RUSSIAN JOURNAL *of* EARTH SCIENCES

METHANE IN THE WATER COLUMN OF THE GDANSK DEEP (BALTIC SEA): SEASONAL AND VERTICAL VARIABILITY

M. O. Ulyanova[1,2*] **and A. O. Korneeva**[1,2]

[1]Shirshov Institute of Oceanology RAS, Moscow, Russia
[2]Immanuel Kant Baltic Federal University, Kaliningrad, Russia
* **Correspondence to:** Marina Ulyanova, marioches@mail.ru

Abstract: The study of the vertical distribution of methane dissolved in water and related parameters (water temperature and salinity, dissolved oxygen concentration) was carried out in 2021–2023 at the offshore carbon supersite Rosyanka in the Gdansk Deep of the Baltic Sea. Measurements with such frequency (a total of 16 surveys) were carried out in the region for the first time. Methane concentrations varied over a fairly wide range (0.000–1.122 μmol/L), and increased with depth, which is a typical distribution for the Baltic Sea and is associated with the vertical stratification of the water column. Single maximum values were characteristic of the layer extending from the bottom to the upper boundary of the halocline, which indicates the flow of methane from bottom sediments into the water column. In the near-surface layer (5–15 m), a weakly pronounced peak in methane concentrations was observed, which is a manifestation of the "oceanic methane paradox". No pronounced seasonality was detected in the vertical distribution of dissolved methane; the correlation between temperature, salinity, oxygen, and methane content turned out to be low.

Keywords: dissolved methane, carbon supersite, thermohaline conditions, hypoxia.

Citation: Ulyanova, M. O., and A. O. Korneeva (2024), Methane in the Water Column of the Gdansk Deep (Baltic Sea): Seasonal and Vertical Variability, *Russian Journal of Earth Sciences*, 24, ES5001, EDN: RPYLFX, https://doi.org/10.2205/2024es000938

RESEARCH ARTICLE

Received: 16 February 2024
Accepted: 16 October 2024
Published: 23 October 2024

Introduction

According to [*IPCC*, 2023], global surface temperature in 2011–2020 was around 1.1 °C higher than in 1850–1900 (1.09 [0.95–1.20] °C), with larger increases over land (1.59 [1.34–1.83] °C) than over the ocean (0.88 [0.68 up to 1.01] °C). The observed warming is caused by human activity: warming from greenhouse gases, dominated by carbon dioxide and methane, is partially masked by aerosol cooling.

Many environmental changes caused by past and future greenhouse gas emissions are irreversible on timescales of centuries and millennia, especially in the ocean, ice sheets, and global sea level. Ocean acidification, ocean oxygen loss, and global average sea level will continue to rise into the 21st century at rates dependent on future emissions. Issues related to reducing anthropogenic greenhouse gas emissions and climate conservation occupy an important place on the agenda of most world powers, including the Russian Federation, which was documented through the adoption of the Paris Agreement [*Voigt*, 2023]. The market for greenhouse gas emission quotas, which emerged after the entry into force of the Kyoto Protocol, provides for taking into account not only emissions, but also carbon absorption (sequestration), which allows Russia to enter it as a supplier of carbon units. In this regard, in 2021, a network of so-called carbon supersites is being created in Russia to develop and test technologies for monitoring the carbon balance, as well as assessing the state of natural systems, the quality of water resources and other parameters [*Bashirova et al.*, 2023].

At the end of the last century, the main sources of atmospheric methane were the following [*Heilig*, 1994]: emissions as a result of anaerobic decomposition in 1) natural wetlands; 2) rice fields; 3) emissions from livestock production systems (including internal fermentation and animal waste); 4) biomass burning; 5) anaerobic decomposition of organic waste in landfills; and 6) fossil methane emissions from fossil fuel exploration and transportation. In the modern world, the problem of global climate change cannot be solved without quantitative assessments of methane flow from the ocean. According to various estimates, the effective contribution of methane flux from the ocean surface to global emissions ranges from 0.005 to 3% [*Cicerone and Oremland*, 1988; *Conrad and Seiler*, 1988; *Reeburgh*, 2007b; *Kirschke et al.*, 2013] or from 5 to 25 million tons/year [*Saunois et al.*, 2016; *Weber et al.*, 2019; *Bange et al.*, 1994]. Discrepancies in flux estimates may be due to insufficient knowledge of the biogeochemical cycle of methane in the ocean [*Lein and Ivanov*, 2009]. In the last quarter of the 20th and first quarter of the 21st centuries, methane research developed mainly in two directions: assessment of distribution in the main ocean reservoirs – bottom sediments and water, as well as the development of molecular biological and isotope methods.

This study aims to study the variability (monitoring) of the vertical distribution of methane in the water column in the south-eastern part of the Baltic Sea in 2021–2023. In 2021, the offshore site of the Rosyanka carbon supersite was opened [*Bukanova et al.*, 2022], where research was carried out.

Study area

The carbon supersite is located in the territorial waters of the Russian Federation, the sea depth is 64–87 m, and the area is influenced by the flow of the largest river in the region Vistula, as well as in close proximity to the outflow of the Kaliningrad Lagoon and the Pregolya River. The location of the offshore carbon supersite in the South-Eastern Baltic Sea (Figure 1) is determined by the following factors:

- an unprecedentedly high level of water eutrophication, and, as a consequence, high rates of primary bioproduction and phytoplankton biomass [*Kudryavtseva and Aleksandrov*, 2019]. On a global scale, a pronounced regional maximum in CO_2 sequestration due to photosynthesis is observed in the Baltic Sea. The intensity of photosynthesis is highest in the southern part of the sea, where the offshore site of the carbon supersite is located [*Mosharov et al.*, 2022, 2024];
- closeness of the gassy sediments area which influences the methane distribution in the water;
- transboundary of the sea and high anthropogenic load [*Ulyanova and Danchenkov*, 2016].

The semi-closeness of the Baltic Sea and the episodic influx of salty North Sea waters through the Danish Straits [*Mohrholz*, 2018] lead to significant stratification of the water column (warm and fresh surface waters, cold and fresh intermediate waters, cold and salty bottom waters, as well as two transitional water masses [*Rak*, 2016; *Krechik et al.*, 2017] and limited vertical mixing. The development of a noticeable redox shift (from oxygen to sub- or anoxic conditions) and the formation of biogeochemical conditions for the existence of methanogenic bacteria and anaerobic oxidation of methane is typical for the Baltic deep basins [*Nausch et al.*, 2016; *Kanapatskiy et al.*, 2022]. The Gdansk Deep is characterized by the occurrence of periods of stagnation of water, which are renewed during large Baltic inflows (Major Baltic inflow) of salty, oxygenated water from the North Sea [*Elken*, 1996; *Piechura and Beszczynska-Moller*, 2003; *Markus Meier*, 2007]. Surface sediments of the Gdansk Deep, located in predominantly stagnant conditions, have been studied from the point of view of the distribution of organic matter and diagenesis processes. In the center of the Gdansk Deep, geochemical studies of pore waters and seismoacoustic studies of the seafloor reveal large areas with high concentrations of dissolved and free gas occurring in an organic-rich layer of post-glacial sediments [*Majewski and Klusek*, 2011; *Brodecka et al.*, 2013; *Ulyanova et al.*, 2013; *Jaśniewicz et al.*, 2018]. Methane, being part of the organic carbon cycle, participates in biogeochemical processes occurring in silty sediments. The relevance of studying areas of distribution of gas-saturated sediments is due to their important role as a source of methane as a greenhouse and media-forming gas for the water column and atmosphere.

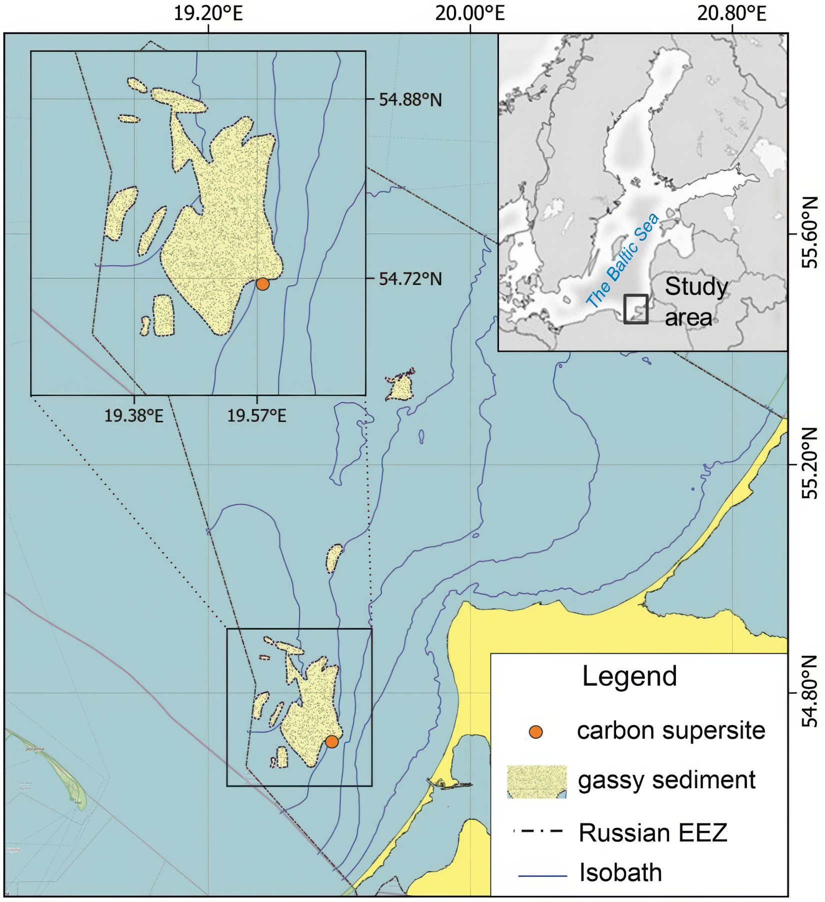

Figure 1. Scheme of the monitoring station (carbon supersite) location in the South-Eastern part of the Baltic Sea. Isobaths are lined every 20 m.

