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BIOGEOCHEMICAL CHARACTERISTICS OF SHALLOW METHANE SEEPS OF CRIMEAN COASTAL AREAS IN COMPARISON WITH DEEP-SEA SEEPS OF THE BLACK SEA

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Methane gas bubble emissions (seeps) are widespread phenomenon in the World Ocean, *inter alia* in Black Sea basin. The relevance of the research of methane seeps is due to their important role as a source of methane – greenhouse and environment-forming gas – for water column and atmosphere. The article presents a comparative analysis of the data from our biogeochemical 10-year studies of shallow gas seeps of the Crimean Peninsula and data on deep-sea gas seeps of the Black Sea. During 10-year period, apart from carrying out hydroacoustic research, the following parameters were determined: bubble gas component composition, methane carbon isotopic composition, microbial community structure of bacterial mats, covering gas bubble emission sites, and gas fluxes from separate seeps. During long-term monitoring, 14 separate gas bubble emission sites were detected and described in Crimean coastal areas; they were located from Cape Tarkhankut in the west of the peninsula to the Dvuyakornaya Bay in the southeast. Crimean coastal seeps were mostly of biogenic origin, with a seasonal type of gas bubble emission. Laspi Bay seeps were classified as emissions of deep gas of thermocatalytic genesis. A significant variation was recorded in values of isotopic composition of methane carbon $\delta^{13}C\text{-}CH_4$ of bubble gas in coastal shallow areas (−94…−34 ‰), which indicates different conditions for bubble gas generation and maturation in seabed sediments. Similar to deep-sea seeps, coastal gas bubble emissions were accompanied by bacterial mats of diverse structure, with different dominating species. As shown, formation of stable bacterial biomass, usually consisting of sulfide- and sulfur-oxidizing bacteria, requires a fluid flux of reduced dissolved gases, while pointwise bubble gas discharge does not provide sufficient concentration gradients and mechanically disrupt community structure. Various methods were used to estimate the size spectra of bubbles, as well as fluxes from separate seeps. Gas flux values varied from 1.8 $L\cdot day^{-1}$ (the Martynova Bay) to 40 $L\cdot day^{-1}$ (the Laspi Bay). The environment-forming effects, related to gas bubble emission in coastal areas, are discussed: effect of seeps on oxygen conditions in seabed sediments and in water column above gas emission sites, vertical water mixing due to gas lift effect, and fluid discharge at gas emission sites.

Keywords: methane seeps, genesis, isotopic composition, bacterial mats, hydroacoustic methods, environment-forming gas, Crimean shelf, Black Sea

Methane gas bubble emissions are a widespread phenomenon in the World Ocean; according to geological classification, these are "cold seeps" (Judd & Hovland, 2007). The relevance of the research of methane seeps is due to their important role as a source of methane – greenhouse and environment-forming gas – for water column and atmosphere. Assessing the contribution of marine methane to global warming is a challenging task due to the non-uniformity of distribution of these sources and high sporadicity of gas influx. Recently, special attention has been paid to studies of methane of polar regions due to their sensitivity to the processes of global climatic change (Römer et al., 2014 ; Sergienko et al., 2012). Thus, on Siberian Arctic shelf, many gas emission sites have been discovered; they are considered to be related to thawing of permafrost zones and “unpacking” of gas hydrates, buried there. At the same time, new seep sites are found in the southern areas at shallow depths (Pimenov et al., 2013 ; Shik, 2006 ; Sciarra et al., 2019 ; Tarnovetskii et al., 2018).

In the Black Sea, methane seeps were found in all areas from shallow coastal ones to a depth of 2084 m (Egorov et al., 2011, 2003 ; Naudts et al., 2006). Geographic coordinates of more than 4380 sites of bottom bubble methane discharge have been established, and it was shown that separate streams can produce gas fluxes of up to 510 $L \cdot min^{-1}$ (Egorov et al., 2011). It was determined that gas bubble streams can significantly affect concentration of dissolved methane in water column and result in gas lift upwelling (Egorov et al., 1999). As shown, production of organic matter by methanotrophic bacteria can reach tens of percent of primary production and affect biological productivity of marine ecosystems (Egorov et al., 2011). The downward transport of bottom water into seabed sediments, resulting from fluid advection, turbulent diffusion, convection, and bioirrigation, is also an important process in “cold seeps”, since it transports oxidized components, capable to act as electron acceptors in the early diagenesis, to the reduced environment. At active methane emission sites in the oxic zone of the Black Sea, bacterial mats were found at the seabed, whereas in the deep-sea reduced zone, carbonate structures of up to 4 m high were recorded (Gulin et al., 2005 ; Michaelis et al., 2002), with their genesis being related to the functioning of microbial consortia of methanotrophic archaea and sulfate-reducing bacteria (Boetius et al., 2000). It should be noted that gas emissions can cause potential environmental adverse effects, *e. g.* lead to methane ignition in case of natural disasters or even losing buoyancy of ships (Egorov et al., 2005 ; Shnyukov, 2005).

Interest in the studying shallow seeps is due to the fact that bubble gas, unlike deep-sea one, is not completely dissolved in water column and enters the atmosphere. Another difference between shallow Black Sea seeps and deep-sea ones is an oxidized environment, where gas emission and accompanying biogeochemical processes occur. The geochemical gradients are formed at the interface between seabed sediments and water column, and this establishes conditions for growth of aerobic chemolithotrophs. On the other hand, the sites of bubble gas discharge off the Crimean coast can be potentially hazardous areas, since with an increase in seismic activity of the area, gas emission volume can increase manifold (Shnyukov, 2005).

The aim of the research was to generalize and analyze current data on localization and biogeochemical characteristics of shallow seeps of Crimean coastal areas in comparison with deep-sea seeps of the Black Sea.

MATERIAL AND METHODS

Our data of 2010–2019 was analyzed, and literature data, concerning the problem under study, was reviewed. During 10-year period, the authors carried out hydroacoustic research, isotopic studies of bubble gas, phylogenetic studies of microbial communities of bacterial mats, covering shallow gas emission sites in Crimea, and assessment of gas fluxes from separate seeps.

The search for gas bubble emissions in coastal areas was carried out on small vessels using echo sounders JFC-46, SeaCharter 480 DF, and Lowrance Elite-7 Ti at operating frequency of 200 kHz, as well as a Garmin-300 echo sounder at 210 kHz. To process acoustic data and form a database of electronic echograms of methane seeps, a licensed WaveLens software was used (Artemov, 2006). Visual observations and filming were carried out to assess size ranges of bubbles and fluxes from separate streams, with an underwater controlled TV camera MiniRover MK-II, as well as a GoPro 3/4 video camera, with the help of deep divers and surface-supplied divers (Malakhova et al., 2015). Bubble gas samples for subsequent component and mass spectral analysis were collected with cone traps and stationary pyramidal bottom traps (Malakhova, 2014). Bubble gas fluxes were assessed by various methods: trap one (Malakhova, 2014), as well as active (Malakhova et al., 2015) and passive hydroacoustics (Budnikov et al., 2020). Seabed sediment sampling was carried out by divers directly at gas emission sites using an acrylic ground tube with a vacuum seal, allowing to sample the surface layer of seabed sediments without disrupting its structure. Methane content in bottom water, seabed sediments, and bubble gas was measured using HP-5890 and "Kristall-2000" gas chromatographs (Russia) with a flame ionization detector after phase equilibrium degassing of the samples (Bol'shakov & Egorov, 1987). Methane $\delta^{13}C$ value was measured using a TRACE GC gas chromatograph (Germany), combined with a Delta Plus mass spectrometer (Germany). The composition of microbial communities was determined by high-throughput sequencing of 16S rRNA genes (Bryukhanov et al., 2018 ; Pimenov et al., 2018).

RESULTS AND DISCUSSION

Localization and edaphic characteristics of shallow seep sites. Localization of gas bubble emission sites off the Crimean coast is shown in Fig. 1. Coordinates, depth, sediment type, and presence of bacterial mats in the areas of recorded seeps are listed in Table 1.

