atmospheric Surface Layer

The concentration of CO_2 in the atmospheric surface layer of the study area varied in the range from 422.10 to 477.37 ppm, with an average of 426.56 ppm and a median of 425.57 ppm.

The concentration of CH_4 varied in the range from 2.029 to 2.070 ppm, with an average of 2.032 and a median of 2.029 ppm.

Several episodes of simultaneous increases in CO_2 and CH_4 concentrations were identified during the study period. Increases in concentrations were noted during the daily mooring in the waters of Kievka Bay. Some episodes of increased concentrations were observed only during a certain period of time, therefore they are not permanent and were caused by a sharp change in the influencing factors.

The main factors include the influence of atmospheric transport from highly urbanized areas or changes in natural environmental parameters (wind direction and speed, atmospheric pressure, air humidity, air and surface water temperature, increased physical mixing of water masses (storms), etc.). According to NOAA monitoring data, the average global concentration of CO_2 and CH_4 in October 2022 was 416.17 and 1.92 ppm, respectively. The data obtained generally exceed the average monthly concentrations for October for both CO_2 and CH_4.

4. Conclusion

As a result of the conducted research, for the first time for the transitional autumn period of the year in the area of Kievka Bay, gas geochemical fields of greenhouse gases in the bottom-water-atmosphere system were comprehensively studied. The obtained data can be used to compile a detailed balance of greenhouse gas emissions/sinks in the marine ecosystems of the region. In Figure 4, all data are summarized in a single diagram showing the predominant influence of coastal sources of climatically active gases in the marine ecosystem.

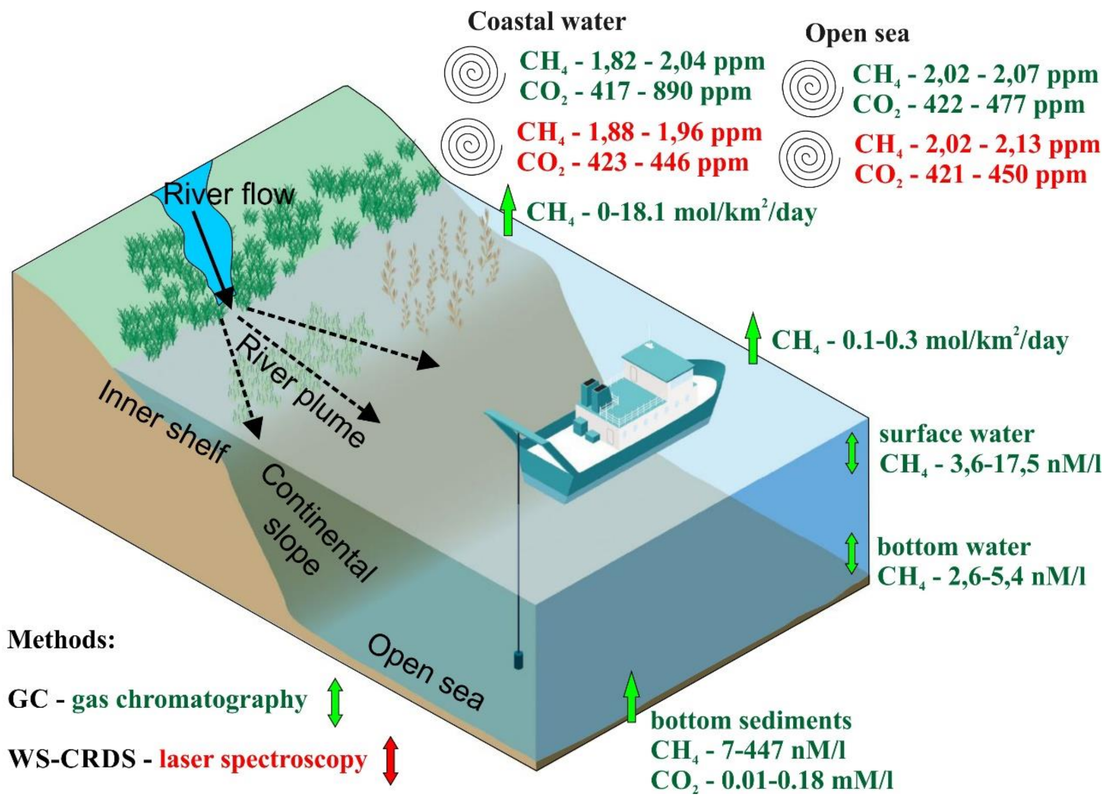

Figure 4.
Schematic diagram of the distribution of methane and carbon dioxide in the section between Kievka Bay and the edge of the shelf.

In general, the studies have revealed methane emissions into the atmosphere of varying intensity (from weak to high), which characterizes Kievka Bay as a low-intensity source of methane emissions into the atmosphere during the autumn transition period of the year. The detected local anomalies can be formed due to the influence of the river runoff of the Kievka River and surface coastal runoff, modern biochemical processes in organic saturated bottom sediments of the central part of the bay, as well as hydrological seasonal conditions of water exchange. The obtained data emphasize the high dynamism of measuring the parameters under study in natural ecosystems, which predetermines the need for further improvement and automation of approaches to measurements. Increasing the discreteness of measurements is the key to understanding daily and ecosystem patterns in gas exchange processes and sources of greenhouse gases in the land-sea system.

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Transparency:

The authors confirm that the manuscript is an honest, accurate, and transparent account of the study; that no vital features of the study have been omitted; and that any discrepancies from the study as planned have been explained. This study followed all ethical practices during writing.

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