The high productivity of the South-Eastern Baltic Sea waters, combined with a significant supply of allochthonous organic matter [*Mosharov et al.*, 2022], promotes intense microbial processes of destruction of organic matter in the sediments. The terminal phase of decomposition of organic matter under anaerobic conditions with the participation of sulfate reducers and methanogens is accompanied by the formation of a significant amount of biogases – hydrogen sulfide and methane [*Geodekyan et al.*, 1989, 1990]. In the Gdansk Basin, the area of silts with contents of more than 1% (up to 5% in the surface horizon 0–5 cm) of Corg is confined to silts of Gdansk Deep [*Emelyanov*, 2002].

The Baltic Sea is among the seas with the fastest warming in the world in recent decades. Linear trends of seasonal and interannual sea surface temperature increase for 2003–2012 in the open part of the South–Eastern Baltic is estimated at a rate of 0.70 ± 0.27 °C/decade [*Bukanova et al.*, 2015] and 0.01 °C/year for 2005–2019 [*Stont et al.*, 2015, 2020]. These changes affect biogeochemical conditions, such as euxinic areas (lack of oxygen and increased levels of free hydrogen sulfide), as well as pelagic and bottom marine ecosystems, where methane conversion processes are active.

Two barriers limiting the release of greenhouse gases from marine basins are anaerobic and aerobic oxidation in sediments and the water column [*Reeburgh*, 2007a,b] and limited vertical mixing in the density gradient zone, which often leads to the accumulation of gases in deeper parts of the water column [*Gentz et al.*, 2014]. The latter barrier is especially important in the highly stratified Gdansk Deep [*Jakobs et al.*, 2014].

Materials and methods

The research was carried out at station located in coordinates 54°43.20′ N, 19°34.80′ E in different seasons 2021–2023 (Table 1). Each survey included vertical hydrophysical sounding and water sampling.

Table 1. Surveys dates

2021	2022	2023
28.04.2021	02.03.2022	26.04.2023
30.06.2021	28.04.2022	09.05.2023
29.08.2021	28.06.2022	10.07.2023
01.10.2021	12.07.2022	16.08.2023
30.10.2021	23.08.2022	22.11.2023
	05.11.2022	20.12.2023
	24.12.2022	

Vertical hydrophysical sounding (temperature, salinity, pressure) was carried out each survey using SonTek CastAway and Sea&Sun Technology CTD 90M probes.

Water sampling from various horizons (0, 2.5, 5, 7.5, 10, 15, 20, 25, 30, above thermocline, under thermocline/above halocline, under halocline, 10 m above bottom, 4 m above bottom, 1 m above bottom) was carried out using a 5-liter Niskin bottle. Total number of samples was 200 probes. Samples for dissolved gases were taken immediately after lifting the bottle aboard the vessel. The sampling discreteness for oxygen determination did not always coincide with the sampling discreteness for methane. Determination of the concentration of dissolved oxygen was carried out by the Winkler titrimetric method using a manual titrator-dispenser Aquilon ATP-1D. To determine methane, water was poured through a silicone tube into penicillin vials with a volume of 25–30 ml, with a fixative (dry KOH) previously placed in them to suppress microbial processes. Then, using a special plexiglass dispenser, the same volume of water (3 ml) was squeezed out of the vial, and closed with a gas-tight butyl rubber stopper and rolled with an aluminum lid. The gas phase in head-space consisted of air. Samples in penicillin vials were stored upside down and transported to the coastal laboratory at a temperature of +4 °C. Gas components in seawater samples were determined on a Crystallux–4000M chromatograph using the phase-equilibrium degassing method, the so-called headspace analysis [*Bolshakov and Egorov*, 1987]. The measurement of methane content on a gas chromatograph is performed with an error of 2%. A standard sample of artificial gas mixture in helium was used for calibration.

Results

Interannual vertical variability of dissolved methane concentrations

2021

The following methane concentrations were measured in 2021: min 0.000, max 0.173, median 0.002 µmol/L. In April, the distribution of methane in the 0–25 m layer was generally uniform (Figure 2). At a horizon of 10–15 m, a slight increase in gas concentration to 0.003 µmol/L was noted. In the near bottom layer, the methane concentration increased by an order of magnitude – to 0.087 µmol/L. In June, the vertical distribution of methane was typical for the open sea: a minimum value of 0.001 µmol/L was observed at the surface, and with increasing depth there was an increase up to a maximum at the horizon of 15 m (0.005 µmol/L); in the near bottom water, methane concentrations reached 0.032 µmol/L at a depth of 4 m above the bottom and 0.173 µmol/L directly above the bottom. In August, a pronounced peak of methane was noted in the near bottom layer (0.069 µmol/L), and at a horizon of 10 m another “mini” peak was recorded – 0.002 µmol/L. The distribution of methane on October 1 was atypical: the maximum (0.151 µmol/L) was observed not near the bottom, but above the halocline (51 m horizon). Concentrations in the upper quasi-homogeneous layer were minimal, with the exception of a slight peak at 5 m (0.001 µmol/L). At the end of October, the minimum for the entire research period was recorded – 0.0002 µmol/L at a horizon of 15 m; high concentrations were again found above the bottom (0.136 µmol/L). In November, maximum was observed near the bottom (0.133 µmol/L), caused by the flux of methane from the sediments; at overlying horizons, methane concentrations changed slightly.

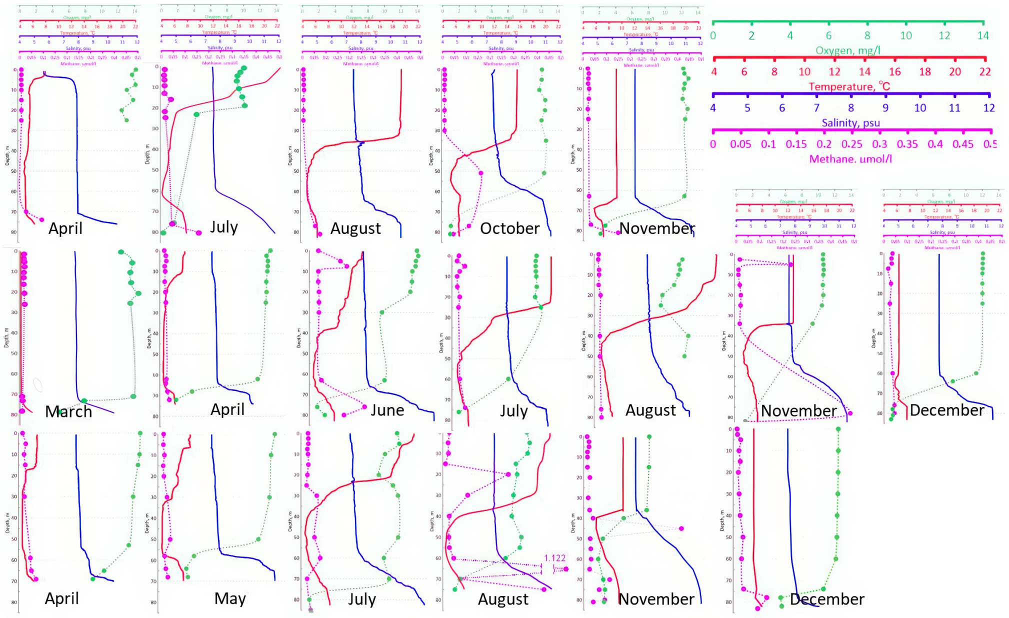

Figure 2. Vertical distribution of temperature, salinity, concentrations of dissolved oxygen and methane at the carbon supersite in 2021–2023.

