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Comparison of methane distribution in bottom sediments of shallow lagoons of the Baltic and Black Seas

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Abstract. In 2015, geoacoustic and gas-geochemical studies of bottom sediments of the Vistula Lagoon of the Baltic Sea and the Sevastopol Bay of the Black Sea were carried out. A comparative analysis showed differences in the particle size distribution and methane content in the sediments of the studied basins. Maximum methane concentrations were observed in the sediments of the central part of the Sevastopol Bay (1856 μmol dm^3), characterized by the highest content of aleuropelite fraction. The diffusion flux of methane at the water-bottom interface was directed from the sediment to water and varied from 0.004 to 0.132 mmol/(m^2 day) in the Sevastopol Bay, and from 0.005 to 0.030 mmol/(m^2 day) in the Vistula Lagoon. The value of methane solubility in pore waters for the Vistula Lagoon, calculated for the average depth of the basin, is significantly lower

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compared to the same value for the Sevastopol Bay. Despite this, bubble outgassing was not recorded in the Vistula Lagoon, unlike the Sevastopol Bay.

Introduction

The problem of global climate change is now recognized as one of the most acute facing the world community. Methane is a greenhouse gas and its distribution requires a detailed quantitative assessment. Globally, methane from the ocean to the atmosphere is negligible, despite the rapid gas formation in the sediments of the continental shelf. High rates of sediment accumulation in shallow coastal areas [*Thang et al.,* 2013] usually lead to a decrease in the lifetime of organic matter in the sulfate reduction zone, which increases the methane formation zone to deeper sediment layers. Besides, methanotrophs are less active under conditions of intense sedimentation [*Dale et al.,* 2008]. As a result, it is coastal shallow water areas that are the main sources of ocean methane release into the atmosphere, and the anthropogenic eutrophication, which affects both studied reservoirs, leads to an increase in methane flux from bottom sediments [*Egger et al.,* 2016].

Methane, as part of the organic carbon cycle, is involved in biogeochemical processes taking place in silts. A large proportion of anaerobic oxidation of methane occurs in sediments of passive continental margins, where dissolved methane in pore waters is transported mainly due to molecular diffusion. Estimates of the exchange of chemical elements at geochemical barriers, both horizontal (coast-sea, river-sea, upwelling, etc.) and vertical (surface water microlayer, water-sediment surface, upper "active" layer of sediments (up to 1–5 cm) and others), serve as the basis for understanding the cycle of substances [*Vershinin and Rozanov,* 2002].

The Baltic Sea, including the two largest and most productive lagoons – the Curonian and Kaliningrad (Vistula) lagoons, is an area of high anthropogenic pressure. This also applies to the Sevastopol Bay of the Black Sea. These shallow basins are buffer zones between rivers and the open sea and they accumulate organic matter and pollutants from the land. The presence of increased concentrations of methane creates a special geochemical background. The study of the lagoons reveals differences in the behavior of methane in water basins with various hydrochemical characteristics.

The research aims to compare the distribution of methane in the bottom sediments of shallow lagoons of the Baltic and Black Seas, which differ in geo- and hydrochemical conditions.

Physic-Geographical Comparison of the Studied Water Areas

The circulation of water in the lagoon is one of the most important factors affecting the physical and biochemical processes. Shallow depths, mixing in the water column, river runoff, and exchange with the open sea – the main factors affecting the hydrochemical regime – differ between the Vistula Lagoon of the Baltic Sea and the Sevastopol Bay of the Black Sea (Table 1).

Vistula Lagoon of the Baltic Sea

The water of the lagoon is usually saturated with oxygen, however, during the period of intensive "blooming" (peaks in April and July–August) oxygen completely disappears, being replaced by hydrogen sulfide [*Alexandrov,* 2010]. Increased nutrient loading in recent decades and limited water exchange have led to the eutrophication of the lagoon, as the shallow basins near densely populated coastal areas are primarily sub-

Table 1. Hydrological and Geochemical Characteristics of the Vistula Lagoon and Sevastopol Bay

Parameter	Vistula Lagoon [*Alexandrov*, 2010]	Sevastopol Bay
Average depth	2.7 m	11.3 m [*Stokozov*, 2010]
Connection with the sea	Restricted water exchange through narrow strait (width about 400 m)	Restricted water exchange through jetties (width about 400 m)
Sedimentation rate	0.4 mm/year [*Chechko*, 2006]	2.3–9.3 mm/year [*Gulin*, 2014]
Average salinity	3.8 ‰	17 ‰
Content C_{org}	$< 2\%$	0.31–7.09 [*Moiseenko and Orekhova*, 2011]
Trophic status	Eutrophic	Mesotrophic [*Gubanov et al.*, 2002]

ject to anthropogenic stress [*Wulff et al.,* 1990]. The consumption of oxygen in combination with the enrichment of bottom sediments with organic matter increases the occurrence of anaerobic conditions and promotes methanogenesis.

Vistula Lagoon is a typical lagoon with simplified morphology. In the coastal part of the lagoon, to a depth of 1.5–2 m, sediments are represented by sand and sandy loam (Figure 1A). Their thickness does not exceed several meters. In the deeper parts of the lagoon the silts are located, the thickness of which reaches 10 m. These deposits formed in the Litorina and Post-Litorina stages of the Baltic Sea development.

The structure of the sedimentary cover of the Kaliningrad Lagoon has not been sufficiently studied [*Otmas and Kokhanova*, 2015]. The study area is located within the boundaries of the Mamonovskaya depression, which stands out as a large negative structure of the submeridional direction, occupying mainly the Gdansk Deep, forming a generally depressed structural bay [*Otmas et al.,* 2017]. Mostly in the system of discontinuous dislocations, the Mamonovskaya depression linkage with neighboring second-order tectonic elements [*Otmas et al.,* 2006].

