ISSN 0026-2617, Microbiology, 2015, Vol. 84, No. 6, pp. 838–845. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © T.V. Malakhova, T.A. Kanapatskii, V.N. Egorov, L.V. Malakhova, Yu.G. Artemov, D.B. Evtushenko, S.B. Gulin, N.V. Pimenov, 2015, published in Mikrobiologiya, 2015, Vol. 84, No. 6, pp. 743–752.

EXPERIMENTAL ARTICLES

Microbial Processes and Genesis of Methane Gas Jets in the Coastal Areas of the Crimean Peninsula

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Received May 25, 2015

Abstract—Hydroacoustic techniques were used for detection and mapping of gas jet areas in the coastal regions of the Crimean Peninsula. Gas jet areas in the bays Laspi, Khersones, and Kazach'ya were chosen for detailed microbiological investigation. The first type of gas jets, observed in the Laspi Bay, was probably associated with discharge of deep thermogenic methane along the faults. Methane isotopic composition was characterized by $\delta^{13}C$ of –35.3‰. While elevated rates of aerobic methane oxidation were revealed in the sandy sediments adjacent to the methane release site, no evidence of bacterial mats was found. The second type of gas emission, observed in the Khersones Bay, was accompanied by formation of bacterial biofilms of the "*Thiodendron*" microbial community type, predominated by filamentous, spirochete-like organisms, in the areas of gas seepage. The isotopic composition of methane was considerably lower there (–60.4‰), indicating a considerable contribution of modern microbial methane to the gas bubbles discharged in this bay. Activity of the third type of gas emission, the jets of the Kazach'ya Bay, probably depended directly on modern microbial processes of organic matter (OM) degradation in the upper sediment layers. The rates of sulfate reduction and methanogenesis were 260 and 34 μmol dm^{-3} day^{-1}, respectively. Our results indicate different mechanisms responsible for formation of methane jets in the Laspi Bay and in the coastal areas of the Heracles Peninsula, where the bays Kazach'ya and Khersones are located.

Keywords: sulfate reduction, methane oxidation, methanogenesis, jet gas emissions, Black Sea

DOI: 10.1134/S0026261715060053

Cold gas jets along the continental shelves of marine basins have been reported worldwide (Judd, 2004), including the Black Sea (Egorov et al., 2011). Investigation of jet emissions of natural gas from sea bottom is important due to their role as a source of methane for the water column and the atmosphere. Assessment of the contribution of natural sources of greenhouse gases to global warming is complicated by heterogeneous distribution of these sources and the sporadic nature of gas emission. Until recently, gas jets were considered the second most important source (after bogs) of atmospheric methane (Etiope and Sherwood Lollar, 2013). Discovery of mud microvolcanoes in the floodplain of the Mukhrina River (Khanty-Mansi Autonomous Okrug), with methane flows exceeding those from the same area of mid-taiga bogs by orders of magnitude (Belova et al., 2013), may, however, result in reevaluation of the role of gas jets as sources of atmospheric methane.

In the present work, shallow-water jets of the southwestern Crimean coast were investigated. Due to the high sulfate reduction rates in the sediments of highly productive coastal areas, pore water sulfate is rapidly consumed, and terminal oxidation of over 50% of precipitated organic matter (OM) is carried out by methanogenic archaea (Jorgensen et al., 1990). Methane synthesized in the anoxic zone is partially consumed by aerobic methanotrophic microorganisms inhabiting the upper oxidized sediment layer and the water column (Ivanov et al., 2002). Anaerobic methane oxidation (AOM) in the anoxic zone, which is carried out by a consortium of sulfate-reducing bacteria and methanotrophic archaea (Hoehler et al., 1994; Boetius et al., 2000), is the main barrier preventing methane release into the water column and the atmosphere. However, a considerable portion of methane synthesized in the shallow-water sediments was shown to be released into the atmosphere as jet emissions (Hovland et al., 1993; Judd, 2004). The Black Sea's northwestern shelf is characterized by wide occurrence of methane jet emissions, which have a significant effect on the biogeochemical processes in this region (Amouroux et al., 2002; Egorov et al., 2011).