2022

The following methane concentrations were measured in 2022: min 0.002, max 0.465, median 0.013 µmol/L. In March, methane concentrations changed slightly, from 0.009 µmol/L at a horizon of 7.5 m to 0.018 µmol/L 10 m above the bottom (see Figure 2). This homogeneous distribution is likely caused by active mixing, cooling and decreased biological activity characteristic of the upper quasi-homogeneous layer, which extended to a depth of 70 m in March (see text below). No subsurface peak was detected. In April, the methane profile was also quite uniform, methane concentrations changed slightly, from 0.004 at the sea surface to 0.025 µmol/L at a horizon of 72 m. The upper quasi-homogeneous layer extended to a horizon of 60 m, deeper than which there was an increase in methane concentrations. At the beginning of June, the distribution of methane changed – two characteristic peaks appeared. The first was in the subsurface horizon up to 7.5 m, where the concentration gradually increased by almost an order of magnitude from 0.023 at the surface to 0.140 µmol/L at a horizon of 7.5 m. The reason for the increased concentrations here may be the vital activity of zooplankton. Deeper, the concentration is distributed uniformly up to 75 m, where a second peak is recorded – 0.213 µmol/L, separated from the bottom by 4 m, which can be explained by the supply of gas from the sediments. In July, two peaks were also identified at approximately the same horizons, however, less pronounced than in June. Methane concentrations varied from 0.007 at the sea surface to 0.04 µmol/L 4 m above the bottom. In August, concentrations varied within the range of 0.002–0.016 µmol/L. The maximums are insignificantly expressed. In November, the distribution of methane was characterized by a significant spread of concentrations. Two high (an order of magnitude different from the rest) concentrations of dissolved methane were recorded – at the horizon of 5 m (0.220 µmol/L) and 4 m from the bottom (0.465 µmol/L). The peak of methane concentration in the near bottom layer was separated from the bottom by 4 m, which may indicate its advective transport. On September 26th, 2022, the detonations at the gas pipelines Nord Stream 1 and 2 in the Bornholm Deep resulted in some of the largest non-natural releases of methane known. Detected methane concentrations up to 4 orders of magnitude above the natural Baltic Sea background [*Abrahamsson et al.*, 2024]. However the possibility of detonations influence at methane concentration in the Gdansk Deep is unlikely. The model simulation showing a primarily westward transport from the northern explosion sites, and an eastward transport from the southern one [*Abrahamsson et al.*, 2024]. The distance from the detonations location and our monitoring point is large (about 300 km), and the Slupsk Furrow which connects the Bornholm and Gdansk Basins is shallower than these basins so it prevents the free exchange of near-bottom water between the basins. In December, the concentration changed very little and (as in March–April) had a fairly uniform vertical distribution. Concentrations were high at the sea surface (0.022 µmol/L). No pronounced maximum was observed in the bottom layer.

2023

The following methane concentrations were measured in 2023: min 0.002, max 1.122, median 0.018 µmol/L. In April, the concentration of dissolved methane varied from 0.002 at the sea surface to 0.056 µmol/L at the bottom (see Figure 2). At horizons of 5 and 15 m a weak peak was observed (0.013–0.015 µmol/L). In May, the maximum value was in the layer above the halocline – 0.035 µmol/L, after which there was a decrease in concentration 10 m from the bottom, followed by a gradual increase. The minimum value was in the surface layer. In July, the maximum of dissolved methane was again observed above the halocline (60 m horizon, 0.064 µmol/L), exceeding the concentrations at the bottom by more than twice. In August, the annual maximum methane concentration was recorded at two horizons: 20 m (above the thermocline) and under halocline 65 m (0.258 and 1.122 µmol/L respectively). The layer of near bottom hypoxia (oxygen concentration 1.2–1.8 mg/L) extended to a horizon of 68 m. In November, methane concentrations dropped sharply again. Against this background, a maximum (0.394 µmol/L) stands out in the upper part of the anomalously elevated halocline (to a depth of 35 m). In December, against a generally low background, a small near-bottom maximum in methane concentration coincided the upper border of the halocline which reached anomaly depth – 75 m. Most possible it was caused by observed incidents of deep convection above the steep southern slope of the Gdansk Deep.

The vertical distribution of methane dissolved in water varied over a fairly wide range – from 0.000 (25 m horizon in June 2021, several horizons in 0–30 m layer in August and October 2021, and August 2022) to 1.122 (under halocline 65 m in August 2023) µmol/L. In accordance with other studies [*Bange et al.*, 2010; *Schmale et al.*, 2010; *Ma et al.*, 2020], we found that methane concentrations generally increased with depth, indicating a predominant release of methane from bottom sediments into the water column. However, a weak peak in methane concentration distribution was observed in the near-surface layer (5–15 m).

Relationship with hydrological and hydrochemical parameters

The bottom layer is characterized by euxinic conditions below the halocline (65–75 m), i.e. there is a lack of oxygen and an increased level of free hydrogen sulfide [*Ulyanova et al.*, 2022a,b, 2023]. Euxine basins are often highly stratified, with an oxygenated, highly productive thin surface layer and anoxic sulfide bottom water. According to the data obtained, in all surveys below the halocline, the oxygen concentration decreased with depth, while the amount of methane increased in the bottom layer (see Figure 2), which indicates a large-scale flux of methane from the sediment into the water [*Thießen et al.*, 2006; *Laier and Jensen*, 2007]. Microbial methanogenesis by methanogenic archaea directly in the euxinic water of the bottom layer cannot be ruled out, however, previous studies of sediments in the study area showed that the intensity of methane oxidation in the mud was significantly higher than methanogenesis, which is possible due to the additional supply of methane from the underlying sedimentary horizons [*Pimenov et al.*, 2010]. In general, the distribution of dissolved oxygen and methane depends significantly on vertical density stratification, controlled by salinity distribution. Stratification of the water prevented upward mixing of methane-rich waters. In the Baltic Sea, the flux of methane from deep layer to the sea surface is strongly hindered by microbial oxidation of methane in the transition zone of oxygen/anoxic conditions below the constant halocline [*Jakobs et al.*, 2014; *Berndmeyer et al.*, 2013]. The minimum oxygen concentration was observed in the bottom layer, that is, it coincided with the layer of maximum methane concentrations. A noticeable change in the concentrations of dissolved gases most often coincided with a layer of salinity gradient.

The subsurface methane maximum (well expressed, for example, in June–July and November 2022) was not accompanied by a noticeable change in oxygen concentrations. The summer subsurface peak can be explained by the fact that at the carbon supersite, the food load of zooplankton on phytoplankton was maximum in the summer and was determined both by feeding activity and the dominance of large crustaceans with a filtration type of feeding [*Mosharov et al.*, 2022]. The maximum value of zooplankton biomass was determined in June, and it was significantly (5–14 times) higher than in other seasons. The integral values of biomass of primary production, chlorophyll *a*, bacterio- and phytoplankton were maximum in autumn.

For each survey, the correlation coefficients of methane with hydrological and hydrochemical parameters were calculated (Figure 3). A positive correlation is observed between methane and salinity, negative – with water temperature and dissolved oxygen concentration in most cases. December 2023 is interesting, when all three relationships had a high correlation, which is explained by the almost complete absence of vertical variability of all parameters caused by storm mixing (November–December 2023 were characterized by strong storms in the south-eastern Baltic) and convection. For some dates the correlation coefficients were low (up to ±0.4), especially for methane and temperature, so they should not be taken into account.

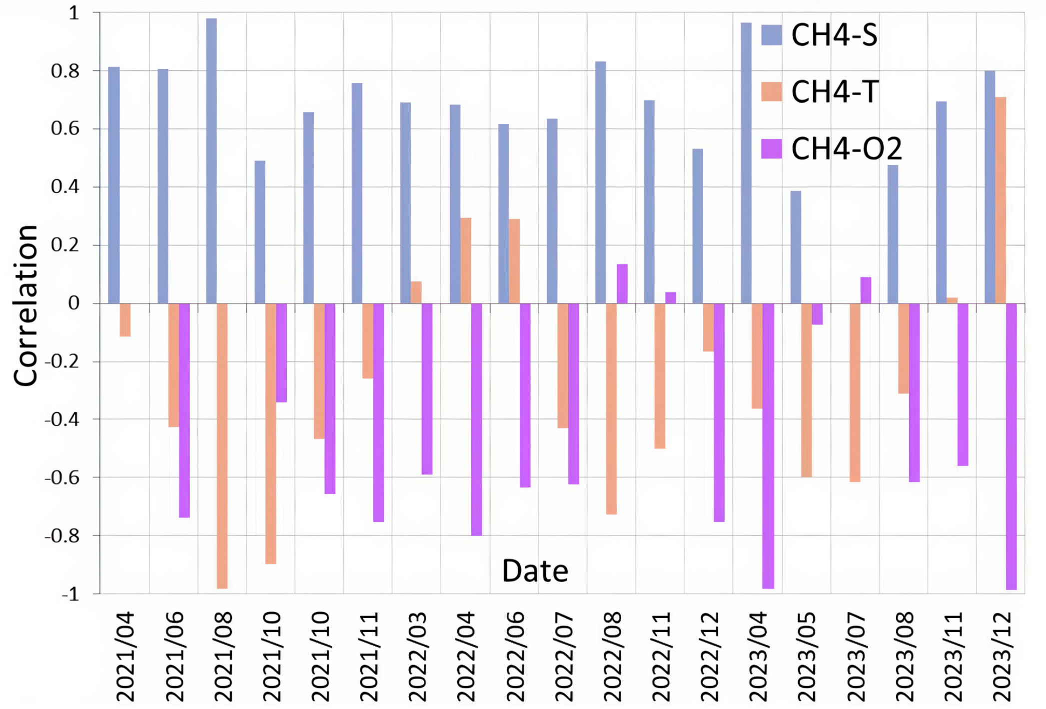

Figure 3. The correlation between methane, salinity, water temperature and dissolved oxygen.