A significant part (25%) of organic matter comes

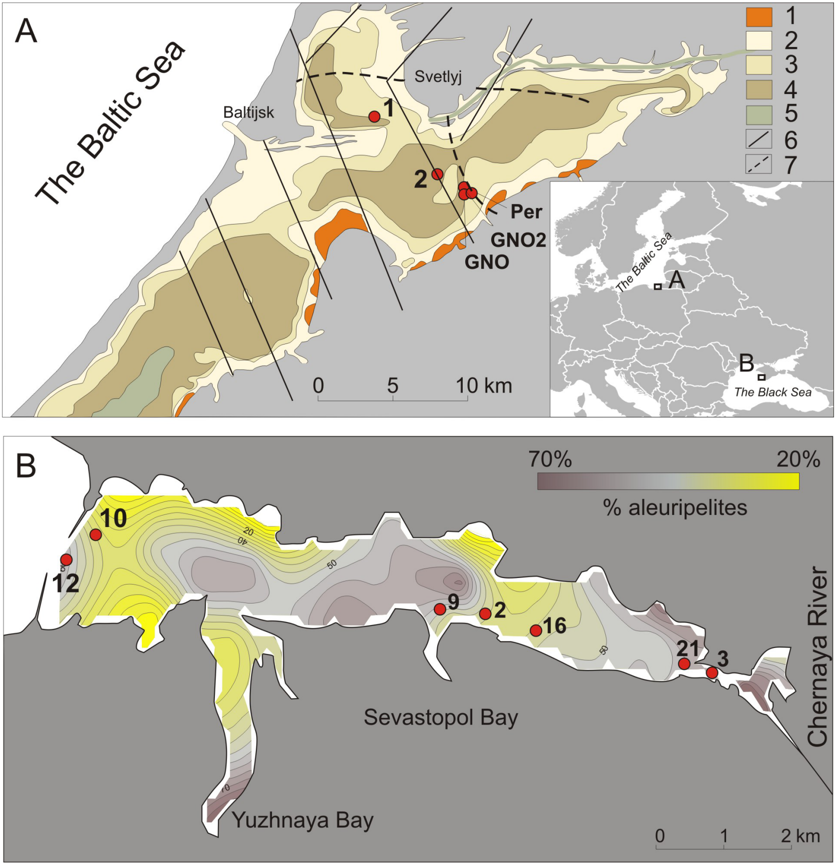

Figure 1. Map of the study areas in the Black and Baltic Seas; A) Station location and types of bottom sediments in the northeastern part of the Vistula Lagoon (Baltic Sea), surface layer 0–7 cm [*Chechko,* 2006]; B) The distribution of the finely dispersed fraction (% aleurite-pelite), surface layer 0–5 cm [*Moiseenko et al.,* 2010] and the location of the stations in the Sevastopol Bay (Black Sea); Legend: 1 – boulder-gravel; 2 – sand; 3 – large aleurite; 4 – fine silt; 5 – aleurite-pelitic mud; 6 – faults [*Dunaev,* 2018]; 7 – borders of tectonic elements of the second order [*Otmas et al.,* 2017]

to the Vistula Lagoon from the open sea. Current conditions of sedimentation in this area are characterized by the outflow of the sediment into the open sea [*Pustelnikovas,* 1998], resulting in a low sedimentation rate (0.4 mm/year) [*Chechko,* 2006]. The distribution of bottom sediments in the lagoon belongs to the “circumcontinental” type [*Emelyanov,* 2002], when fine sediments are confined to the central, deeper regions, and sands are distributed along the periphery.

Sevastopol Bay of the Black Sea

The Sevastopol Bay is located along the fault line, stretching from the city of Sevastopol to the city of Simeiz [*Ivanov et al.,* 2009] and it is a rather deeply cut in sublatitudinal elongated trough-shaped depression about 6.5 km long, with a width of 1.4 km and an existing depth of the sea of up to 19 m. Its steep slopes and parent bottom are composed of Neogene-Paleogene limestones, marls and clays, and the seabed filled with unconsolidated Quaternary sediments. Their thickness ranges from 28 in the bay apex to 40 m in the estuary, where they are mainly represented by detritus-shell sand. To the east, they are replaced by sandy loam and clayey silts, contributing to the accumulation of organic matter (Figure 1B). The sublatitudinal tectonic breaks that formed the graben of the Sevastopol Bay discontinue lithified Neogene–Paleogene rocks, and the time of movement along them refers to Quaternary activation [*Bondarev et al.,* 2015]. At the same time, orthogonal and diagonal breaking faults were activated, which are traced along modern draws and bays adjacent the Sevastopol Bay, the largest of which passes through the Yuzhnaya Bay. Along the same submeridional faults, the other largest bays of the Heracles Peninsula are laid.

The hydrological and hydrochemical parameters of the Sevastopol Bay are characterized by significant spatial and temporal variability, which is determined by the intensity of its water exchange with the adjacent waters of the Black Sea, the peculiarities of the water circulation within the bay, and the flow regime of the Chernaya River and waste water [*Ivanov et al.,* 2006]. In the water of the bay, there is an excess of nutrients, which is an order of magnitude higher than in the open areas of the Black Sea, a lack of oxygen in the bottom layer, increased values of the total suspended matter, pH and total alkalinity [*Minkovskaya et al.,* 2007]. This hydrochemical regime contributed to the eutrophication of the waters of the Sevastopol Bay in the 90s of the last century. In recent years, the problem of improving the quality of the waters of the Sevastopol coast and classifying them as transitional from oligotrophic to mesotrophic has been discussed [*Gubanov et al.,* 2002].

Materials and Methods

Methods

Geoacoustic studies in the Sevastopol Bay were carried out by a portable single-beam Simrad EA 400SP sonar echo sounder (frequency 38 and 200 kHz). In the Vistula Lagoon, geoacoustic profiles were obtained with a dual-beam profilograph Knudsen Chirp 3212 (frequency from 3.5 to 210 kHz).