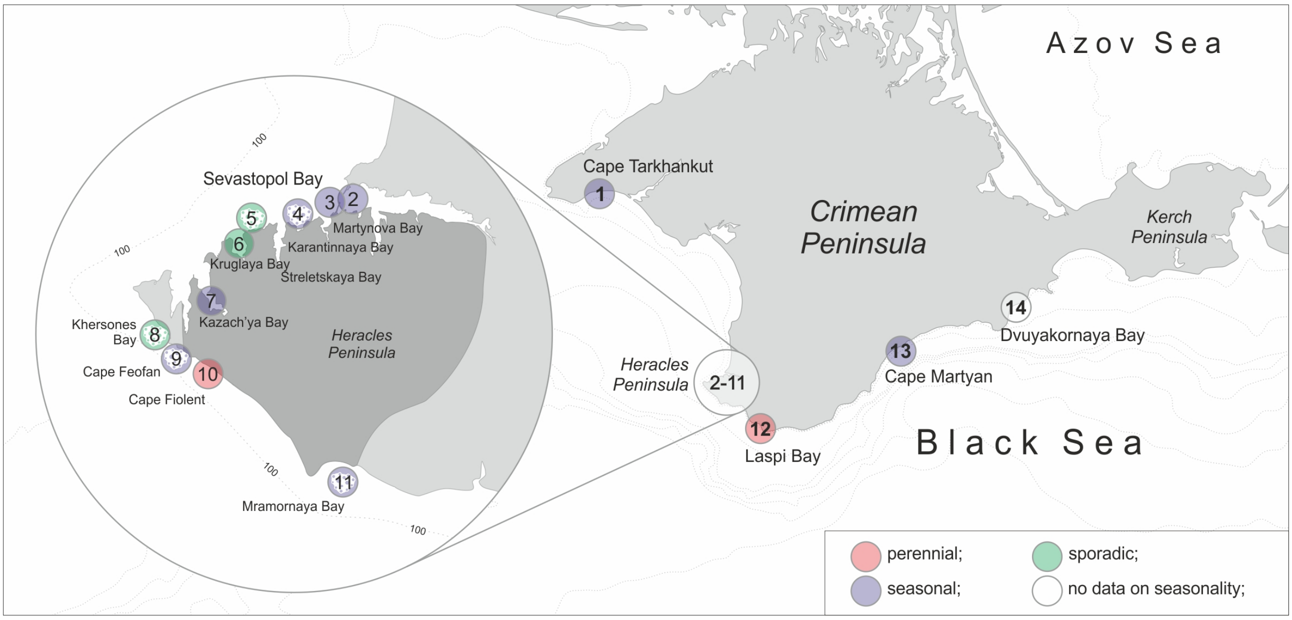

Fig. 1. Map of methane seep sites off the Crimean coast; white markers within the circles indicate presence of bacterial mats at the sites

Table 1. Localization and depth of gas emission sites, seep types, seabed sediment types, and characteristics of microbial communities

Station No.	Research area	Coordinates	Depth, m	Seep type	Sediment type	Microbial communities	References
1	Cape Tarkhankut	45°21′45″N, 32°44′57″E	4	Seasonal	Dark gray / black silt	No data	[49]
2	Sevastopol Bay	44°37′19″N, 33°30′38″E	17–18	Seasonal	Silted sand	No data	[9 ; 19]
3	Martynova Bay	44°36′57″N, 33°30′11″E	5	Seasonal	Gas-saturated detrital sediment	+	[37 ; 38]
4	Karantinnaya Bay	44°36′37″N, 33°29′44″E	0,5	Seasonal	Dark gray reduced sand	++	New data
5	Streletskaya Bay open area	44°36′40″N, 33°27′42″E	10	Sporadic	Dark gray reduced silt under a curd-type white mat	+++	[32]
6	Kruglaya Bay	44°35′57″N, 33°26′49″E	1,5	Sporadic	Detrital sediment, covered with macrophytes	+	New data
7	Kazach'ya Bay	44°33′57″N, 33°24′39″E	1,5	Seasonal	Detrital sediment, covered with macrophytes	+	[38]
8	Khersones Bay	44°33′53″N, 33°23′57″E	5	Sporadic	Local patches of highly reduced silty gas-saturated sand	++	[31 ; 38]
9	Cape Feofan	44°33′34″N, 33°24′01″E	10	Seasonal	Gas-saturated detrital sediment at the bottom of a rocky crack, covered with a biofilm	+++	New data
10	Cape Fiolent	44°31′21″N, 33°28′01″E	2	Year-round	Coarse sand with pebbles	+	New data
11	Mramornaya Bay	44°30′03″N, 33°30′51″E	6	Seasonal	Gas-saturated detrital sediment at the bottom of a rocky depression, covered with a biofilm	++	[42]
12	Laspi Bay	44°25′15″N, 33°42′25″E	3	Year-round	Bedrock, covered with coarse sand	–	[1 ; 16 ; 23 ; 38 ; 40]
13	Cape Martyan	44°30′15″N, 34°14′02″E	2,5	Seasonal	Coarse sand with pebbles	+	[5]
14	Dvuyakornaya Bay	44°59′00″N, 35°21′18″E	2,5–4	No data	Sand, covered with a layer of detritus-bacterial mat	+++	[12 ; 22]

Note:
– indicates, that bacterial mats were not found;
+ indicates traces of bacterial communities in the form of the finest whitish films;
++ indicates distinct mats, covering a small area, with a significant amount of biomass;
+++ indicates abundant bacterial mats, covering a large area.

Association of seeps with seabed morphometric and geological structures. Previously, the relationship between gas bubble emissions and morphometric and geological structures of the seabed was shown (Shnyukov et al., 2005 ; Artemov et al., 2007 ; Römer et al., 2012). For example, for deep-sea seeps of biogenic origin in Kerch area, several patterns of spatial distribution were identified, depending on geomorphological structure. In the area of the upper continental margin, being steep and cut by ravines, seeps were found mainly along the ridges, oriented down the slope. In paleo-Don valley area, the slope was affected by extensive landslides. Gas emissions were associated there with areas of ruptured sediments; they were detected mainly along the ledges of underwater landslides (Zander et al., 2020). Same as in Kerch area, in paleo-Dnieper water area, gas emissions were found mostly at the tops of mountain ranges, formed by sedimentary rocks, on canyon walls, dotted with ditches, and on the slopes of underwater landslides (Artemov et al., 2007). At the same time, a few seeps were detected at the bottom of canyons (Egorov et al., 2011). A thorough analysis of geological patterns of active methane gas emission sites, performed in (Naudts et al., 2006), showed as follows: gas bubble emissions in paleo-Dnieper area do not depend on the system of faults, as stated in (Kruglyakova et al., 2004); they depend on stratigraphic and sedimentary factors.

The seeps, in turn, can affect small-scale morphology of seabed, creating specific structures during gas emission; these occur either as local depressions (pockmarks) or, conversely, as elevations of sediment level due to excessive pressure of gas, accumulating under the surface. Pockmarks are caused by fine sediments dispersion, resulting from gas seepage at fluid and gas bubble emission sites, whereas the increase in sediment level is caused by bubble gas, mainly of microbial origin, accumulating under “dome” surface. Such geomorphological peculiarities of seabed can serve as distinguishing features during prospecting and exploration.

A distinctive feature of coastal shallow seeps is a thin layer of sedimentary material, often being sandy sediments or silted sand (Table 1). Low thickness of these sediments, insignificant amount of organic matter in them, and, as a consequence, low intensity of microbial processes mostly preclude identification of such upper sedimentary layers as genetically related to gas emission occurrences. Despite the biogenic origin of most Crimean coastal seeps, their source was located in the underlying layers, as shown in (Egorov et al., 2012).

In this regard, the Sevastopol Bay stands out, with its morphology, contributing to the accumulation of a sedimentary layer with the thickness ranging from 28 m in the apex to 40 m in the mouth (Bondarev et al., 2015). On the roadstead, more than 20 sites of periodically active gas bubble streams were recorded; most of them were detected in the areas of geodynamic nodes (Eremeev et al., 2007 ; Malakhova et al., 2020a, 2015). Echograms of the seeps, found in this and other areas of the Crimean shelf, are shown in Fig. 2.

It is important to note that not all geological blocks possess the necessary and sufficient conditions for formation of gas and fluid emissions. The main conditions are as follows: lack of degassing of underlying horizons, lack of gas traps, and either low or extremely high degree of crustal fragmentation, preventing formation of visible gas emission fluxes. Thus, repeated hydroacoustic surveys of Karan block seaward part, located along the Georgievsky fault (one of the largest tectonic faults), did not reveal any gas bubble emissions in the area. This is probably due to a combination of the conditions, mentioned above.

In general, the locality of coastal gas emissions, their association with the mapped fault structures, and gas discharge occurrence in the surf zone from the sediments, depleted in organic matter, where stationary anaerobic conditions are not maintained due to mixing, indicate a certain trigger, starting the mechanism of gas bubble emission. Such a trigger can be submarine discharge of fresh groundwater (Kravchenko, 2008 ; Whiticar, 2002), resulting in the rise of fluid fluxes, enriched in nutrients and reduced gases, from the aquifers along the system of micro-faults. At local sites, with especially intense fluxes, strongly reducing conditions are created; these, with temperature along, contribute to development of anaerobic microbial communities and formation of gas-saturated silts.