Dissolved methane and temperature

When comparing the distribution of methane with hydrophysical parameters, it was revealed that most of the measurements occurred during the cold period, when the water temperature was below 10 °C. Increased methane concentrations tend to this temperature (Figure 4 upper). The relationship between methane concentrations and water temperature during the study period (2021–2023) is characterized by a weak linear relationship ($R^2 = 0.018$). The relationship is shown separately for the subsurface (0–5 m) with high temperature variability (3.5–21.7 °C) and near-bottom layer (near the bottom and bottom +4 m), which is less susceptible to the influence of synoptic variability.

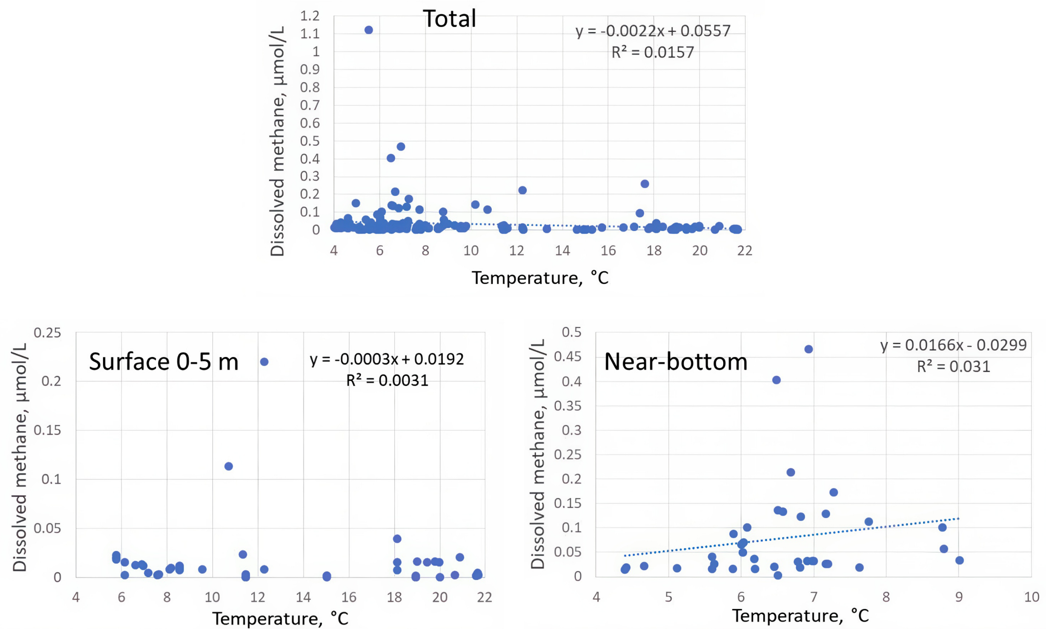

Figure 4. The relationship between methane and water temperature throughout the entire water column (upper), subsurface 0–5 m (left) and in the bottom layer (right).

Dissolved methane and salinity

Water salinity in the study area ranged from 5.6 to 12.0 psu, with most methane measurements occurring at 7–8 psu (Figure 5). The relationship between methane concentrations and salinity is characterized by a weak linear relationship ($R^2 = 0.082$). The relationship is shown separately for the near-bottom layer (near the bottom and bottom +4 m).

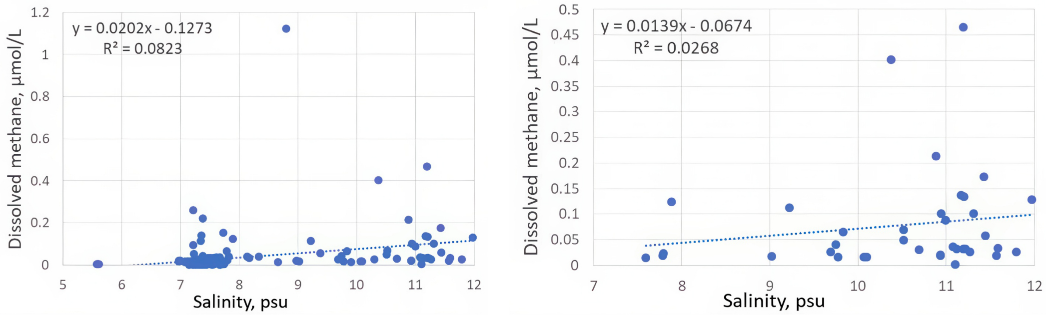

Figure 5. The relationship between methane and salinity throughout the entire water column (left) and in the bottom layer (right).

Dissolved methane and oxygen

Figure 6 shows that the relationship between the dissolved methane and oxygen concentrations is characterized by a weak linear relationship (R^2 = 0.214). The relationship is shown separately for the near bottom layer (near the bottom and bottom +4 m). Two groups are distinguished: most of the measured values fall into the group with high oxygen concentrations and low methane concentrations, which corresponds to the surface layer of the sea. High concentrations of methane at high concentrations of oxygen are most possible associated with "oceanic methane paradox" caused by the vital activity of phyto- or zooplankton in the subsurface layer or transport by subsurface currents. To reliably answer the question about the origin of methane in oxygenated water, it is necessary to study the isotopic composition of methane, since the isotopic structure of methane emitted by phytoplankton is clearly different from methane produced by methanogenic archaea [*Klintzsch et al.*, 2023]. The second group – suboxic conditions and low methane concentrations – manifests itself in the bottom layer below the halocline. Single high concentrations of methane here are associated with a maximum that is either directly above the bottom or is separated from the bottom by 4–6 m. In other areas of the Baltic Sea (for example, Kiel and Eckernförde bays) the correlation between dissolved oxygen and methane was significantly higher (R^2 = 0.764) and there was a seasonal shift in the $CH_4 - O_2$ relationship associated with changes in water masses [*Gindorf et al.*, 2022]. It has been established that not only in bottom sediments, but also in water above gas emission points, a significant decrease in oxygen concentration can be observed [*Malakhova et al.*, 2021].

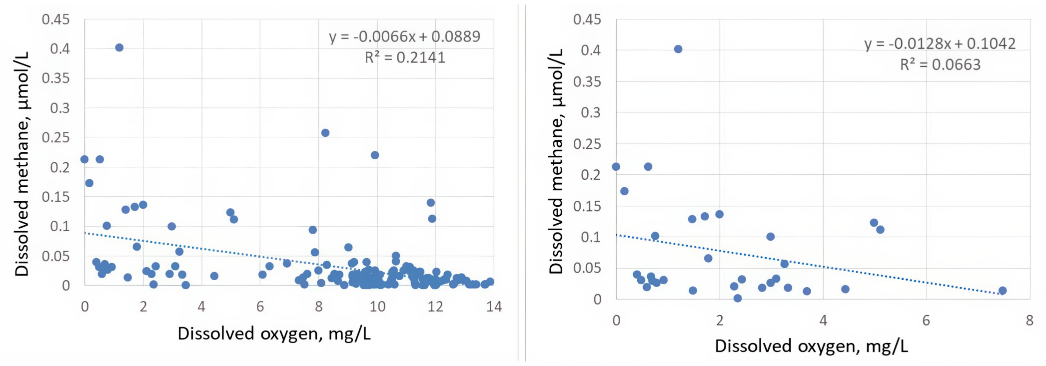

Figure 6. The relationship between methane and oxygen throughout the entire water column (left) and in the bottom layer (right).

The change in oxygen concentration in areas where methane seeps from sediments (silt sediments in the study area) occurs due to a combination of several processes: consumption for aerobic oxidation of methane by the microbial community; consumption for the oxidation of hydrogen sulfide, released both in the composition of bubble gas and as a result of fluid emission from gas-saturated sediments; the interchange of bubble gas components with dissolved oxygen in the water, and the subsequent removal of oxygen along with the bubble into the atmosphere.