The sampling of bottom sediments and near-bottom water was carried out by a hermetic Niemistø corer. Immediately after corer appearing on board, the samples were taken for gas analysis.

Water from the corer were drained through a silicone tube in penicillin vials of 30 ml volume, with pre-placed in them solid potassium hydroxide to inhibit microbial processes. The same volume of water was squeezed out by special organic glass dispensers of and closed a gastight stopper is made of butyl rubber. Samples from sediments were taken with 2 ml of a plastic syringe with a trimmed tip. Then the sediments were placed in a methane bottle with clamp, filled with degassed water and has a standard volume of water, closed with a butyl rubber stopper.

The methane concentration in the water and bottom sediments was measured by the method of phase-equilibrium degassing [*Sakagami et al.,* 2012], known in the literature as “headspace analysis”. The methane concentration in the gas phase of water samples and bottom sediments of the Vistula Lagoon was determined using a Crystal 2000 gas chromatograph (Meta-Chrom, Russia) with a flame ionization detector and helium as a carrier gas. The relative error in the determination of independent measurements was about 8%. Determination of methane concentrations in water and bottom sediments of the Sevastopol Bay was carried out on an chromatograph HP 5890, the relative error of 7%.

Determination of sulphate content in silt waters.

Silt water was obtained by centrifuging sediments at 8000 rpm for 10 min in a TsUM-1 centrifuge (Russia). Quantitative determination of the sulfate ion in the pore sediment water was carried out using a Stayer ion chromatograph (Russia).

The methane diffuse flux

(J) at the water-bottom interface was calculated from the concentrations of methane (C) in pore waters according to Fick's first law:

$$J = \phi \cdot D_s \cdot dC/dz$$

where J is the diffuse methane flux, mmol/(m^2 day); D_s is the coefficient of molecular diffusion of methane in the sediment, cm^2/day; ϕ is the sediment porosity, dC/dz is the methane concentration gradient in the upper centimeters of the sediment layer (C is the concentration of dissolved methane in pore water, z is the depth below the sediment surface), mmol/cm [*Frenzel et al.,* 1992].

The solubility of methane in pore water was estimated from the calculation of the solubility coefficient of Bunsen [*Yamamoto et al.,* 1976], which depends on the temperature and salinity of the environment:

$$\ln\beta = A_1 + A_2\frac{100}{T} + A_3\ln\frac{T}{100} +$$

$$+S\left[B_1 + B_2\frac{T}{100} + B_3\left(\frac{T}{100}\right)^2\right]$$

where β is the Bunsen coefficient, $\mathrm{ml}\cdot\mathrm{ml}^{-1}$; T – water temperature, K; S – salinity of water, ‰.

To calculate the solubility of methane, an *in situ* pressure correction was also introduced in accordance with Henry's first law, according to [*Albert et al.,* 1998]. The salinity and temperature of pore water over the entire depth of the studied columns were taken equal to the values for bottom water at the corresponding stations.

Materials

Geoacoustic profiling of bottom sediments of the Sevastopol Bay was carried out in October 2015 (Figure 2). Based on the results of geoacoustic sounding, as well as the available data on the release of bubble gas from the sediment into the water column [*Egorov et al.,* 2012], columns of bottom sediments at 7 stations were sampled (Figure 2, Table 2).

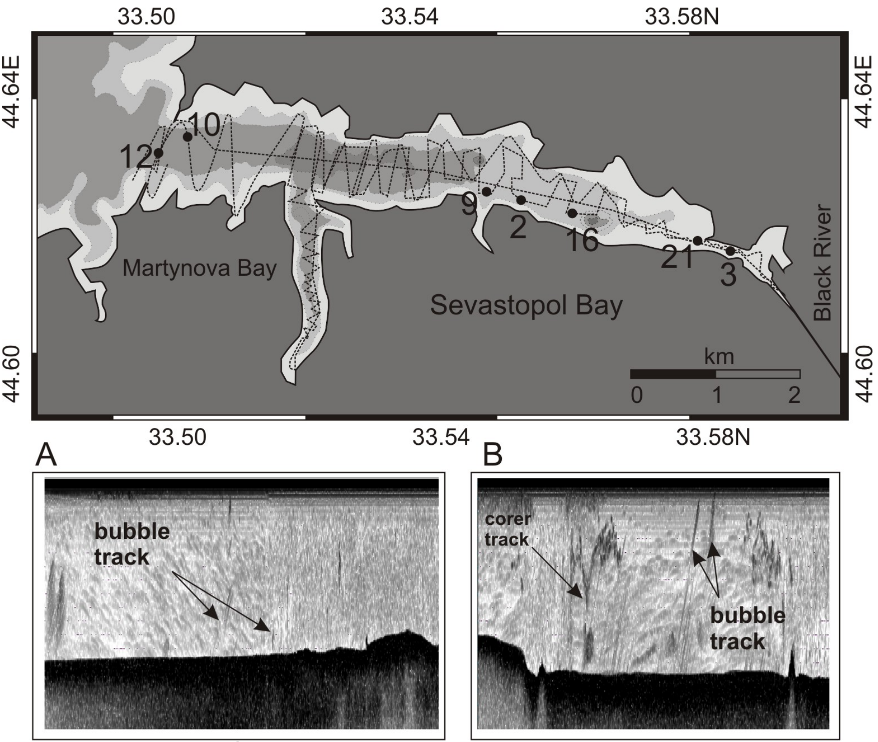

Figure 2. Map of coverage of the Sevastopol Bay with geoacoustic profiles with a single-beam echosounder Simrad EA 400SP (38 kHz) and the location of sampling stations (above); A – Acoustic image of the outflows of bubble gas into the water column in the area of station 2 (coordinates 44.6166 N, 33.5632 E); B – The acoustic image of the outflows of bubble gas into the water column during sampling of bottom sediments in the central part of the bay northwest of station 9 (coordinates 44.6211 N, 33.5597 E) on geoacoustic profiles processed by WaveLens software [*Artemov,* 2006].