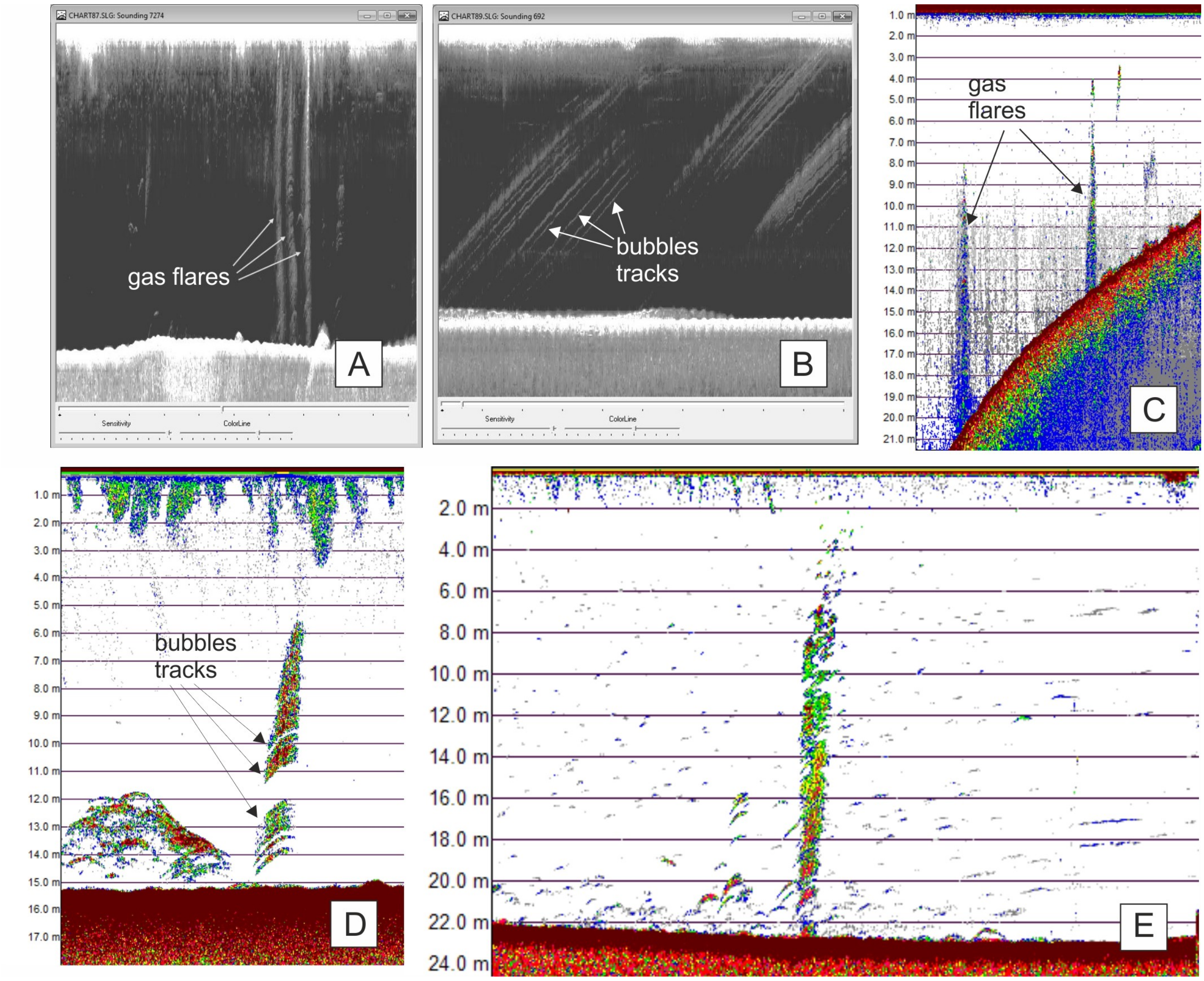

Fig. 2. Echograms of methane gas bubble emissions in Crimean Peninsula coastal areas: A and B – the Sevastopol Bay, October 2011 (SeaCharter 480 DF echo sounder); C – the Laspi Bay, July 2017 (SeaCharter 480 DF); D – sea area of the specially protected natural area "Cape Martyan", September 2019 (Lowrance Elite-7 Ti echo sounder); E – the Streletskaya Bay, September 2006 (SeaCharter 480 DF)

Frequency and intensity of Crimean coastal seep fluxes. Long-term monitoring of Crimean coastal seeps made it possible to identify several types of their activity. By gas emission frequency, seeps can be divided into seasonal, year-round, and sporadic ones (see Table 1).

The seeps of the Heracles Peninsula and Cape Tarkhankut (Tarnovetskii et al., 2018) were classified as **seasonal** ones, with both gas emissions and adjacent bacterial mats recorded during the warm season: from June to October. The highest spatial density of methane gas bubble emissions was registered in Sevastopol Bay alignment: in the area of about 500 m^2, by the acoustic method, 23 gas flares at depths of 17–18 m were detected in October 2011 (Egorov et al., 2012). Regular acoustic observations, carried out in the area of Sevastopol bays in different years in winter and spring, did not result in revealing presence of gas flares. As shown, these gas emissions were caused by bubble methane discharge into surface horizons of sediments from deeper layers of sedimentary strata and did not originate from the upper sediment layer (Egorov et al., 2012). The potential forecast for methane occurrence transformation in this area is associated with development of a layer of gas-saturated sediments, charged by bay outflows, *inter alia* Chernaya River runoff, and with formation of conditions for all-season activity of methane seeps, similar to that observed in paleo-Dnieper area: one of the world's most intense sites of bubble methane discharge, located 105–125 km northwest of the area described. There, more than 2200 permanent local methane gas bubble emission sites in the depth range of 35–835 m have been detected; their spatial density distribution on the shelf (depths up to 90 m) can reach 300 km^{-2} (Egorov et al., 2011).

The seeps at Cape Fiolent and in the Laspi Bay were classified as **year-round** ones, with gas occurrences recorded both in the warm and cold seasons since 2004 (Shik, 2006) (Fig. 3C). In the Laspi Bay, more than 20 separate gas bubble emission sites were detected both hydroacoustically and visually (Malakhova et al., 2015).

Sporadic seeps were recorded only once (they were not detected during subsequent monitoring). Thus, gas bubble emissions in the Kruglaya and Khersones bays were of irregular character and weak activity. Subsequently, in these areas, local sites of gas-saturated sediments were recorded, with bubble gas, emitting under mechanical action on them (Fig. 3D). In the center of such sites, highly reduced conditions were formed (Eh = −330…−245 mV) in seabed sediments, resulting in active sulfate reduction and methanogenesis, as well as in formation of stable fluxes of hydrogen sulfide and methane into seabed layers of water column (Bryukhanov et al., 2018). It was determined that formation of such areas of gas-saturated sediments (sulfurets) and scale of gas occurrences depend on the ambient temperature. Thus, a decrease was recorded in the area of seabed coverage with sulfurets in the Khersones Bay, as well as their formation only by the end of the summer season of the abnormally cold 2018.