Previously, in the study area, minimum oxygen concentrations were also observed at points with maximum (up to 0.48 µmol/L) methane concentrations [*Pimenov et al.*, 2008]. For comparison, typical values of methane concentration in water in the shallow coastal waters of the Gdansk Basin (sea depth up to 50 m) were in the range of 0.008–0.040 µmol/L [*Pimenov et al.*, 2010].

In November 2021, August 2022 and May, July 2023, increased methane concentrations were observed below the thermocline. The strong influence of the thermohaline structure on the water column methane distribution has been shown both for seasonal and for daily dynamics studies [*Malakhova et al.*, 2024]. The formation of a thermocline in summer leads to the accumulation of a methane "reserve" below this upper density limit [*Gülzow et al.*, 2013]. Recent studies have revealed periodic accumulation of methane in oxic waters just below the thermocline during the summer months [*Jakobs et al.*, 2014; *Schmale et al.*, 2017]. Stable carbon isotopes indicated a biogenic in situ origin of methane, while clonal sequences pointed to methanogenic archaea as potential producers [*Schmale et al.*, 2017]. However, the rate of methane production associated with zooplankton alone was not sufficient to fully explain the observed methane enrichment. Using the example of the Central Baltic Sea, it is shown that zooplankton contributes to the enrichment of methane in the subthermocline due to 1) direct methanogenesis in the digestive tract of copepods and/or 2) indirect participation in methane production due to the release of methane precursor substances into the water with subsequent microbial decomposition to methane outside bodies of copepods [*Stawiarski et al.*, 2019]. Calculations also showed that methane was consumed below the thermocline and was not transported to the upper sea, suggesting that other sources in the mixed layer are required to maintain the observed air-sea methane flux [*Schmale et al.*, 2017].

Vertical mixing directly affects the vertical transport of reduced compounds (e.g., iron II, manganese II, ammonia or methane) from the lower hypoxic layers towards the redox zone, where most of the methane is consumed by microbial consumption [*Reissmann et al.*, 2009; *Jakobs et al.*, 2014]. The halocline prevents the process of vertical mixing of the upper layer with the bottom layer, therefore, below the halocline, vertical transport is initiated by wind phenomena that excite several types of deep-sea movements (for example, internal waves). In addition, the intensity of vertical mixing can also be influenced by the proximity of the coast [*Axell*, 1998]. Thus, methane accumulates in a layer that is not subject to intense vertical mixing.

In addition to vertical mixing processes, methane distribution can potentially be influenced by variability in methanogenesis in sediments. The availability of organic matter is an important factor for methane formation. However, the seasonality of this influencing factor is not expressed, since in the upper meter layer, where sulfate ions are present and the process of sulfate reduction occurs, no significant methane formation occurs [*Piker et al.*, 1998]. Deep-water basins, in particular the Gdansk Basin, are characterized by high rates of transport of organic matter (formed by primary production and coastal erosion) into deep-water zones, where it is partially mineralized, thereby reducing the oxygen concentration in the water [*Reissmann et al.*, 2009]. Conditions of absence or deficiency of oxygen (O_2 <2 mL/L) in the deep-sea zone promote the burial of organic matter, and, consequently, the microbial formation of methane in sediments. In the hydrogen sulfide zone, areas of gas-saturated sediments with flows of dissolved methane directed into the water are unique oases of life due to the material and energy properties of methane for the microbial component, and in coastal oxidizing conditions, on the contrary, they are zones of inhibition.

Methane anomalies in oxic conditions are well known as the “oceanic methane paradox” [*Reeburgh*, 2007b]. Studies have shown that pelagic methane production in the presence of oxygen may result from the metabolism of methylated compounds (e.g., methylphosphonates [*Karl et al.*, 2008], dimethylsulfoniopropionate [*Damm et al.*, 2010]) or the activity of methanogenic archaea in the presence of photoautotrophs [*Grossart et al.*, 2011]. Methane production is associated with anoxic microniches within inorganic particles or fecal pellets [*Karl et al.*, 2008]. Mesozooplankton (copepods) can create a local anoxic microenvironment in the intestine [*Tang et al.*, 2011]. The rate of methane production by zooplankton depends on the type of organism and the diet of phytoplankton. These studies indicate that the above various mechanisms of methane formation should be considered significant as a source of methane in the aerobic layer of the water column.

Our data confirm that biogenic methane production in the oxygen-saturated layer is a common feature not only for the central part of the Baltic Sea during the summer period [*Schmale et al.*, 2017], but also for the southern part of the Gdansk Basin, where the carbon supersite is located.

Seasonal variability

Analyzing some statistical parameters of the distribution of all obtained methane measurements, it can be concluded that the seasonal course of methane distribution in the Gdansk Basin takes place. The maximum, both average (0.048 μmol/L) and absolute values were obtained in the summer (Table 2). Median values were the same in summer and winter (0.016 μmol/L), the minimum concentrations were observed in spring. For the surface layer, the maximum concentrations were observed in winter, the minimum – in spring and autumn.

Table 2. Seasonal statistic of methane concentrations (μmol/L)

	Spring		Summer		Autumn		Winter*	
	Total	Surface (0–1 m)	Total	Surface (0–1 m)	Total	Surface (0–1 m)	Total	Surface (0–1 m)
Number of measurements	40	4	80	7	64	4	32	3
Mean	0.015	0.004	0.048	0.011	0.037	0.004	0.023	0.015
Median	0.011	0.003	0.016	0.015	0.009	0.004	0.016	0.012
Minimum	0.002	0.002	0.000	0.000	0.000	0.000	0.004	0.010
Maximum	0.087	0.009	1.122	0.023	0.465	0.008	0.123	0.022

* A hydrological winter in the South-Eastern Baltic Sea includes December–March [*Bernikova et al.*, 2007].

Maximum methane concentrations (0.022 μmol/L) in the surface layer (0–1 m) were observed in both June and December 2022 (Figure 7). However, in general, the surface layer in all seasons was characterized by minimum methane concentrations, with the exception of June 2022, when the minimum values were at a horizon of 10 m (0.007 at 10 m versus 0.015 μmol/L at 0 m). The bottom layer was characterized by a wide range of values: from 0.016 to 0.402 μmol/L. High concentrations at the near bottom layer were observed in the summer and autumn of 2021, as well as in July 2022. In winter 2022, concentrations at the surface and at the bottom were comparable. In winter 2023 near bottom methane concentrations were an order of magnitude higher than at the surface which may be associated with the abnormal deep location of the halocline.

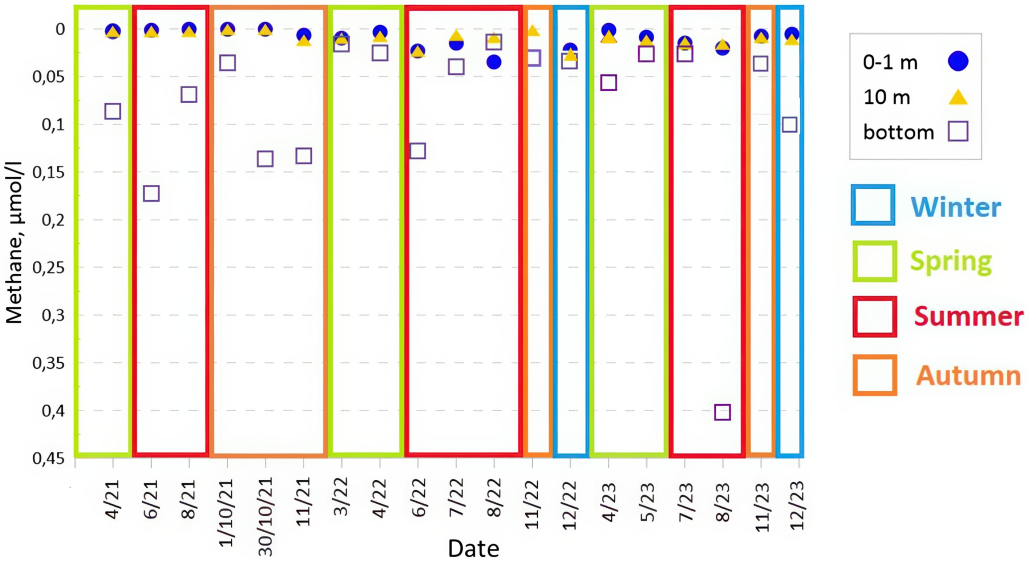

Figure 7. Seasonal variability of the distribution of methane dissolved in water in the surface (0–1 m), subsurface (10 m) and bottom layers.