Table 2. The Coordinates and Depths of the Sampling Stations

Vistula Lagoon				Sevastopol Bay			
Station	Depth, m	N	E	Station	Depth, m	N	E
1	4	54.648	20.044	10	7	44.625	33.519
2	4.1	54.616	20.109	16	11	44.614	33.579
GNO	4	54.595	20.13	2	7	44.616	33.563
GNO2	4	54.595	20.133	9	7.7	44.617	33.557
Per	4	54.597	20.133	3	4	44.612	33.59
				21	3	44.614	33.583
				12	18	44.622	33.511

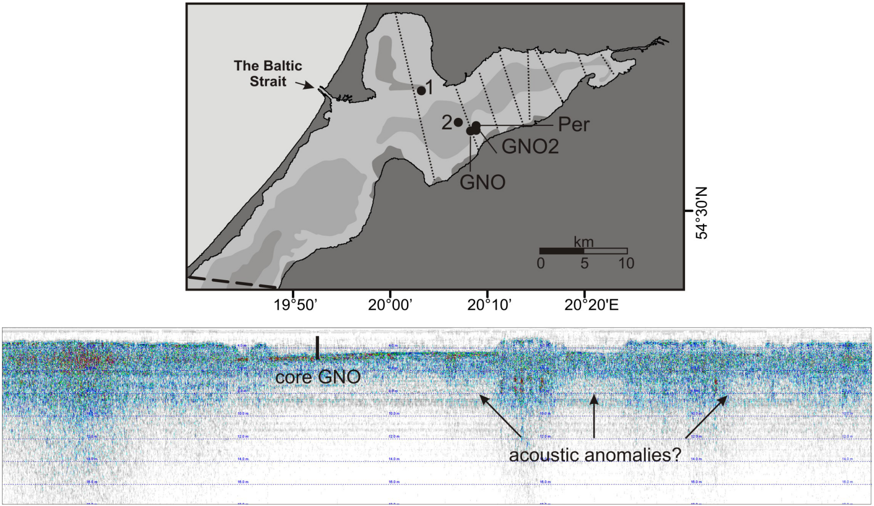

Figure 3. Map of the coverage of the Vistula Lagoon with geoacoustic profiles with a two-channel Knudsen Chirp 3212 profilograph (3.5–210 kHz) and the location of sampling stations (above); geoacoustic signs (acoustic transparency) of gas saturation of bottom sediments of the Vistula Lagoon, obtained on a profile through the GNO station.

Bottom sediments in the Vistula Lagoon (the Baltic Sea) were sampled at 5 stations (see Table 2), two of which (1 and 2) had already been studied earlier (July 2011, September 2012 and 2013), while the remaining three (GNO, GNO2 and Per) were studied for the first time in July 2015 based on the results of the interpretation of geoacoustic profiles (Figure 3).

Results and Discussions

Vistula Lagoon (the Baltic Sea)

Geoacoustic profiles obtained in December 2014 visually showed signs of gas saturation of sediments (Figure 3), similar to those observed in the open part of the Baltic Sea (Gdansk Deep) [*Ulyanova et al.,* 2013]. Darkness directly below the bottom surface, caused by increased reflection of the sound wave in near-surface sediments, below which acoustic windows are traced, appearing as white spots of intense absorption of the acoustic signal, may indicate the presence of increased gas concentrations.

Gas Geochemical Studies

The studied sediments were represented by silty sands (Figure 4). The fragments of shells were found in all samples.

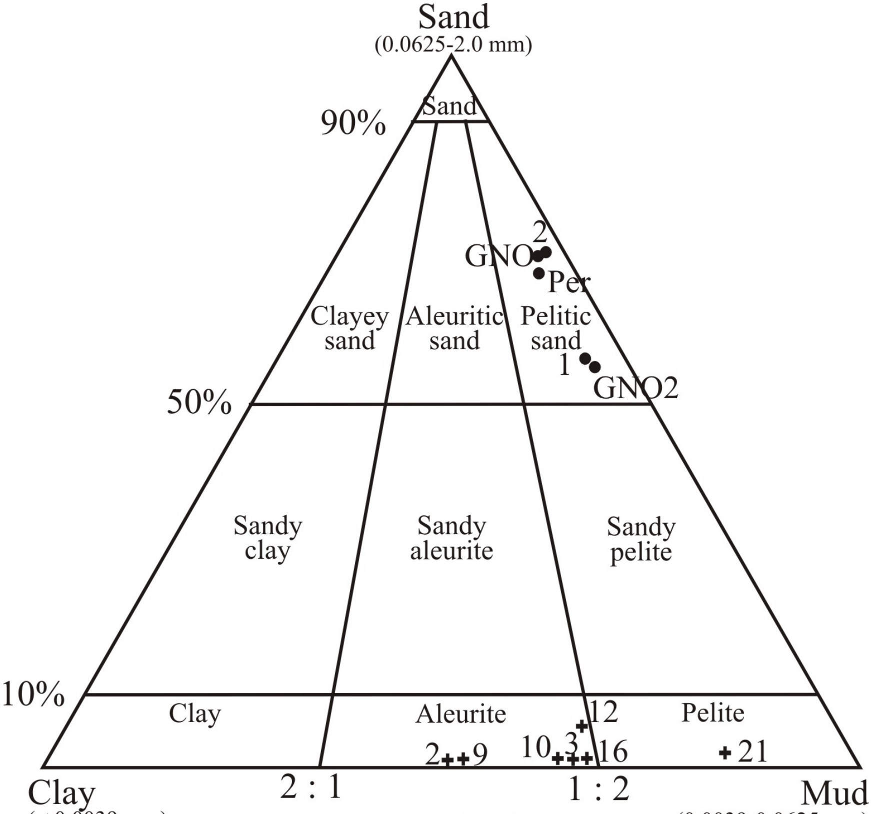

Figure 4. Distribution of bottom sediments of the Vistula Lagoon (points) and the Sevastopol Bay (crosses) according to the granulometric type.