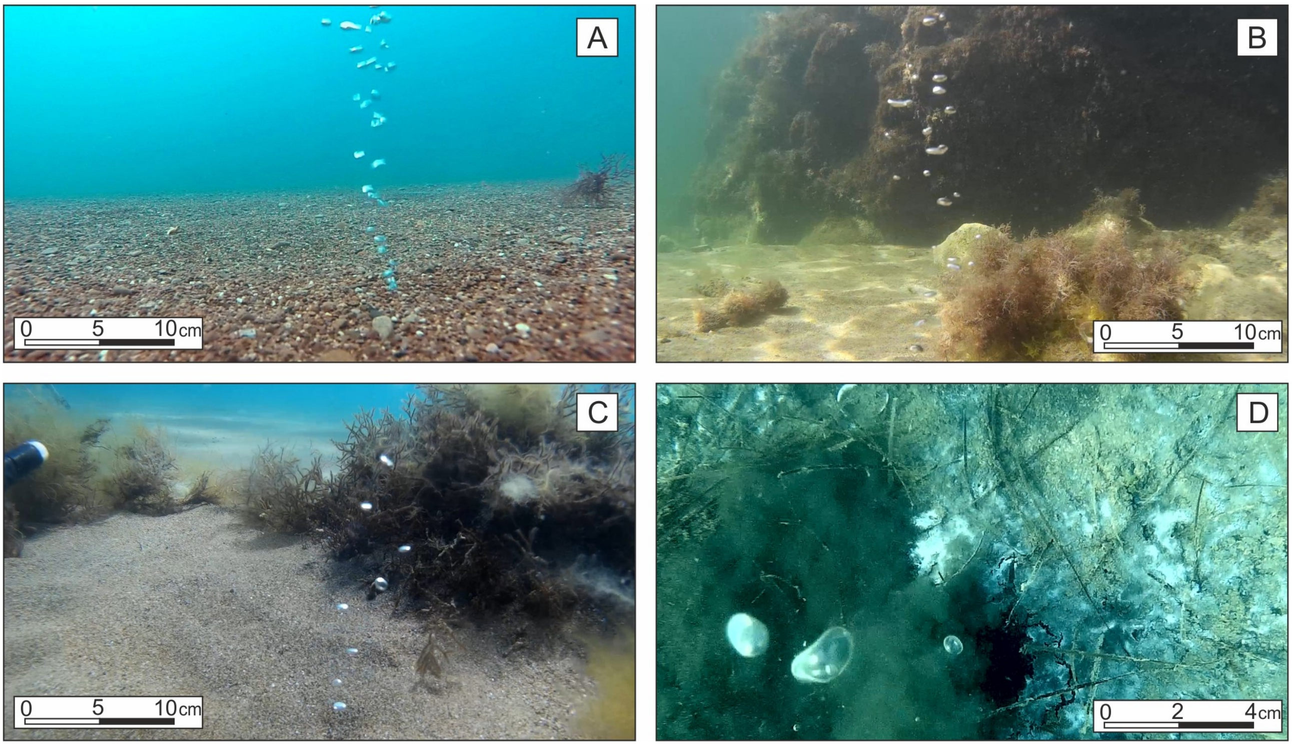

Fig. 3. Underwater photos of gas bubble emissions of Crimean coastal areas: A – Cape Martyan (2019); B – Cape Fiolent (2019); C – the Laspi Bay (2019); D – the Kruglaya Bay (2018)

Quantitative estimates of bubble gas volumes, reaching the surface and entering the atmosphere, are of importance for analyzing the contribution of greenhouse gases to the pool. The assessment was performed in the Martynova Bay in July 2009, using a pyramidal trap to collect bubble gas from seabed sediments. Time dynamics of gas volumes, emerged from Martynova Bay seabed, is shown in Fig. 4. Bubble gas flux during the exposure varied from 1.8 to 14 L·day^{-1}, averaging 4.5 L·day^{-1} (Malakhova, 2014).

In the Laspi Bay, to estimate the daily fluxes of gas bubble emission, a passive acoustic method, proposed by the authors, was used. It is based on the relationship between the frequency of the audio signal, produced by a gas bubble, when emerging from the outlet underwater channel, and bubble size (Budnikov et al., 2020). As shown for two seeps studied, the average bubble diameters were 7 and 5 mm. Given the intensity of bubble gas discharge, the calculated gas flux at these sites was 40 and 6 L·day^{-1}, respectively (Budnikov et al., 2020).

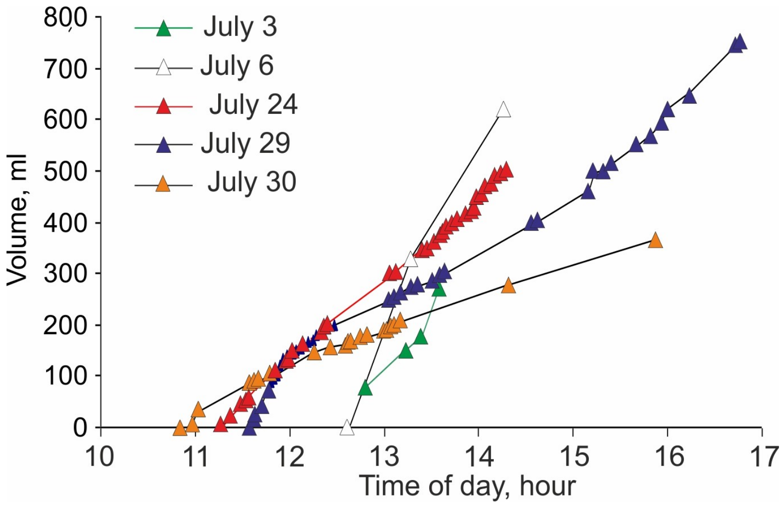

Fig. 4. Volume of bubble gas, emerged from 1 m^2 of seabed sediments in the Martynova Bay, measured by the trap method (July 2009)

Bubble gas hydrocarbon composition and genesis. There are two points of view on the source of methane of gas bubble emission. According to a geological hypothesis, degassing of Black Sea seabed passes through a system of geological faults and/or through an intermediate link: gas hydrate deposits in seabed sediments, resulting from gas discharge of hydrocarbon deposits. The arguments of geological hypothesis supporters are as follows: forecast estimates of high total prospective gas content in the area, presence of detected gas fields on Black Sea shelf in close proximity to methane gas bubble emission sites, and estimates of methane flux from gas emission sites (Shnyukov, 2005 ; Shnyukov et al., 2005). According to a biogenic hypothesis, the source of methane is microbial production in seabed sediments, which is confirmed by carbon stable isotopic composition of Black Sea methane, sampled at many gas-producing areas, such as paleo-Don and paleo-Dnieper ones (Lein & Ivanov, 2009).

Methane predominated in component composition of bubble gas of Crimean coastal areas (Table 2), but its amount was much lower than in bubble gas of deep-sea areas of the Black Sea. In the Kruglaya Bay, for example, methane in bubble gas accounted for 55 %, while at Cape Martyan it accounted only for 38 %. A significant amount of methane homologues was found only in Laspi Bay seeps.

One of the indicators of low-temperature (microbial) or high-temperature genesis of methane is the isotopic composition of its carbon and hydrogen (Whiticar, 1999). Of particular interest is a considerable variation of values in the isotopic composition of methane carbon $\delta^{13}C\text{-}CH_4$ in bubble gas, ranging from −94 to −34 ‰ in shallow coastal areas (Table 2, Fig. 5). A wide range of values is recorded both for gas samples of different areas and for gas samples of one area, *e. g.* for seeps of the Heracles Peninsula (−84…−58 ‰ $\delta^{13}C\text{-}CH_4$). High variability of $\delta^{13}C\text{-}CH_4$ was also established for bubble gas of Cape Tarkhankut: in different years, it ranged from −65 to −48 ‰ (Tarnovetskii et al., 2018). The variation may be explained by several factors. Microbial methane oxidation in the upper horizons of the sedimentary layer results in the change of $\delta^{13}C\text{-}CH_4$ isotopic composition due to selective consumption of methane with the lighter carbon isotope ^{12}C by methanotrophs (Whiticar, 1999). On the other hand, the cause may be the mixing of isotopically heavy gas from deep layers with a near-surface isotopically light gas of microbial origin, so that the isotopic ratio of $\delta^{13}C\text{-}CH_4$ depends on the contribution of these two sources (Pape et al., 2010).

Table 2. Hydrocarbon (CH_4, %; C_1/C_{2+}) and isotopic ($\delta^{13}C\text{-}CH_4$, ‰ PDB; $\delta D\text{-}CH_4$, ‰ SMOW) composition of bubble gas of Crimean coastal areas and deep-sea areas of the Black Sea

Station No.	Research area	CH_4, %	C_1/C_{2+}	$\delta^{13}C\text{-}CH_4$, ‰ PDB	$\delta D\text{-}CH_4$, ‰ SMOW	Reference
			Crimean coastal areas			
1	Cape Tarkhankut	n. d.*	n. d.	−65…−48	n. d.	[49]
3	Martynova Bay	57	$1.7 \cdot 10^4$	−56.7	−340.1	our data
4	Karantinnaya Bay	73	$21 \cdot 10^4$	−58	n. d.	-”-
6	Kruglaya Bay	54–55	n. d.	−94.5…−92.4	n. d.	-”-
8	Khersones Bay	66–72	10^4	−84…−58	n. d.	-”-
9	Cape Feofan	68.5–75.5	10^4	−83.4…−67.2	n. d.	-”-
10	Cape Fiolent	n. d.	n. d.	−60.3	n. d.	-”-
11	Mramornaya Bay	n. d.	n. d.	−67.54…−67.1	n. d.	-”-
12	Laspi Bay	92	31	−43…−36	n. d.	-”-
13	Cape Martyan	38	10^4	−89…−84	n. d.	-”-
			Deep-sea areas of the Black Sea			
	Vodyanitsky Mud Volcano	99.8	n. d.	−61	−170.8	[46]
	Dvurechensky Mud Volcano	n. d.	n. d.	−66…−62	−209…−185	[29]
	Helgoland Mud Volcano	n. d.	n. d.	n. d.	−217.4	our data**
	Kerch seep	99.2	2372	−66.6	−248	[44]
	Batumi seep	99.9	4267	−53.5	−175	[41]
	Kolkheti seep	n. d.	566	−51.1…−45.0	−192	[43]
	Pechori Mound	n. d.	299	−52.2…−45.8	−224…−216	[43]
	Ordu Ridge	n. d.	1998	−72.6…−68.5	−224.2…−221.5	our data

Note:
* – no data;
** – data for deep-sea areas of the Black Sea was obtained during the Summer Student Fellowship 2011 at the MARUM University (Bremen, Germany).