Black Sea shallow-water jets were originally found on the Bulgarian coast (Dimitrov et al., 1979). They have been since observed throughout the Azov–Black Sea coast: on Bulgarian (Dimitrov, 2002), Caucasian (Tkeshelashvili et al., 1997; Kruglyakova et al., 2009),

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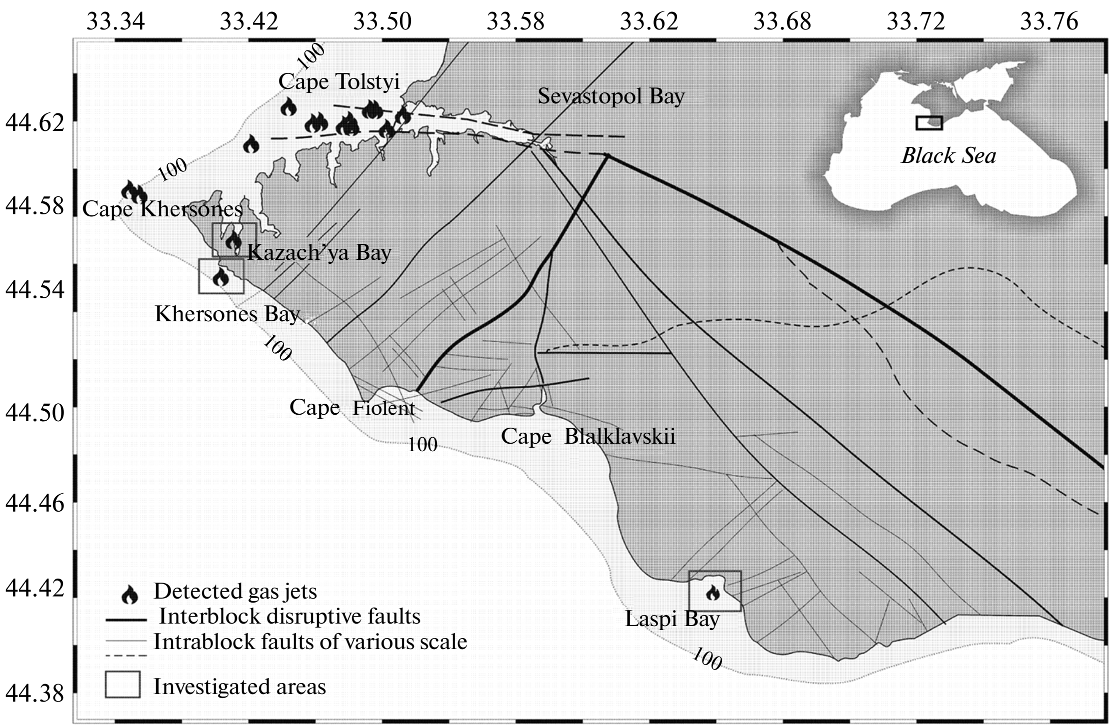

Fig. 1. Schematic map of the studied polygon showing the major faults and methane gas seeps. The structural and tectonic elements presented according to Ivanov et al. (2009) and Shestopalov et al. (2008).

and Crimean coasts (Egorov et al., 2011), as well as in the Sea of Azov (Pasynkov et al., 2009). Isotopic analysis revealed that methane of these jet emissions was often of biogenic origin (Egorov et al., 2012, Pimenov et al., 2013). Recent research, however, does not rule out discharge of thermogenic gas in the coastal areas of the southern Crimean shore (Lysenko and Shik, 2013).

The goal of the present work was to carry out mapping of the gas emission areas in southwestern Crimean areas, comparative assessment of gas flows from methane jets, and determination of the rates of microbial processes in the seepage areas.

MATERIALS AND METHODS

Field research was carried out from July to October 2014 from a small vessel equipped with a mobile acoustic complex containing a SeaCharter 480 DF echosounder with a GPS receiver, a hydroacoustic antenna, and a universal setup for antenna attachment. The investigated area is schematically presented on the map (Fig. 1). The results of hydroacoustic mapping were processed using the SonarViewer V2.1.2 software package and a WaveLens package for analysis of acoustic information (Artemov, 2006).

Bottom sediments were collected using a tubular sampler preserving the structure of the upper 50-cm sediment layers. The hydrological parameters of the water (temperature, salinity, and density) were determined in situ using an SD204 CTD probe (SAIV A/S, Norway). Methane content in near-bottom water and in the sediments was determined by headspace analysis using a Kristall-2000 gas chromatograph (Russia) equipped with a flame ionization detector. The measurement error did not exceed 5%.