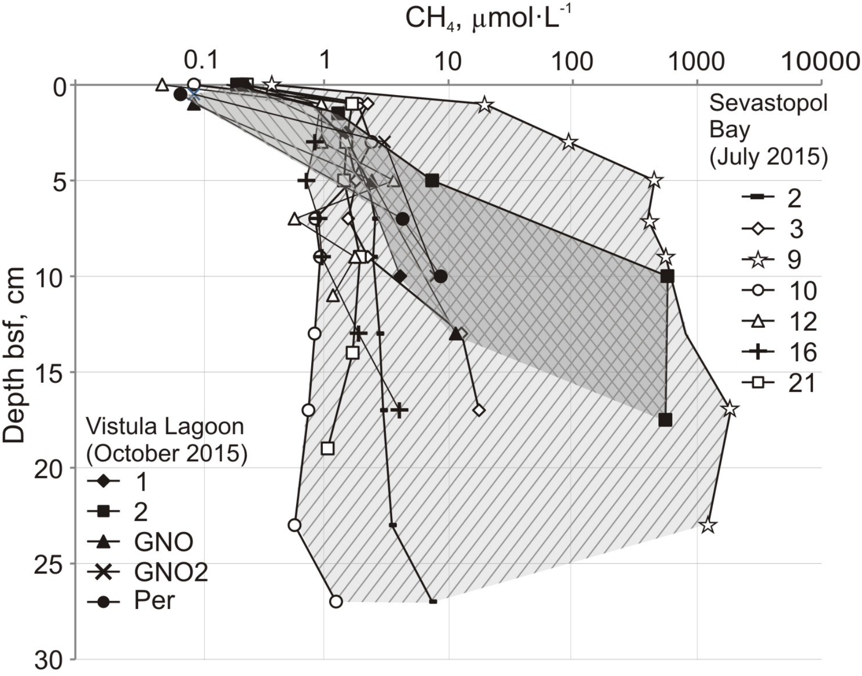

Figure 5. Comparison of methane distribution profiles in bottom sediments of the Vistula Lagoon in July 2015 and the Sevastopol Bay in October 2015; The numbers indicate the numbers of points. Shaded areas indicate concentration ranges for the respective study areas.

Table 3. The Content of Methane and Sulfates in the Sediments of the Vistula Lagoon (2011 data are taken from [*Pimenov et al.*, 2013], 2012 from [*Ulyanova et al.*, 2013]).

Point/ Depth, m	Horizon, cm	CH_4, µmol/dm^3				SO_4^{2-}, mmol/l		
		06–2011	09–2012 18/22*	09–2013	07–2015	06–2011	09–2013	07–2015
1/4.0	Near-bottom water				0.23			
	0–5	242	2.8/6.2	144	1.5	2.92	2.92	1.7
	5–10	357	5.3/5.9	160	4.1	2.85	3.23	3.6
	17–22	372	18.7/–	263	–	1.83	2.19	–
	22–27	361	–	269	–	1.67	2.08	–
	27–32	332	–	310	–	1.15	1.98	–
2/4.1	Near-bottom water				0.20			
	0–3	93.2	3.3/2.5	194	1.3	2.4	4.9	3.2
	3–8	95.9	12.2/5.3	202	7.4	2.38	5.31	–
	8–12	95.2	129/124	274	578	1.71	3.23	1.1
	15–20	106	399/521	2276	555	1.43	1.15	1.0
	20–25	111	–	8515	–	1.11	0.42	–
	25–30	–	–	8523	–		0.42	–
GNO/4.0	Near-bottom water				0.09			
	0–2				2.42			2.61
	3–8				11.44			2.49
	9–13				15.63			1.98
GNO2/4.0	Near-bottom water				0.09			–
	0–1				3.07			–
	2–4				7.90			
	5–10				14.73			
Per/4.0	Near-bottom water				0.07			
	0–1				4.28			3.13
	2–6				8.65			–
	7–12				16.07			2.79

Note: Methane concentration was measured by phase-equilibrium degassing using a Crystal 2000 gas chromatograph. The sulfate ion in the pore water of sediments was determined using a Stayer ion chromatograph.
* September 18, 2012 / September 22, 2012.

The content of methane and sulfates in the sediments of the Vistula Lagoon differed within the area (Table 3, Figure 5). In the summer season of 2015, maximum methane values were recorded for silt sand of point 2 on the horizon 5–15 cm (578 to 555 μmol/dm^3), which were accompanied by the exhaustion of sulfates (from 3.2 mmol/l in the surface layer 0–2 cm to the minimum in 2015 about 1 mmol/l). The minimum methane content in the surface layer was fixed at the same point and amounted to 1.3 μmol/dm^3, and it was quite high compared to sulfates.