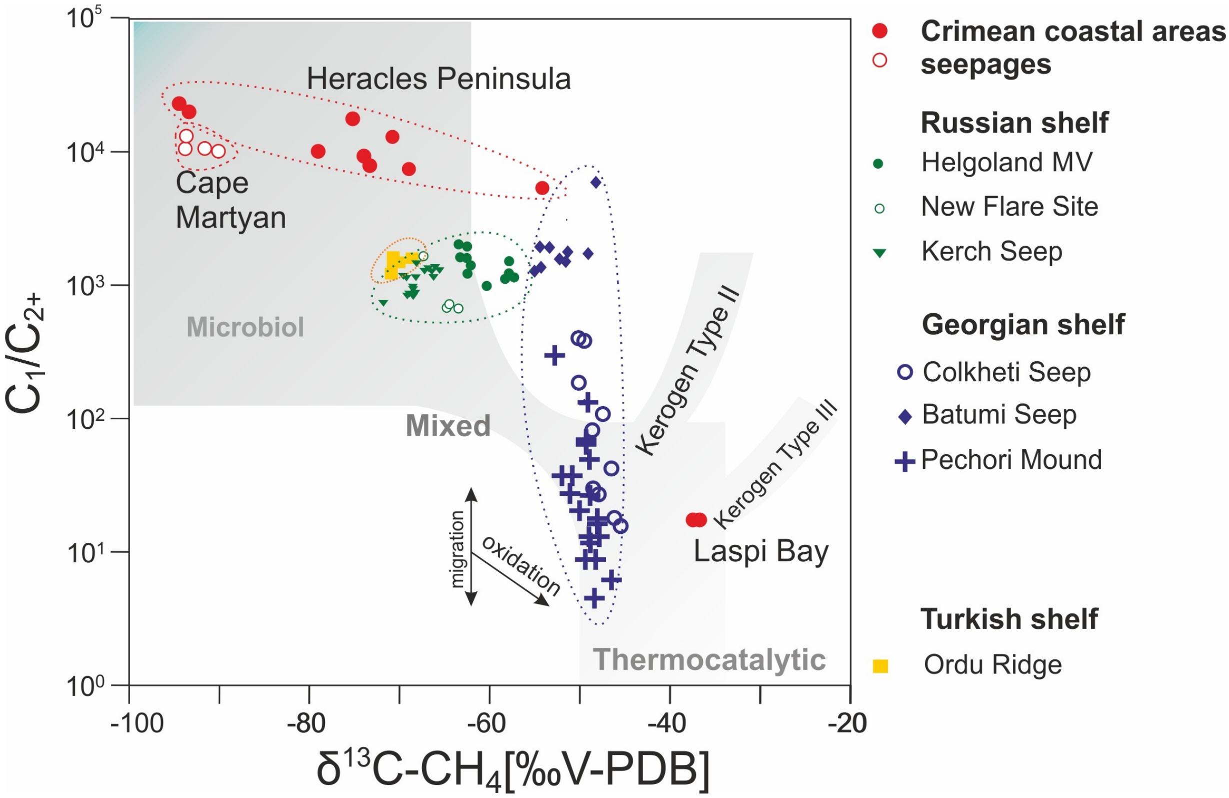

Fig. 5. Bernard diagram (Bernard et al., 1976), illustrating hydrocarbon (C_1/C_{2+}) and isotopic ($\delta^{13}C\text{-}CH_4$) ratios of bubble gas of Crimean coastal areas and deep-sea areas of the Black Sea

The ratio of methane homologues in seeps to the ratio of heavy ^{13}C carbon isotope in them ($C_1/C_{2+}/\delta^{13}C\text{-}CH_4$) shows that methane of most seeps of Crimean coastal areas, except for Laspi Bay gas, is of biogenic origin (Fig. 5). To date, sedimentary strata depth is unclear, from which isotopically light microbial methane is discharged in the areas like Cape Martyan and Cape Fiolent, where the upper layer of sandy sediments is characterized by low methane content and relatively low rates of microbial processes (Malakhova et al., 2015).

Bernard diagram (Fig. 5) illustrates as follows: methane from deep-sea areas of the Russian shelf (Kerch seeps, Sorokin Trough mud volcanoes) is in the sector, which characterizes the gas as microbial one, whereas methane from the Georgian shelf (Pechori Upland, Kolkheti seep) is either within thermocatalytic methane sector or in close proximity to it. The character of values distribution on the diagram indicates as follows: for the gas of the Georgian shelf, the change in its hydrocarbon composition is most likely caused by fractionation of homologues during gas migration through the sediment. For coastal seeps and seeps of the Russian shelf, the isotopic ratio $\delta^{13}C\text{-}CH_4$ changes more, which indicates microbial oxidation.

The ratio of stable hydrogen isotopes δD of methane in combination with $\delta^{13}C$ provides additional information on the type of gas formation (Whiticar, 1999). Values of $\delta D\text{-}CH_4$ of deep-sea gas samples ranged −248…−170 ‰ (see Table 2). According to the typification, proposed in (Whiticar, 1999), biogenic methane, sampled in Kerch seeps area (Russian shelf) and Ordu Ridge area (Turkish shelf), is formed *via* the hydrogenotrophic pathway ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$). This type of methane generation is dominant in marine ecosystems, while the acetoclastic pathway, characterizing the seep in the Martynova Bay (δD-CH_4 −340.1 ‰, see Table 2), is more common in freshwater and in the sediments of highly contaminated areas, where a significant amount of acetate ions accumulates in pore water during organic matter decomposition by primary destructors (Whiticar, 1999).

Bacterial mats and phylogenetic variety of microorganisms of gas emission areas. Long-term observations of the seeps of the Heracles Peninsula and Cape Tarkhankut showed that most of gas emissions, as well as accompanying bacterial mats, were of seasonal type (Table 1). A noticeable bacterial mass was usually accumulated in the second half of June and remained, as a rule, until October. The thickness of seabed coverage with bacterial films varied, increasing towards the end of the summer and sometimes reaching tens of square meters. Photographs of bacterial fouling in the gas-emitting areas of the Crimean coast are shown in Fig. 6.

Fig. 6. Underwater photos of bacterial mats in Heracles Peninsula water area, detected in 2017–2018. A – bacterial biofilm in a rocky depression in the Mramornaya Bay (Pimenov et al., 2018); B – filamentous fouling on living algae thalli, Cape Feofan; C – curd-type bacterial mat on sandy sediments in the Khersones Bay (Bryukhanov et al., 2018); D – massive bacterial mats, detected in Streletskaya Bay open area in July 2018 (Budnikov et al., 2019)

It was noted that in areas of intense gas bubble emissions (the Laspi Bay, Cape Fiolent), there were either no bacterial films, or only their traces, in the form of the finest whitish films (Table 1). Apparently, formation of a stable bacterial biomass requires a stable fluid flux, containing dissolved gases, with obligatory presence of reduced sulfur, same as in the case of mats in the Mramornaya Bay (Fig. 6A). Here, in rocky depressions, filled with dispersed detrital gas-saturated sediments, white bacterial mats with a characteristic cotton-like structure developed, with the basis, formed by sulfide-oxidizing epsilonproteobacteria of the genus *Arcobacter* (Pimenov et al., 2018). At the same time, bubble gas, emitting pointwise from the seabed, was not creating sufficient concentration gradients and could mechanically disrupt the structure of the forming community. Hence, for the entire observation period (since 2012), we did not register any biofilm formation in Laspi Bay gas emission area. However, by high-throughput 16S rRNA gene sequencing in the surface horizons of Laspi Bay sediments, we identified sulfur-oxidizing epsilonproteobacteria of the family Thiovulaceae (8.2 %). Deeper, in the horizons of 10–15 cm, archaea of the phylogenetic cluster ANME-2a/b (19.2 %) and bacteria of the family Desulfobacteraceae (12.2 %), mediating anaerobic methane oxidation, were the most numerous ones. Bacterial mats in the Khersones Bay, represented by white flocs, developing on gas-saturated sands, had the largest coverage area (Fig. 6C, D). According to the results of electron microscopic and molecular biological studies, the basis of bacterial mats was formed by filamentous sulfur bacteria of the family Thiotrichaceae and epsilonproteobacteria of the family Helicobacteraceae (Bryukhanov et al., 2018).

Environment-forming effect of gas bubble emissions. The environment-forming and ecological effects, related to Black Sea methane seeps, include the effect of bubble methane flux on water gas composition, water hydrochemical structure, and formation of carbonate edifices, as well as the effect of methane seeps on microbial processes and microbial community structure (Egorov et al., 2011). The environment-forming roles of deep-sea and shallow seeps are similar, but there are some differences.