It is known [*Gindorf et al.*, 2022] that within the upper 1 m of the water column there are methane concentration gradients, and the difference in concentrations between 0.1 and 1 m (difference in order) was greater than between 1 and 2 m (average difference between gradients ~ 1 nmol/L). The direction of the gradients varied: sometimes there were higher concentrations in the uppermost layer, in other cases there were increases with depth or intermediate maxima. Concentrations measured in Niskin bottle samples (1–2 m horizon) were generally higher than in surface samples (mean difference between bottle and surface sample concentrations: 1.2 ± 0.4 nmol/L). Thus, in our study, speaking about the surface layer, it can be assumed that the analyzed samples show a certain average concentration between the immediate subsurface layer (0–10 cm) and the surface layer (1 m), since the length of the bottle used for sampling was 0.5 m.

According to a study of the South-Western Baltic Sea, maximum methane concentrations were usually observed in October, at the end of seasonal hypoxia, favorable for microbial methane production. Due to the long anoxic period, significant accumulations of methane (0.6 μmol/L) in the bottom layer were observed in autumn [*Ma et al.*, 2020]. This is higher than the values obtained in this study, but the order of magnitude is the same. A study of the North-Eastern Baltic Sea (Estonian sea area sub-basins) the median highest concentrations in the upper layer were observed in April (0.008–0.014 μmol/L), and authors gave three possible reasons of methane concentrations variability: physically disturbed organic-rich sediments, river plumes, and upwelling were identified as processes causing hot spots of methane emission [*Lainela et al.*, 2024]. However in our case the upwelling is inappropriate as influencing factor as the depth of area is too deep. As well as river plumes – the site is far away from the coast. The high concentration of methane in bottom water is most likely the result of methanogenesis in anoxic sediments [*Bange et al.*, 2010], which produces gas that partially leaks into the water [*Reindl and Bolałek*, 2012; *Donis et al.*, 2017]. Summer stratification prevents methane from reaching the surface, and therefore it accumulates below the pycnocline. In the water column, methane is effectively oxidized, and only a small part of it reaches the surface layer [*Steinle et al.*, 2017].

Seasonal variability in the distribution of methane in water at the carbon supersite is observed, however not very pronounced. The same conclusion was made for some other indicators of the marine ecosystem of the study point. For example, the ratio of the integral (for the euphotic layer) biomass values of the main components of the marine biocenosis (phyto-, zoo- and bacterioplankton), which determine the formation of the flow of organic carbon particles, changed slightly throughout the year [*Mosharov et al.*, 2022]. While the parameters of the biological components themselves change significantly. In summer, organic carbon particles synthesized by phytoplankton practically do not form a downward flow, but remain within the upper active layer of water in the form of biomass and metabolites of bacterio- and zooplankton.

Ecotoxicological effect of high CH_4 concentrations

The zone of acute toxicity where fatal intoxication of a reliably recorded number of aquatic organisms within 2–4 days is inevitable, begins at a methane concentration level of about 45 μmol/L and higher [*Galchenko*, 2001]. One of the latest studies of biomarkers revealed that the non-typical methane community species (mussel *Mytilus galloprovincialis*) was more sensitive to methane than to low oxygen concentration, supporting the effects of methane on the mussel's immune system [*Kladchenko et al.*, 2024]. The highest concentrations of methane at the carbon supersite was comparable to the biogeochemical threshold of ecological tolerance of hydrobionts for methane (0.45 μmol/L (the same value is accepted as an approximate value of the maximum permissible concentration of dissolved methane in the marine environment [*Mishukova et al.*, 2007]). For comparison, the value of methane dissolved in water in the bottom layer (0.5–1 m from the bottom) in the Gdansk Basin above the pockmark and gas-saturated sediments was 0.22–0.67 μmol/L, which is comparable with this study and determines the bottom horizon water as a zone of threshold effects and environmental tolerance. In both the surface and bottom layers in 2022, according to the results of summer, autumn and winter surveys for the Russian sector of the South-Eastern Baltic Sea (from shallow waters of 10 m up to depths of 110 m), methane concentrations varied in the range of 0.000–0.205 μmol/L [*Korneeva and Ulyanova*, 2023]. Thus, in general, the distribution of methane in the carbon supersite corresponds to background values for the South-Eastern Baltic Sea.

Conclusion

Studies of dissolved in water methane and related parameters (water temperature and salinity, dissolved oxygen concentration) were carried out in all seasons in 2021–2023 at one point located in the Gdansk Deep of the Baltic Sea on the offshore carbon supersite Rosyanka. A total of 16 surveys were completed. Measurements with such frequency in the study are were performed for the first time.

The vertical distribution of dissolved methane in water varied over a fairly wide range – from 0 to 1.112 μmol/L. Methane concentrations increased with depth, which is a typical distribution for the sea and is associated with the vertical stratification of the water column. The layer from the bottom to the upper boundary of the halocline is the most saturated with methane: values above 0.1 μmol/L accounted for about 5% of all measured values and occurred in the halocline and under it. Thus, the CH_4 flux from bottom sediments into the water column was predominant.

However, in the near-surface layer (5–15 m) a weakly pronounced peak in methane concentrations was observed ("oceanic methane paradox"). Most likely it is associated with biological processes.

Most of the measured values fall into the group with high oxygen and low methane concentrations, which corresponds to the surface layer of the sea. High concentrations of methane at high concentrations of oxygen are associated with the "oceanic methane paradox". The second group is confined to the bottom layer with euxinic conditions and high methane concentrations – manifested in the bottom layer in and below the halocline. The lack of oxygen is the possible reason why the more saline near bottom waters were saturated with methane.

Some pronounced seasonality was detected in the vertical distribution of dissolved methane. The maximum, both average and absolute values were obtained in the summer, Median values were the same in summer and winter, the minimum concentrations were observed in spring. For the surface layer, the maximum concentrations were observed in winter, the minimum – in spring and autumn. A positive correlation was between methane and salinity, negative – with water temperature and dissolved oxygen concentration in most cases.

Acknowledgments. Hydrophysical conditions and oxygen content were analyzed with a support of the state assignment of IO RAS (Theme No. FMWE-2024-0025). The methane research was supported by the state task of the Ministry of Education and Science of the Russian Federation, topic No. FZWM-2024-0015 (IKBFU). The authors thank the staff of the IO RAS for providing primary hydrophysical data and determination of dissolved oxygen: V. Krechik, E. Bubnova, A. Muratova.

References

Abrahamsson, K., E. Damm, G. Björk, et al. (2024), Methane plume detection after the 2022 Nord Stream pipeline explosion in the Baltic Sea, *Scientific Reports*, *14*(1), https://doi.org/10.1038/s41598-024-63449-2.

Axell, L. B. (1998), On the variability of Baltic Sea deepwater mixing, *Journal of Geophysical Research: Oceans*, *103*(C10), 21,667–21,682, https://doi.org/10.1029/98JC01714.

Bange, H. W., U. H. Bartell, S. Rapsomanikis, and M. O. Andreae (1994), Methane in the Baltic and North Seas and a reassessment of the marine emissions of methane, *Global Biogeochemical Cycles*, *8*(4), 465–480, https://doi.org/10.1029/94GB02181.

Bange, H. W., K. Bergmann, H. P. Hansen, et al. (2010), Dissolved methane during hypoxic events at the Boknis Eck time series station (Eckernförde Bay, SW Baltic Sea), *Biogeosciences*, *7*(4), 1279–1284, https://doi.org/10.5194/bg-7-1279-2010.

Bashirova, L., V. Sivkov, M. Ulyanova, A. Gavrikov, and A. Artamonov (2023), Climate and environmental monitoring of the Baltic Sea: general principles and approaches, *Reliability: Theory & Applications. Special Issue*, *5*(75), 164–171, https://doi.org/10.24412/1932-2321-2023-575-164-171.

Berndmeyer, C., V. Thiel, O. Schmale, and M. Blumenberg (2013), Biomarkers for aerobic methanotrophy in the water column of the stratified Gotland Deep (Baltic Sea), *Organic Geochemistry*, *55*, 103–111, https://doi.org/10.1016/j.orggeochem.2012.11.010.

Bernikova, T. A., V. F. Dubravin, H. N. Nagornova, and Z. I. Stont (2007), Climatic seasons of the Southern Baltic Sea, in *V International Scientific Conference "Innovations in Science and Education - 2007". Part 1*, pp. 53–55, KSTU, Kaliningrad (in Russian).

Bolshakov, A. M., and A. V. Egorov (1987), On the use of the phase-equilibrium degassing technique in gasometric studies, *Oceanology*, *27*(5), 861–862 (in Russian).

Brodecka, A., P. Majewski, J. Bolałek, and Z. Klusek (2013), Geochemical and acoustic evidence for the occurrence of methane in sediments of the Polish sector of the southern Baltic Sea, *Oceanologia*, *55*(4), 951–978, https://doi.org/10.5697/oc.55-4.951.

Bukanova, T. V., Z. I. Stont, and O. A. Gushchin (2015), Variability of sea surface temperature in the South-East Baltic according to MODIS data, *Sovremennye problemy distantsionnogo zondirovaniya Zemli iz kosmosa*, *12*(4), 86–96 (in Russian), EDN: UITZRP.