In the sediments of the remaining points of the Vistula Lagoon, methane concentrations did not exceed 16 μmol/dm^3. Values of methane content obtained in September 2013 at a horizon of up to 20 cm of point 2 were maximum for the entire observation period 2011–2015 (see Table 3). For comparison, it should be noted that for the southern part of the Vistula Lagoon (the water area of Poland), the maximum concentration of methane was recorded in the southwestern part and amounted to 6450 μmol/dm^3, the minimum in the southeastern part, 7.1 μmol/dm^3 [*Reindl and Bolałek,* 2017]. The rest of the Polish water area is characterized by values of 7–37 μmol/dm^3, which is slightly higher than the values obtained for the Russian part of the Vistula Lagoon in 2015. The maximum concentration obtained for the Polish water area is identical to the values in Eckernförde Bay, the Baltic Sea, and is explained by weak hydrodynamics and low salinity area. In the Curonian Lagoon (southern part) of the Baltic

Sea, the methane concentration in the surface layer of sediments varies in the range 1.6–1000 μmol/dm^3 [*Pimenov et al.,* 2013b; *Ulyanova et al.,* 2013].

The sulfate-methane transition zone was recorded at two points: at point 2 at a horizon of 5 cm and at a GNO points at a horizon of 11 cm. The amount of methane in bottom water varied slightly (0.07 to 0.23 μmol/l). Thus, the areas selected based on the results of geoacoustic profiling did not confirm the presence of increased gas concentrations in bottom sediments. However, it must be borne in mind that sampling was performed several months after profiling. Changing seasons and, consequently, hydrological parameters could contribute to the release of gas.

For the first time, the solubility of methane in pore waters was calculated for the Vistula Lagoon: 2.12 mmol/l for point 1, 2.04 mmol/l for point 2 and 2.00 mmol/l for other points. It is known that with a change in temperature, the rate of molecular motion changes and, consequently, the solubility of various substances in liquids also changes. The solubility of gases decreases with increasing temperature. A significant effect on the solubility of gases in water is exerted by pressure. The amount of gas dissolving in water increases in direct proportion to the increase in its partial pressure, i.e. gases obey Henry's law. The pressure of the gas phase at any point in the bottom sediments will depend on changes in atmospheric and hydrostatic pressure. Therefore, under slightly changing conditions in the water area, the solubility values can be considered comparable. In general, in the Vistula Lagoon under the observed conditions, there was no excess of methane concentration in pore waters over its solubility.

The diffusion flux of methane at the water-bottom interface varied from 0.005 at point 1 to 0.030 mmol/(m^2 day) at point Per (Figure 6). At point 2, the value was 0.008 mmol/(m^2 day), at the points of GNO and GNO2 – 0.017 and 0.021 mmol/(m^2 day), respectively.

When comparing the magnitude of the diffusion flux at points 1 and 2 with the previously obtained data (2011–2013), we can conclude that in July 2015, there was a minimal methane flux from the surface sediment layer to the water of the Vistula Lagoon.

Sevastopol Bay (the Black Sea)

Geoacoustic Research

There were no reliable signs of the presence of gas-saturated layers of bottom sediments in the Sevastopol Bay. Sites visually similar to the areas of gas-saturated sediment distribution were studied, but insignificant

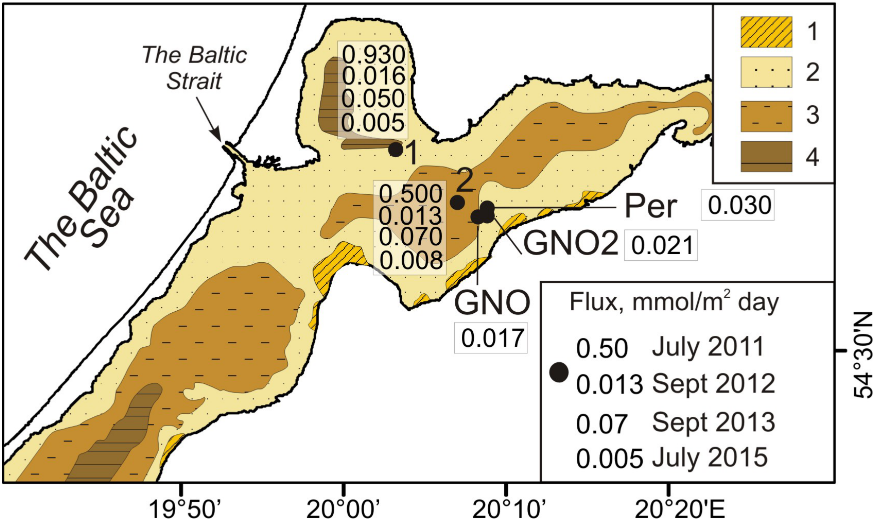

Figure 6. Diffusion flux of methane from the surface layer of sediments to bottom water in the Vistula Lagoon according to the results of surveys 2011–2013 – points 1 and 2 [*Ulyanova et al.*, 2013], 2015 – all points; Legend: 1 – boulder-pebble; 2 – sand; 3 – aleurite; 4 – mud.

methane contents confirmed the assumption that there were no elevated gas concentrations. It should be noted that stratification of sediments also was not recorded, although the study area is partially characterized by the predominance of aleuritic-pelitic sediments on the bottom surface, and according to the technical characteristics of the echo-profiler, several upper thin layers of sediments should be expected to be displayed. At the same time, at points 9 and 2, acoustic anomalies in the water column were observed, similar to bubble outgassing (see Figure 2A, Figure 2B). Stream gas emissions were repeatedly recorded earlier in the coastal waters of the Heracles Peninsula, including the Sevastopol Bay [*Egorov et al.,* 2011; *Malakhova et al.,* 2015; *Pimenov et al.,* 2013a]. It has been established that the mechanism of formation of biogenic methane seeps can be different. Bubble gas can form directly in the upper layers of bottom sediments due to intense microbial processes, such as in Kazachya Bay; and in deeper layers of the sedimentary layer, as in the case of the estuarine part of the Sevastopol Bay [*Malakhova et al.,* 2015].

In Figure 2B, the track from the bubbles was recorded after the contact of the corer with the bottom at point 9. Most likely, the mechanical effect on the sediments released a certain amount of gas in bubble form. The grain-size composition of the sediment at point 9 ensures that microbubbles are collected on the surface of the bounding layer, consisting of a sediment with small-diameter pores (Figure 4). Whereas in the sandy sediments of the Vistula Lagoon, dissolved gas and microbubbles pass unhindered at the water-bottom sediment interface without forming sufficiently large accumulations.