The defining difference between shallow and deep-sea seeps of the Black Sea is an oxidized environment, where gas emission and accompanying biogeochemical processes occur. In hydrogen sulfide zone, gas emission sites are a kind of oases of life due to matter and energy properties of methane for microbial trophic chains, whereas in coastal oxidizing conditions, on the contrary, they are zones of inhibition. Thus, as shown in (Ivanova, 2017), in seep areas at Cape Tarkhankut and in the Dvuyakornaya Bay, the meiofauna was characterized by considerably lower abundance and differed in taxonomic composition from the population of surrounding sands due to hydrogen sulfide contamination and acute hypoxia / anoxia.

It has been established that not only in seabed sediments, but also in water above gas emission sites, a significant decrease in O_2 concentration can be observed. Vertical profiling of water column above gas emission site at Cape Feofan showed a notable decrease in O_2 content in the seabed water layer, with a minimum reaching 0.2 $mg \cdot L^{-1}$ (Malakhova et al., 2020a). Minimum salinity values were revealed as well, which may indicate seep-related pulse-wise freshwater discharge. It was recorded that these patterns of distribution of hydrological indicators are determined by presence of gas bubble emissions and geomorphology of the area studied. The key factors of the intensive development of hypoxic phenomena in the seabed water layer are the high degree of isolation of underwater canyons, representing Cape Feofan underwater relief, and, as a result, the slowed down water exchange with the open area (Malakhova et al., 2020a).

Previously, it was calculated that energy dissipation above gas bubble emission sites can be the cause of a micro-upwelling effect (Egorov et al., 2011). Thus, the effect of bubble flux was shown on temperature distribution in water column above gas emission sites in paleo-Dnieper area (Egorov et al., 2011).

In 2018, the authors of this article carried out an experiment in coastal water area, aimed at simulating the effect of gas bubble emissions on stratified layers of water column (Ivanova et al., 2018). The results showed as follows: the generated gas stream, with the flux of several liters per minute, transports colder layers of water from the seabed almost to the surface (Ivanova et al., 2018).

Of particular interest is the assessment of the contribution of fluid emission at methane gas emission sites to total gas flux. It should be noted that the quantitative data on methane influx from seabed sediments in the form of fluid discharge or diffusion fluxes is still not sufficiently complete. Data of direct *in situ* measurements is particularly scarce, which is due to the difficulty of experiments in sea area.

In 2019, the trap method was used to measure methane fluid discharge from seabed sediments in the Laspi Bay near the area of gas bubble emissions; the values reached 74.3 $mmol \cdot m^{-2} \cdot day^{-1}$ (Malakhova et al., 2020b). According to the calculations, the integral fluid discharge in the Laspi Bay can be comparable to the flux from gas bubble emissions, since the maximum fluid flux per 1 m^2 of the seabed is only 3.5 times lower than the flux from a single seep (Malakhova et al., 2020b).

Conclusion. A comparative analysis of our data on the biogeochemical research of shallow seeps of the Crimean Peninsula and data on deep-sea gas bubble emissions of the Black Sea is presented. It is shown that gas bubble emissions are widespread in Crimean coastal areas: they are located within the territory from Cape Tarkhankut in the west of the peninsula to the Dvuyakornaya Bay in the southeast.

Long-term monitoring of the activity of coastal gas emissions made it possible to distinguish seasonal, year-round, and sporadic seeps. Most of Crimean coastal seeps were of a biogenic origin, with the source of gas emission both in the upper layers of seabed sediments and much deeper. Methane predominated in component composition of bubble gas in Crimean coastal areas. However, compared to its content in deep-sea areas of the Black Sea, exceeding 99 %, its content in coastal gas emissions was significantly lower (55 % in the Kruglaya Bay and 38 % near Cape Martyan). A significant number of homologues were found only in Laspi Bay seeps, classified, according to their isotopic and hydrocarbon composition, as those producing gas of thermocatalytic origin, in contrast to other seeps, where the main amount of methane is formed as a result of methanogenic archaea activity. A significant variation was observed in values of isotopic ratio of methane carbon $\delta^{13}C\text{-}CH_4$ of bubble gas in shallow coastal areas (from −94 to −34 ‰); this confirms the assumption about different conditions for bubble gas generation and maturation of seabed sediments, as well as different rates of microbial oxidation and methane formation at separate gas bubble emission sites.

Like deep-sea seeps, coastal ones were often accompanied by bacterial mats. In the areas with bubble gas, freely emitting from the sand, there were either no bacterial films, or only their traces, in the form of the finest whitish films. It was shown as follows: formation of stable bacterial biomass, usually consisting of sulfide- and sulfur-oxidizing bacteria, requires a fluid flux of reduced dissolved gases, while pointwise bubble gas discharge does not provide sufficient concentration gradients and can mechanically disrupt the structure of the forming community.

Various methods were used to estimate the size spectra of bubbles, as well as fluxes from separate streams. Gas flux values varied from 1.8 $L \cdot day^{-1}$ (the Martynova Bay) to 40 $L \cdot day^{-1}$ (the Laspi Bay).

The environment-forming effects, related to gas bubble emissions in coastal areas, are described: oxygen conditions in both seabed sediments and water column above gas emission sites, vertical water mixing due to gas lift effect, and volumes of fluid discharge at gas emission sites.

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REFERENCES

1. Artemov Yu. G., Evtushenko D. B., Moseichenko I. N. Localization of gas bubble streams from the bottom of the Laspi Bay. *Sistemy kontrolya okruzhayushchei sredy*, 2018, iss. 11 (31), pp. 69–73. (in Russ.)
2. Bol'shakov A. M., Egorov A. V. Using of phase-equilibrium degassing method for gasometric studies. *Okeanologiya*, 1987, vol. 27, no. 5, pp. 861–862. (in Russ.)
3. Bondarev I. P., Lomakin I. E., Ivanov V. E. Osobennosti formirovaniya i razvitiya Sevastopolskoi bukhty. *Geologiya i poleznye iskopaemye Mirovogo okeana*, 2015, no. 4, pp. 16–31. (in Russ.)
4. Budnikov A. A., Ivanova I. N., Malakhova T. V., Kirillov E. V. Measurement hydrological parameters of water over methane seep in Laspi Bay during continuous *in situ* experiments. *Uchenye zapiski fizicheskogo fakul'teta Moskovskogo universiteta*, 2019, no. 3, art. no. 193090 (7 p.). (in Russ.)
5. Egorov V. N., Plugatar Y. V., Malakhova T. V., Sadogursky S. Y., Moseichenko I. N. Gas seeps detection in the offshore area near Cape Martyan. *Bulletin of the State Nikita Botanical Gardens*, 2018, no. 126, pp. 9–13. (in Russ.). https://doi.org/10.25684/NBG.boolt.126.2018.01
6. Egorov V. N., Polikarpov G. G., Gulin M. B., Artemov Yu. G., Stokozov N. A., Gulin S. B. Vliyanie struinykh metanovykh gazovydelenii iz dna Chernogo morya na melkomasshtabnye protsessy vertikal'nogo peremeshivaniya vod. *Dopovidi NAN Ukrainy*, 1999, no. 8, pp. 186–190. (in Russ.)
7. Egorov V. N., Artemov Yu. G., Gulin S. B. *Methane Seeps in the Black Sea: Environment-forming and Ecological Role* / G. G. Polikarpov (Ed.). Sevastopol : "EKOSI-Gidrofizika", 2011, 405 p. (in Russ.)
8. Egorov V. N., Artemov Yu. G., Polikarpov G. G., Gulin S. B., Malakhova L. V., Malakhova T. V. Assessment of potential environmental hazard caused by methane gas seeps from the Black Sea floor. *Morskoj ekologicheskij zhurnal*, 2005, vol. 7, no. 1, pp. 23–29. (in Russ.)
9. Egorov V. N., Pimenov N. V., Malakhova T. V., Artemov Yu. G., Kanapatsky T. A., Malakhova L. V. Biogeochemical characteristics of methane distribution in sediment and water at the gas seepage site of Sevastopol bays. *Morskoj ekologicheskij zhurnal*, 2012, vol. 11, no. 3, pp. 41–52. (in Russ.)
10. Egorov V. M., Polikarpov G. G., Gulin S. B., Artemov Ju. G., Stokozov M. A., Kostova S. K. Modern conception about forming-casting and ecological role of methane gas seeps from bottom of the Black Sea. *Morskoj ekologicheskij zhurnal*, 2003, vol. 2, no. 3, pp. 5–26. (in Russ.)
11. Eremeev V. M., Egorov V. M., Polikarpov G. G., Artemov Yu. G., Gulin S. B., Nezhdanov O. I., Evtushenko D. B., Popovichev V. M., Stokozov M. O. New stream gas flow from the sea ground in Sevastopol water area. *Visnyk NAN Ukrainy*, 2007, no. 4, pp. 47–50. (in Ukr.)]
12. Ivanova E. A. Meiobenthos ecology within the methane seeps of the Black Sea: Results of taxonomical study and direct microscopic. *Ekosistemy*, 2017, no. 10 (40), pp. 28–34. (in Russ.)