Bukanova, T. V., E. S. Bubnova, and S. V. Aleksandrov (2022), Remote monitoring of the offshore site of the Rosyanka carbon polygon (the Baltic Sea): First results, *Sovremennye problemy distantsionnogo zondirovaniya Zemli iz kosmosa*, *19*(6), 234–247, https://doi.org/10.21046/2070-7401-2022-19-6-234-247 (in Russian).

Cicerone, R. J., and R. S. Oremland (1988), Biogeochemical aspects of atmospheric methane, *Global Biogeochemical Cycles*, *2*(4), 299–327, https://doi.org/10.1029/GB002i004p00299.

Conrad, R., and W. Seiler (1988), Methane and hydrogen in seawater (Atlantic Ocean), *Deep Sea Research Part A. Oceanographic Research Papers*, *35*(12), 1903–1917, https://doi.org/10.1016/0198-0149(88)90116-1.

Damm, E., E. Helmke, S. Thoms, et al. (2010), Methane production in aerobic oligotrophic surface water in the central Arctic Ocean, *Biogeosciences*, *7*(3), 1099–1108, https://doi.org/10.5194/bg-7-1099-2010.

Donis, D., S. Flury, A. Stöckli, et al. (2017), Full-scale evaluation of methane production under oxic conditions in a mesotrophic lake, *Nature Communications*, *8*(1), https://doi.org/10.1038/s41467-017-01648-4.

Elken, J. (1996), *Deep water overflow, circulation and vertical exchange in the Baltic Proper*, 91 pp., Estonian Mar. Inst., Tallinn.

Emelyanov, E. M. (Ed.) (2002), *Geology of the Gdansk Basin. Baltic Sea*, 496 pp., Yantarny skaz, Kaliningrad (in Russian).

Galchenko, V. F. (2001), *Methanotrophic bacteria*, 500 pp., GEOS, Moscow (in Russian).

Gentz, T., E. Damm, J. Schneider von Deimling, et al. (2014), A water column study of methane around gas flares located at the West Spitsbergen continental margin, *Continental Shelf Research*, *72*, 107–118, https://doi.org/10.1016/j.csr.2013.07.013.

Geodekyan, A. A., V. Y. Trotsyuk, V. I. Avilov, et al. (1989), New data on the methane content in modern sediments of the Baltic Sea, *Reports of the USSR Academy of Sciences*, *250*(1), 160–164 (in Russian).

Geodekyan, A. A., V. Y. Trotsyuk, and A. I. Blazhchishin (1990), *Geoacoustic and gas lithogeochemical studies in the Baltic Sea. Geological features of fluid flow discharge areas*, 164 pp., IO AN USSR, Moscow (in Russian).

Gindorf, S., H. W. Bange, D. Booge, and A. Kock (2022), Seasonal study of the small-scale variability in dissolved methane in the western Kiel Bight (Baltic Sea) during the European heatwave in 2018, *Biogeosciences*, *19*(20), 4993–5006, https://doi.org/10.5194/bg-19-4993-2022.

Grossart, H.-P., K. Frindte, C. Dziallas, W. Eckert, and K. W. Tang (2011), Microbial methane production in oxygenated water column of an oligotrophic lake, *Proceedings of the National Academy of Sciences*, *108*(49), 19,657–19,661, https://doi.org/10.1073/pnas.1110716108.

Gülzow, W., G. Rehder, J. Schneider von Deimling, T. Seifert, and Z. Tóth (2013), One year of continuous measurements constraining methane emissions from the Baltic Sea to the atmosphere using a ship of opportunity, *Biogeosciences*, *10*(1), 81–99, https://doi.org/10.5194/bg-10-81-2013.

Heilig, G. K. (1994), The greenhouse gas methane (CH4): Sources and sinks, the impact of population growth, possible interventions, *Population and Environment*, *16*, 109–137.

IPCC (2023), *Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, 184 pp., IPCC, Geneva, Switzerland, https://doi.org/10.59327/IPCC/AR6-9789291691647.

Jakobs, G., P. Holtermann, C. Berndmeyer, et al. (2014), Seasonal and spatial methane dynamics in the water column of the central Baltic Sea (Gotland Sea), *Continental Shelf Research*, *91*, 12–25, https://doi.org/10.1016/j.csr.2014.07.005.

Jaśniewicz, D., Z. Klusek, A. Brodecka-Goluch, and J. Bolałek (2018), Acoustic investigations of shallow gas in the southern Baltic Sea (Polish Exclusive Economic Zone): a review, *Geo-Marine Letters*, *39*(1), 1–17, https://doi.org/10.1007/s00367-018-0555-5.

Kanapatskiy, T. A., M. O. Ulyanova, T. R. Iasakov, O. V. Shubenkova, and N. V. Pimenov (2022), Microbial Processes of Carbon and Sulfur Cycles in Sediments of the Russian Sector of the Baltic Sea, in *The Handbook of Environmental Chemistry*, Springer Berlin Heidelberg, https://doi.org/10.1007/698_2021_818.

Karl, D. M., L. Beversdorf, K. M. Björkman, et al. (2008), Aerobic production of methane in the sea, *Nature Geoscience*, *1*(7), 473–478, https://doi.org/10.1038/ngeo234.

Kirschke, S., P. Bousquet, P. Ciais, et al. (2013), Three decades of global methane sources and sinks, *Nature Geoscience*, *6*(10), 813–823, https://doi.org/10.1038/ngeo1955.

Kladchenko, E. S., E. S. Chelebieva, M. S. Podolskaya, et al. (2024), Shift in hemocyte immune parameters of marine bivalve Mytilus galloprovincialis (Lamarck, 1819) after exposure to methane, *Marine Pollution Bulletin*, *201*, 116,174, https://doi.org/10.1016/j.marpolbul.2024.116174.

Klintzsch, T., H. Geisinger, A. Wieland, et al. (2023), Stable Carbon Isotope Signature of Methane Released From Phytoplankton, *Geophysical Research Letters*, *50*(12), https://doi.org/10.1029/2023GL103317.

Korneeva, A. O., and M. O. Ulyanova (2023), Methane concentrations in the surface and bottom water layers in the southeastern part of the Baltic sea in summer, autumn and winter sesons of 2022, in *Proceedings of the All-Russian Scientific and Practical Conference "Hydrometeorology and Atmospheric Physics: Modern Achievements and Development Trends"*, pp. 300–302, Publishing and Printing Association of Higher Education Institutions, St. Petersburg (in Russian), EDN: SEMUJW.

Krechik, V. A., M. V. Kapustina, E. S. Bubnova, and V. A. Gritsenko (2017), Abiotic conditions of bottom waters in the Gdansk deep of the Baltic sea in 2016, *Scientific notes of the RGGMU*, *48*, 186–194 (in Russian), EDN: ZWUOPX.

Kudryavtseva, E. A., and S. V. Aleksandrov (2019), Hydrological and Hydrochemical Underpinnings of Primary Production and Division of the Russian Sector in the Gdansk Basin of the Baltic Sea, *Oceanology*, *59*(1), 49–65, https://doi.org/10.1134/S0001437019010077.

Laier, T., and J. B. Jensen (2007), Shallow gas depth-contour map of the Skagerrak-western Baltic Sea region, *Geo-Marine Letters*, *27*(2–4), 127–141, https://doi.org/10.1007/s00367-007-0066-2.

Lainela, S., E. Jacobs, S. Stoicescu, G. Rehder, and U. Lips (2024), Seasonal dynamics and regional distribution patterns of CO2 and CH4 in the north-eastern Baltic Sea, *Preprint egusphere-2024-598*, https://doi.org/10.5194/egusphere-2024-598.

Lein, A. Y., and M. V. Ivanov (2009), *Biogeochemical cycle of methane in the ocean*, 546 pp., Nauka, Moscow (in Russian), EDN: QKIMET.

Ma, X., M. Sun, S. T. Lennartz, and H. W. Bange (2020), A decade of methane measurements at the Boknis Eck Time Series Station in Eckernförde Bay (southwestern Baltic Sea), *Biogeosciences*, *17*(13), 3427–3438, https://doi.org/10.5194/bg-17-3427-2020.

Majewski, P., and Z. Klusek (2011), Expressions of shallow gas in the Gdańsk Basin, *Zeszyty naukowe Akademii Marynarki Wojennej*, *4*(187), 61–71.

Malakhova, T. V., I. N. Ivanova, A. A. Budnikov, A. I. Murashova, and L. V. Malakhova (2021), Distribution of Hydrological Parameters over the Methane Seep Site in the Golubaya Bay (the Black Sea): A Connection with Submarine Freshwater Discharge, *Russian Meteorology and Hydrology*, *46*(11), 792–798, https://doi.org/10.3103/S1068373921110091.