Table 4. Methane Content in Sediments and Near-Bottom Water, Diffusion Flux at the Sediment-Water Interface in the Sevastopol Bay of the Black Sea

Point	Horizon, cm	Methane concentration*	Methane diffusion flux mmol m^2/day	Point	Horizon, cm	Methane concentration*	Methane diffusion flux mmol m^2/day
10	near-bottom water	0.09		9	near-bottom water	**0.38**	
	1	1.87	0.012		1	19.43	0.132
	3	2.41			3	92.63	
	5	1.67			5	452.99	
	7	0.85			7	400.24	
	9	0.93			9	558.33	
	13	0.84			13	807.02	
	17	0.75			17	**1856.22**	
	23	0.58			23	1216.33	
	27	1.25					
16	near-bottom water	0.24		3	near-bottom water	0.22	
	1	0.93	0.005		1	2.25	0.014
	3	0.84			3	1.53	
	5	0.72			5	1.82	
	7	0.9			7	1.56	
	9	0.96			9	2.25	
	13	1.89			13	12.75	
	17	4.02			17	17.61	
2	near-bottom water	0.16		21	near-bottom water	0.22	
	1	0.76	0.004		1	1.68	0.01
	3	1.51			3	1.51	
	5	2.15			5	1.45	
	7	2.48			9	1.94	
	9	2.39			14	1.7	
	13	2.69			19	1.07	
	17	2.87		12	near-bottom water	0.05	
	23	3.38			1	0.95	0.006
	27	7.13			3	0.96	
	33	7.33			5	3.63	
	37	8.07			7	0.58	
	45	8.77			9	1.78	
					11	1.18	

Note: Methane concentration was measured by phase-equilibrium degassing using a Crystal 2000 gas chromatograph (for samples of the Vistula Lagoon) and an HP 5890 chromatograph (for samples of the Sevastopol Bay). The diffusion flux was calculated from methane concentrations in pore waters according to Fick's first law.

* µmol/l for water and mmol/dm^3 for sediments.

Gasgeochemical studies.

The investigated sediments of the Sevastopol Bay were represented by clayey aleurite and aleuritic-pelitic clayey silts and siltstones (see Figure 4).

The methane content in the bottom sediments of the Sevastopol Bay differed within the studied area (Table 4, see Figure 5). In October 2015, the maximum methane values were recorded for point 9 at a horizon of 17 cm. The maximum methane concentration in the near-bottom water (0.38 μmol/l) was also observed here. The entire sediment core, samples at point 9, located in the central part of the bay, was characterized by elevated methane concentrations ranging from 19 to 1856 μmol/dm^3. At other points, the methane concentration fluctuated slightly (from 0.58 to 17.61 μmol/dm^3).

The spatial model of methane distribution in the near-surface bottom sediments of estuaries is based on the fact that the concentration of methane in pore water decreases in the sea direction. Nevertheless, there are several exceptions, including for highly eutrophied coastal bays with sufficiently high salinity and extremely high sedimentation rates of organic material. For example, in Eckernförde Bay in Germany and

Cape Lookout in North Carolina, such conditions lead to sulphate depletion in the upper layers of bottom sediments and the methane concentration reaches several mmol/dm^3 at a depth of less than 1 m below the bottom [*Abegg,* 1997]. The formation of bubble methane in these areas is already possible at a depth of several tens of centimeters, where the methane concentration becomes higher than the gas solubility in pore water.

The presence of increased methane concentrations in the sediments of the central part of the bay compared with the peripheral parts can be explained by the peculiarities of sedimentation processes [*Malakhova et al.,* 2018]. The sedimentary matter of the central part of the bay is characterized by a finer granulometric composition of sediments (60–65 % of aleuropelites), and its supply is associated with allochthonous matter [*Malakhova et al.,* 2018], such as rainfall drains, emergency releases of untreated water, which can be a significant source of organic matter. In this regard, increased concentrations of CH_4 at point 9 are due to both a high content of organic carbon in the sediments and an increased dispersion, and, consequently, to the adsorption capacity of the muds.

Above the seep field (point 12), the values both in bottom sediments and in bottom water were among the

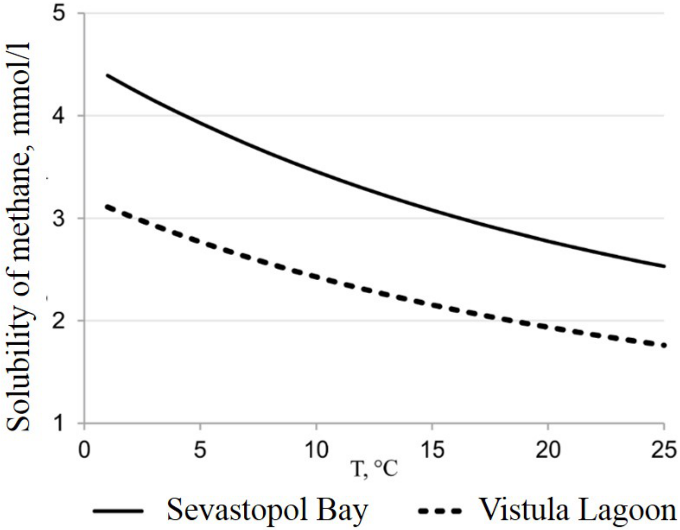

Figure 7. The calculated dependence of the solubility of methane in pore waters on the water temperature for the Sevastopol Bay (average depth 11.3 m, $S = 18$ ‰) and the Vistula Lagoon (average depth 2.7 m, $S = 3.8$ ‰) calculated by Henry's Law.

lowest, however, a sharp increase in methane concentration at a horizon of 4–6 cm (up to 3.63 μmol/dm^3) occurred in comparison with the overlying and underlying layers (0.96 and 0.58 μmol/dm^3, respectively). A similar profile of methane with a maximum in subsurface horizons was previously noted both in this research area [*Egorov et al.,* 2012] and in the study of methane seeps on the Black Sea shelf [*Ivanov et al.,* 2002].