13. Ivanova I. N., Budnikov A. A., Malakhova T. V., Yevtushenko D. B., Bykov Ye. M. Investigation of bubble flame influence on temperature stratification of the water column by *in situ* experiment. *Protsessy v geosredakh*, 2018, no. 17, pp. 231–232. (in Russ.)
14. Kravchenko V. G. Functioning mechanism of underwater gas flares of the Black Sea. *Geologiya i poleznye iskopaemye Mirovogo okeana*, 2008, no. 1, pp. 106–115. (in Russ.)
15. Lein A. Yu., Ivanov M. V. *Biogeochemical Cycle of Methane in the Ocean.* Moscow : Nauka, 2009, 575 p. (in Russ.)
16. Lysenko V., Shik N. Contemporary carbonates formation processes associated with hydrocarbons degassing in the underwater part of the Laspi Bay beach zone (southern coast of Crimea). *Prostranstvo i Vremya*, 2013, no. 2 (12), pp. 151–157. (in Russ.)
17. Malakhova T. V. *Microbial Processes of Methane Cycle and Its Balance in the Sevastopol Coastal Area (Black Sea).* [dissertation]. Sevastopol, 2014, 199 p. (in Russ.)
18. Malakhova T. V., Yevtushenko D. B., Bayandina Yu. S. Struinye metanovye gazovydeleniya: metod registratsii i komp'yuternogo analiza puzyr'kovoi razgruzki dna. In: *Pontus Euxinus 2015* : tezisy IX Vseros. nauch.-prakt. konf. molodykh uchenykh (s mezhdunar. uchastiem) po problemam vodnykh ekosistem, posvyashch. 100-letiyu so dnya rozhd. d. b. n., prof., chl.-korr. AN USSR V. N. Greze, Sevastopol, 17–20 Nov., 2015. Sevastopol : DigitPrint, 2015, pp. 106–107. (in Russ.)
19. Malakhova T. V., Ivanova I. N., Budnikov A. A., Murashova A. I., Malakhova L. V. Hydrological parameters distribution over the methane seep site in the Blue Bay (Black Sea) – Connection with submarine freshwater discharge. *Meteorologiya i gidrologiya*, 2020a. (In press). (in Russ.)
20. Malakhova T. V., Budnikov A. A., Ivanova I. N., Murashova A. I. Methane fluid flow from seafloor: Data from Laspy Bay seepage area compared to other gas emission regions. *Protsessy v geosredakh*, 2020b. (In press). (in Russ.)
21. Pimenov N. V., Egorov V. N., Kanapatskii T. A., Malakhova T. V., Artemov Ju. G., Sigalevich P. A., Malakhova L. V. Sulfate reduction and microbial processes of the methane cycle in the sediments of the Sevastopol Bay. *Mikrobiologiya*, 2013, vol. 82, no. 5, pp. 614–624. (in Russ.)
22. Timofeyev V. A., Ivanova E. A., Gulin M. B. Detecting of a new field of gas seeps in the coastal zone off the Crimea Peninsula, Black Sea. *Morskoj ekologicheskij zhurnal*, 2014, vol. 13, no. 1, pp. 34. (in Russ.)
23. Shik N. V. Gazovye vydeleniya na dne bukhty Laspi. *Geologiya i poleznye iskopaemye Mirovogo okeana*, 2006, no. 1, pp. 135–136. (in Russ.)
24. Shnyukov E. F. Gazogidraty metana v Chernom more. *Geologiya i poleznye iskopaemye Mirovogo okeana*, 2005, no. 2, pp. 41–52. (in Russ.)
25. Shnyukov E. F., Starostenko V. I., Rusakov O. M., Kutas R. I. Glubinnaya priroda gazovykh fakelov zapadnoi chasti Chernogo morya po rezul'tatam geofizicheskikh issledovanii. *Geologiya i poleznye iskopaemye Mirovogo okeana*, 2005, no. 1, pp. 70–85. (in Russ.)
26. Artemov Yu. G., Egorov V. N., Polikarpov G. G., Gulin S. B. Methane emission to the hydro- and atmosphere by gas bubble streams in the Dnieper paleo-delta, the Black Sea. *Morskoj ekologicheskij zhurnal*, 2007, vol. 6, no. 3, pp. 5–26.
27. Artemov Yu. G. Software support for investigation of natural methane seeps by hydroacoustic method. *Morskoj ekologicheskij zhurnal*, 2006, vol. 5, no. 1, pp. 57–71.

28. Bernard B. B., Books J. M., Sackett W. M. Natural gas seepage in the Gulf of Mexico. *Earth and Planetary Science Letters*, 1976, vol. 31, pp. 48–54. https://doi.org/10.1016/0012-821X(76)90095-9
29. Blinova V. N., Ivanov M. K., Bohrmann G. Hydrocarbon gases in deposits from mud volcanoes in the Sorokin trough, North-Eastern Black Sea. *Geo-Marine Letters*, 2003, vol. 23, pp. 250–257. https://doi.org/10.1007/s00367-003-0148-8
30. Boetius A., Revenschlag K., Schubert C. J., Rickert D., Widdel F., Gieseke A., Armann R., Jørgensen B. B., Witte U., Pfannkuche O. A marine microbial consortium apparently mediating anaerobic oxidation of methane. *Nature*, 2000, no. 407, pp. 623–626. https://doi.org/10.1038/35036572
31. Bryukhanov A. L., Vlasova M. A., Perevalova A. A., Pimenov N. V., Malakhova T. V. Phylogenetic diversity of the sulfur cycle bacteria in the bottom sediments of the Chersonesus Bay. *Microbiology (Mikrobiologiya)*, 2018, vol. 87, no. 3, pp. 372–381. https://doi.org/10.7868/S0026365618030060
32. Budnikov A. A., Ivanova I. N., Malakhova T. V., Malakhova L. V. Thermohaline structure of water above the microbial mats site at Sevastopol marine area. In: *Physical and Mathematical Modeling of Earth and Environment Processes* : 4th International Scientifical School for Young Scientists, Ishlinskii Institute for Problems in Mechanics of RAS. Cham, Switzerland : Springer Nature Switzerland AG, 2019, pp. 417–423. (Springer Proceedings in Earth and Environmental Sciences). https://doi.org/10.1007/978-3-030-11533-3_41
33. Budnikov A. A., Malakhova T. V., Ivanova I. N., Linchenko E. V. Application of a passive acoustic method for detection and estimation of shallow-water bubble gas emissions. *Moscow University Physics Bulletin*, 2020, vol. 74, no. 6, pp. 690–696. https://doi.org/10.3103/S0027134919060109
34. Gulin S. B., Greinert J., Egorov V. N., De Batist M., Artemov Yu. G. Observation of microbial carbonate build-ups growing at methane seeps near the upper boundary of the gas-hydrate stability zone in the Black Sea. *Morskoj ekologicheskij zhurnal*, 2005, vol. 4, no. 3, pp. 5–14.
35. Judd A., Hovland M. *Seabed Fluid Flow: The Impact on Geology, Biology and the Marine Environment.* New York : Cambridge University Press, 2007, 475 p.
36. Kruglyakova R. P., Byakov Y. A., Kruglyakova M. V., Chalenko L. A., Shevtsova N. T. Natural oil and gas seeps on the Black Sea floor. *Geo-Marine Letters*, 2004, no. 24, pp. 150–162. https://doi.org/10.1007/s00367-004-0171-4
37. Malakhova L. V., Egorov V. N., Malakhova T. V., Gulin S. B., Artemov Y. G. Methane in the Sevastopol coastal area, Black Sea. *Geo-Marine Letters*, 2010, vol. 30, no. 3, pp. 391–398. https://doi.org/10.1007/s00367-010-0198-7
38. Malakhova T. V., Egorov V. N., Malakhova L. V., Artemov Y. G., Evtushenko D. B., Gulin S. B., Kanapatskii T. A., Pimenov N. V. Microbial processes and genesis of methane gas jets in the coastal areas of the Crimean Peninsula. *Microbiology (Mikrobiologiya)*, 2015, vol. 84, no. 6, pp. 838–845. https://doi.org/10.1134/S0026261715060053
39. Michaelis W., Seifert R., Nauhaus K., Treude T., Thiel V., Blumenberg M., Knittel K., Gieseke A., Peterknecht K., Pape T., Boetius A., Amann R., Jørgensen B. B., Widdel F., Peckmann J., Pimenov N. V., Gulin M. B. Microbial reefs in the Black Sea fueled by anaerobic oxidation of methane. *Science*, 2002, no. 297, iss. 5583, pp. 1013–1015. https://doi.org/10.1126/science.1072502