Malakhova, T. V., A. I. Khurchak, V. V. Voitsekhovskaia, and A. V. Fedirko (2024), Distribution of methane in the upper water layer of the northern Black Sea: Seasonal and daily trends and seawater-air emissions, *Continental Shelf Research*, *281*, 105,320, https://doi.org/10.1016/j.csr.2024.105320.

Markus Meier, H. E. (2007), Modeling the pathways and ages of inflowing salt- and freshwater in the Baltic Sea, *Estuarine, Coastal and Shelf Science*, *74*(4), 610–627, https://doi.org/10.1016/j.ecss.2007.05.019.

Mishukova, G. I., A. I. Obzhirov, and V. F. Mishukov (2007), *Methane contents in fresh and sea waters and it's fluxes on border of water-atmosphere at far Eastern region of Asia*, 157 pp., Dalnauka, Vladivostok (in Russian), EDN: TSJECQ.

Mohrholz, V. (2018), Major Baltic Inflow Statistics - Revised, *Frontiers in Marine Science*, *5*, https://doi.org/10.3389/fmars.2018.00384.

Mosharov, S., I. Mosharova, K. Borovkova, and E. Bubnova (2024), Variability of Primary Productivity as an Initial Link in Carbon Flux Under the Influence of Hydrological Conditions in the Baltic Sea, *Russian Journal of Earth Sciences*, pp. 1–14, https://doi.org/10.2205/2024ES000888.

Mosharov, S. A., I. V. Mosharova, O. A. Dmitrieva, A. S. Semenova, and M. O. Ulyanova (2022), Seasonal Variability of Plankton Production Parameters as the Basis for the Formation of Organic Matter Flow in the Southeastern Part of the Baltic Sea, *Water*, *14*(24), 4099, https://doi.org/10.3390/w14244099.

Nausch, G., M. Naumann, L. Umlauf, et al. (2016), Hydrographic-hydrochemical assessment of the Baltic Sea 2015, *Marine Science Reports*, (101), https://doi.org/10.12754/msr-2016-0101.

Piechura, J., and A. Beszczynska-Moller (2003), Inflow waters in the deep regions of the southern Baltic Sea - Transport and transformations, *Oceanologia*, *46(1)*, 4.

Piker, L., R. Schmaljohann, and J. F. Imhoff (1998), Dissimilatory sulfate reduction and methane production in Gotland Deep sediments (Baltic Sea) during a transition period from oxic to anoxic bottom water (1993-1996), *Aquatic Microbial Ecology*, *14*, 183–193, https://doi.org/10.3354/ame014183.

Pimenov, N. V., M. O. Ul'yanova, T. A. Kanapatskii, V. V. Sivkov, and M. V. Ivanov (2008), Microbiological and biogeochemical processes in a pockmark of the Gdansk depression, Baltic Sea, *Microbiology*, *77*(5), 579–586, https://doi.org/10.1134/S0026261708050111.

Pimenov, N. V., M. O. Ulyanova, T. A. Kanapatsky, et al. (2010), Microbially mediated methane and sulfur cycling in pockmark sediments of the Gdansk Basin, Baltic Sea, *Geo-Marine Letters*, *30*(3–4), 439–448, https://doi.org/10.1007/s00367-010-0200-4.

Rak, D. (2016), The inflow in the Baltic Proper as recorded in January-February 2015, *Oceanologia*, *58*(3), 241–247, https://doi.org/10.1016/j.oceano.2016.04.001.

Reeburgh, W. S. (2007a), Global Methane Biogeochemistry, in *Treatise on Geochemistry*, Elsevier, https://doi.org/10.1016/B0-08-043751-6/04036-6.

Reeburgh, W. S. (2007b), Oceanic Methane Biogeochemistry, *Chemical Reviews*, *107*(2), 486–513, https://doi.org/10.1021/cr050362v.

Reindl, A., and J. Bolałek (2012), Methane flux from sediment into near-bottom water in the coastal area of the Puck Bay (Southern Baltic), *Oceanological and Hydrobiological Studies*, *41*(3), 40–47, https://doi.org/10.2478/s13545-012-0026-y.

Reissmann, J. H., H. Burchard, R. Feistel, et al. (2009), Vertical mixing in the Baltic Sea and consequences for eutrophication - A review, *Progress in Oceanography*, *82*(1), 47–80, https://doi.org/10.1016/j.pocean.2007.10.004.

Saunois, M., P. Bousquet, B. Poulter, et al. (2016), The global methane budget 2000-2012, *Earth System Science Data*, *8*(2), 697–751, https://doi.org/10.5194/essd-8-697-2016.

Schmale, O., J. Schneider von Deimling, W. Gülzow, et al. (2010), Distribution of methane in the water column of the Baltic Sea, *Geophysical Research Letters*, *37*(12), https://doi.org/10.1029/2010GL043115.

Schmale, O., J. Wäge, V. Mohrholz, et al. (2017), The contribution of zooplankton to methane supersaturation in the oxygenated upper waters of the central Baltic Sea, *Limnology and Oceanography*, *63*(1), 412–430, https://doi.org/10.1002/lno.10640.

Stawiarski, B., S. Otto, V. Thiel, et al. (2019), Controls on zooplankton methane production in the central Baltic Sea, *Biogeosciences*, *16*(1), 1–16, https://doi.org/10.5194/bg-16-1-2019.

Steinle, L., J. Maltby, T. Treude, et al. (2017), Effects of low oxygen concentrations on aerobic methane oxidation in seasonally hypoxic coastal waters, *Biogeosciences*, *14*(6), 1631–1645, https://doi.org/10.5194/bg-14-1631-2017.

Stont, Z., T. Bukanova, and O. Goushchin (2015), Variability of sea surface temperature in the South-Eastern Baltic from MODIS data, *Sovremennye problemy distantsionnogo zondirovaniya Zemli iz kosmosa*, *12*, 86–96 (in Russian), EDN: UITZRP.

Stont, Z., T. Bukanova, and E. Krek (2020), Variability of climatic characteristics of the coastal part of the south-eastern Baltic at the beginning of the 21st century, *Bulletin of the Immanuel Kant Baltic Federal University*, *1*(4), 81–94 (in Russian), EDN: CYZSPJ.

Tang, K. W., R. N. Glud, A. Glud, S. Rysgaard, and T. G. Nielsen (2011), Copepod guts as biogeochemical hotspots in the sea: Evidence from microelectrode profiling of Calanus spp, *Limnology and Oceanography*, *56*(2), 666–672, https://doi.org/10.4319/lo.2011.56.2.0666.

Thießen, O., M. Schmidt, F. Theilen, M. Schmitt, and G. Klein (2006), Methane formation and distribution of acoustic turbidity in organic-rich surface sediments in the Arkona Basin, Baltic Sea, *Continental Shelf Research*, *26*(19), 2469–2483, https://doi.org/10.1016/j.csr.2006.07.020.

Ulyanova, M., and A. Danchenkov (2016), Maritime potential of the Russian sector of the south-eastern Baltic Sea and its spatial usage, *Baltica*, *29*(2), 133–144, https://doi.org/10.5200/baltica.2016.29.12.

Ulyanova, M., V. Sivkov, T. Kanapatskij, and N. Pimenov (2013), Seasonal variations in methane concentrations and diffusive fluxes in the Curonian and Vistula lagoons, Baltic Sea, *Geo-Marine Letters*, *34*(2–3), 231–240, https://doi.org/10.1007/s00367-013-0352-0.

Ulyanova, M. O., V. V. Sivkov, L. D. Bashirova, et al. (2022a), Oceanological Research of the Baltic Sea in the 51st Cruise of the PV Akademik Sergey Vavilov (June-July 2021), *Oceanology*, *62*(4), 578–580, https://doi.org/10.1134/S0001437022040130.

Ulyanova, M. O., V. V. Sivkov, L. D. Bashyrova, et al. (2022b), Oceanological Research in the Baltic Sea during the 56th Cruise of the Passenger Vessel Akademik Ioffe, *Oceanology*, *62*(1), 136–138, https://doi.org/10.1134/s0001437022010167.

Ulyanova, M. O., V. V. Sivkov, S. V. Aleksandrov, et al. (2023), Baltic Sea Research on Cruise 61 of the R/V Akademik Ioffe (June-July 2022), *Oceanology*, *63*(5), 752–754, https://doi.org/10.1134/s000143702305017x.

Voigt, C. (2023), The power of the Paris Agreement in international climate litigation, *Review of European, Comparative & International Environmental Law*, *32*(2), 237–249, https://doi.org/10.1111/reel.12514.

Weber, S., J. Beutel, R. Da Forno, et al. (2019), A decade of detailed observations (2008-2018) in steep bedrock permafrost at the Matterhorn Hörnligrat (Zermatt, CH), *Earth System Science Data*, *11*(3), 1203–1237, https://doi.org/10.5194/essd-11-1203-2019.