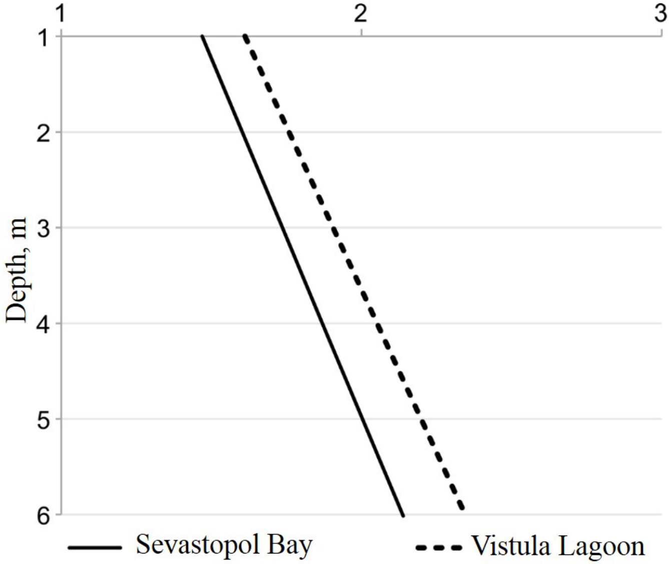

Figure 8. Dependencies of methane solubility on the depth of the station for the Sevastopol Bay ($S = 18‰$) and the Vistula Lagoon (average depth 2.7 m, $S = 3.8‰$) at a water temperature of 22 °C.

The solubility of methane in pore waters calculated for the Sevastopol Bay varied from 1.77 mmol/l for point 3 (the shallowest sampling depth is 3 m) to 3.81 mmol/l for point 12 (maximum depth 18 m), on average for the water area 2.5 mmol/l. Despite the rather high methane concentrations at point 9, even at it the concentration did not exceed the solubility of methane.

The dependencies of methane solubility in pore waters on water temperature (Figure 7) and pressure (Figure 8) were also calculated. The graphs show that the solubility of methane in the Sevastopol Bay exceeds the values in the Vistula Lagoon, which is explained, first of all, by the greater depth of the basin. The difference could be even greater, but the higher salinity of the Sevastopol Bay leads to a decrease in solubility, as the mineralization of water reduces the solubility of hydrocarbons in water.

After the gas phase is formed, the gas movement between the gas and water phases is governed by Henry's law, according to which the concentration of dissolved gas is equivalent to the partial pressure of the gas multiplied by its solubility (Henry's constant), which is inversely dependent on temperature [*Slabaugh and Parsons,* 1976]. Thus, with increasing temperature throughout the summer, the solubility of the gas will decrease, which will lead to the transition of gas from the dissolved to the gaseous phase.

The diffusion flux of methane at the water-bottom boundary in the Sevastopol Bay varied from 0.004 at point 2 to 0.132 mmol/(m^2 day) at point 9 (see Table 4). The results are comparable with studies in 2011, when the methane flow in the open part of the Sevastopol Bay varied from 0.001 to 0.544 mmol/(m^2 day)

[*Malakhova et al.,* 2012]. Moreover, the maximum values both in 2011 and in 2015 were observed in the central part of the bay, characterized by the finest surface sediments. With the exception of sedimentation at point 9, we can say that the methane diffusion flux in the Sevastopol Bay was comparable with the data for the Vistula Lagoon. However, it should be taken into account that there are bubble emissions of methane from the bottom surface in the Sevastopol Bay [*Egorov et al.,* 2012; *Malakhova et al.,* 2013; 2015]. Their formation can be associated with fault systems of the studied water area that promote gas migration [*Bondarev et al.,* 2015; *Kravchenko,* 2008].

Conclusions

The geoacoustic and gas-geochemical studies in the Vistula Lagoon of the Baltic Sea and Sevastopol Bay of the Black Sea revealed the following results:

1. Sampling of the potential area of gassy sediments in the Vistula Lagoon discovered during geoacoustic profiling, did not confirm the presence of elevated methane concentrations. Methane concentrations in sediments and near-bottom water, as

well as the value of methane diffusion flux at the sediment-water interface, were insignificant compared to background area. The change in hydrological characteristics (seasons) that occurred between geoacoustic profiling (December 2014) and sampling of bottom sediments (July 2015) can explain the yield of a significant amount of gas recorded on the profile.

2. The maximum concentrations of methane were observed in the central part of the Sevastopol Bay, which may be due to a finer grain size distribution compared to other sampling sites.

3. Methane concentrations in both studied basins were generally comparable, but did not exceed solubility. It should be noted that lower methane concentrations in the Sevastopol Bay (with the exception of point 9) can be explained by the difference in the sampling season (Baltic Sea – July, Black Sea – October). With increasing temperature throughout the summer, the solubility of the gas decreased, which led to the transition of the gas from the dissolved to the gaseous phase.

4. The diffusion flux of methane at the sediment-water interface was comparable in the Vistula La-

goon and Sevastopol Bay. However, bubbly methane emissions are present only in the Sevastopol Bay, which is probably due to the grain size composition of bottom sediments.

5. For the first time, for the Vistula Lagoon the solubility of methane in pore waters was calculated taking into account Henry's law at different temperatures of the bottom water. The solubility of methane in the Vistula Lagoon was lower than in the Sevastopol Bay, which is explained by the greater depth of the area.

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