40. Naudts L., Greinert J., Artemov Y., Staelens P., Poort J., Van Rensbergen P., De Batist M. Geological and morphological setting of 2778 methane seeps in the Dnepr paleo-delta, northwestern Black Sea. *Marine Geology*, 2006, no. 227, iss. 3–4, pp. 177–199. https://doi.org/10.1016/j.margeo.2005.10.005
41. Pape T., Bahr A., Rethemeyer J., Kessler J. D., Sahling H., Hinrichs K.-U., Klapp S. A., Reeburgh W. S., Bohrmann G. Molecular and isotopic partitioning of low-molecular-weight hydrocarbons during migration and gas hydrate precipitation in deposits of a high-flux seepage site. *Chemical Geology*, 2010, no. 269, iss. 3–4, pp. 350–363. https://doi.org/10.1016/j.chemgeo.2009.10.009
42. Pimenov N. V., Merkel A. Yu., Tarnovetskii I. Yu., Malakhova T. V., Samylina O. S., Kanapatskii T. A., Tikhonova E. N., Vlasova M. A. Structure of microbial mats in the Mramornaya Bay (Crimea) coastal areas. *Microbiology (Mikrobiologiya)*, 2018, vol. 87, no. 5, pp. 681–691. https://doi.org/10.1134/S0026261718050132
43. Reitz A., Pape T., Haeckel M., Schmidt M., Berner U., Scholz F., Liebetrau V., Aloisi G., Weise S. M., Wallmann K. Sources of fluids and gases expelled at cold seeps offshore Georgia, eastern Black Sea. *Geochimica et Cosmochimica Acta*, 2011, vol. 75, no. 11, pp. 3250–3268. https://doi.org/10.1016/j.gca.2011.03.018
44. Römer M., Sahling H., Pape T., Bahr A., Feseker T., Wintersteller P., Bohrmann G. Geological control and magnitude of methane ebullition from a high-flux seep area in the Black Sea – the Kerch seep area. *Marine Geology*, 2012, vol. 319–322, pp. 57–74. https://doi.org/10.1016/j.margeo.2012.07.005
45. Römer M., Torres M., Kasten S., Kuhn G., Graham A. G. C., Mau S., Little C. T. S., Linse K., Pape T., Geprägs P., Fischer D., Wintersteller P., Marcon Y., Rethemeyer J., Bohrmann G. First evidence of widespread active methane seepage in the Southern Ocean, off the sub-Antarctic island of South Georgia. *Earth and Planetary Science Letters*, 2014, vol. 403, pp. 166–177. https://doi.org/10.1016/j.epsl.2014.06.036
46. Sahling H., Bohrmann G., Artemov Y. G., Bahr A., Brüning M., Klapp S. A., Klaucke I., Kozlova E., Nikolovska A., Pape T., Reitz A., Wallmann K. Vodyanitskii mud volcano, Sorokin trough, Black Sea: Geological characterization and quantification of gas bubble streams. *Marine and Petroleum Geology*, 2009, vol. 26, no. 9, pp. 1799–1811. https://doi.org/10.1016/j.marpetgeo.2009.01.010
47. Sciarra A., Saroni A., Etiope G., Coltorti M., Mazzarini F., Lott C., Grassa F., Italiano F. Shallow submarine seep of abiotic methane from serpentinized peridotite off the Island of Elba, Italy. *Applied Geochemistry*, 2019, no. 100, pp. 1–7. https://doi.org/10.1016/j.apgeochem.2018.10.025
48. Sergienko V. I., Lobkovskii L. I., Semiletov I. P., Dudarev O. V., Dmitrievskii N. N., Shakhova N. E., Romanovskii N. N., Kosmach D. A., Nikol'skii D. N., Nikiforov S. L., Salomatin A. S., Anan'ev R. A., Roslyakov A. G., Salyuk A. N., Karnaukh V. V., Chernykh D. B., Tumskoi V. E., Yusupov V. I., Kurilenko A. V., Chuvilin E. M., Bukhanov B. A. The degradation of submarine permafrost and the destruction of hydrates on the shelf of east arctic seas as a potential cause of the "Methane Catastrophe": Some results of integrated studies in 2011. *Doklady Earth Sciences*, 2012, vol. 446, no. 1, pp. 1132–1137.
49. Tarnovetskii I. Yu., Merkel A. Yu., Kanapatskiy T. A., Ivanova E. A., Gulin M. B., Toshchakov S., Pimenov N. V. Decoupling between sulfate reduction and the anaerobic

oxidation of methane in the shallow methane seep of the Black Sea. *FEMS Microbiology Letters*, 2018, vol. 365, iss. 21, article no. fny235. https://doi.org/10.1093/femsle/fny235
50. Whiticar M. J. Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chemical Geology*, 1999, vol. 161, no. 1–3, pp. 291–314. https://doi.org/10.1016/S0009-2541(99)00092-3
51. Whiticar M. J. Diagenetic relationships of methanogenesis, nutrients, acoustic turbidity, pockmarks and freshwater seepages in Eckernförde Bay. *Marine Geology*, 2002, vol. 182, no. 1–2, pp. 29–53. https://doi.org/10.1016/S0025-3227(01)00227-4
52. Zander T., Haeckel M., Klaucke I., Bialas J., Klaeschen D., Papenberg C., Pape T., Berndt C., Bohrmann G. New insights into geology and geochemistry of the Kerch seep area in the Black Sea. *Marine and Petroleum Geology*, 2020, vol. 113, article no. 104162. https://doi.org/10.1016/j.marpetgeo.2019.104162

БИОГЕОХИМИЧЕСКИЕ ХАРАКТЕРИСТИКИ МЕЛКОВОДНЫХ СТРУЙНЫХ МЕТАНОВЫХ ГАЗОВЫДЕЛЕНИЙ В ПРИБРЕЖНЫХ РАЙОНАХ КРЫМА В СРАВНЕНИИ С ГЛУБОКОВОДНЫМИ СИПАМИ ЧЁРНОГО МОРЯ

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Струйные метановые газовыделения (сипы) — широко распространённый феномен в Мировом океане, в том числе в бассейне Чёрного моря. Актуальность исследований метановых сипов обусловлена их важной ролью в качестве источника метана как парникового и средообразующего газа для водной толщи и атмосферы. В работе представлен сравнительный анализ данных собственных биогеохимических исследований мелководных сипов Крымского полуострова, охватывающих последние десять лет, и материалов, посвящённых глубоководным газовыделениям Чёрного моря. В этот период были проведены поисковые гидроакустические исследования, выявлен компонентный состав пузырькового газа, измерен изотопный состав углерода метана, а также молекулярно-биологическими методами определена структура микробного сообщества бактериальных матов, покрывающих площадки газовыделений, и выполнена оценка газовых потоков от отдельных сипов. В течение многолетнего мониторинга обнаружено и описано 14 отдельных газовыделяющих площадок в прибрежных районах Крыма, которые располагались от мыса Тарханкут на западе полуострова до бухты Двуякорная на юго-востоке. Превалирующая часть прибрежных сипов Крыма имела биогенную природу и сезонный характер газовыделений. К глубинному газу термокаталитического генезиса отнесены сипы в бухте Ласпи. Наблюдался значительный разброс величин изотопного состава углерода метана $\delta^{13}C\text{-}CH_4$ пузырькового газа прибрежных мелководных районов (−94…−34 ‰), что указывает на разные условия его генерации и созревания в донных отложениях. Так же, как и глубоководным сипам, прибрежным струйным газовыделениям сопутствовали бактериальные маты разной структуры с различными доминирующими видами. Показано, что для формирования устойчивой бактериальной биомассы, основу которой составляли, как правило, сульфид- и сероокисляющие бактерии, необходим флюидный поток восстановленных растворённых газов, тогда как точечная разгрузка пузырькового газа не обеспечивает достаточных градиентов концентрации и может механически разрушать структуру образующегося сообщества. Различными методами сделаны оценки размерных спектров пузырьков и потоков от отдельных струй. Диапазон значений газового потока варьировал от 1,8 л·сут$^{-1}$ (бухта Мартынова) до 40 л·сут$^{-1}$ (бухта Ласпи). Проанализированы средообразующие эффекты, связанные с выделением пузырькового газа в прибрежных районах: влияние сипов на кислородный режим в донных осадках и в толще воды́ над точками газовыделений; вертикальное перемешивание вод за счёт газлифтового эффекта; флюидная разгрузка на площадках струйных газовыделений.

Ключевые слова: метановые сипы, генезис, изотопный состав, бактериальные маты, гидроакустические методы, средообразующий газ, крымский шельф, Чёрное море