Pore water was obtained by centrifugation of the sediments (5000 *g*, 10 min) on a TsUM-1 centrifuge (Russia). Sulfate content in pore water was measured on a Staier ion chromatograph (Russia).

The rates of microbial processes were determined by the radioisotope method. Immediately after hauling on board, the sediment from a relevant horizon (3 mL) was transferred into a 5-mL cut-off plastic syringe, which was then sealed with a butyl rubber stopper. The radioactively labeled substrate (0.2 mL) was injected through the stopper, and the samples were incubated for 24–48 h at 16–18°C. The incubation temperature was maintained the same as the temperature of near-bottom water determined by a CTD probe at the time of sampling. After incubation, the samples were fixed with 1 mL of 2 N KOH and transferred to the laboratory. The samples were then treated as described previously (Pimenov and Bonch-Osmolovskaya, 2009). The rate of methane oxidation (MO) was determined using ^{14}C methane dissolved in degassed distilled water (1 μCi per sample). The rate of sulfate reduction was determined using ^{35}S sulfate (10 μCi per sample). The samples fixed with KOH and

Table 1. Sampling sites, coordinates, depth (H), component hydrocarbon composition (vol %), C_1/C_{2+}, and isotopic composition ($\delta^{13}C_{CH_4}$, ‰ VPDB) of the bubble gas from Crimean Shallow-water seeps

Name	Coordinates	H, m	C_1, %	C_2, %	C_3, %	C_1/C_{2+}	$\delta^{13}C$-CH_4, ‰ VPDB	Date of detection
Laspi Bay	44.420818° N 33.706990° E	3	92	3	0.01	29	–35.3	2004 (Shik, 2006)
Kazach'ya Bay	44.565867° N 33.410892° E	1.5	99	–*	–	–	–56.3	2014 Present work
Khersones Bay	44.564728° N 33.399350° E	5	99	–	–	–	–60.4	2014 Present work

* Values below the limit of reliable detection.

incubated in a refrigerator for 6 h prior to addition of the substrate were used as the control.

Bubble methane for mass spectral analysis of the carbon isotopic composition ($\delta^{13}C$) was collected in the water into 20-mL penicillin vials. The $\delta^{13}C$ for methane was measured on TRACE GC gas chromatograph (Germany) combined with a Delta plus mass spectrometer (Germany). The error of $\delta^{13}C$ determination did not exceed ~0.1‰.

High-resolution underwater shooting was carried out using a GoPro HERO3+ Black Edition camera with 4K quality of video imaging. Such visualization technique has not been used previously in Crimean coastal waters.

Microscopic investigation of bacterial biofilms (mats) was carried out using an Axio Imager microscope (Germany).

RESULTS

During July–October 2014, several hydroacoustic probings of the sites of shallow-water gas emission in the coastal zone of the Crimean peninsula were carried out (Table 1). Apart from the previously known methane jets in the Laspi Bay (Shik, 2006), new sites of jet gas emission were found (Fig. 1). In the bays Khersones and Kazach'ya, visual inspection by divers revealed areas of bubble gas emission at the depths of 5 and 1.5 m, respectively (Table 1, Fig. 1).

In July 2014, a mobile acoustic complex on board a small vessel was used to observe and map the methane jets originally described ten years earlier (Shik, 2006). Repeated investigation in September and October confirmed localization and activity of the gas emission field in Laspi Bay. The area of bubble gas emission was located in the central part of the Laspi Bay, where it juts into the coast, 15–20 m from the shore. The depth in the area of bubble seepage did not exceed 3 m (Fig. 2a). The gas emission area was located on an abrasion terrace covered by a thin sheath of marine beach deposits (~1 m) consisting of individual boulders, pebbles, gravel, and sand. At the bay, over 20 individual points of jet gas emission from both rocky formations and sand occurred simultaneously. Since the density of seepages varied from 1–2 to a dozen per 1 m^2, the exact number of jets was impossible to determine. According to the results of video imaging, the flow from a jet (30 to 120 bubbles per minute) consisted of 5–30-mm bubbles. The surfacing rate of individual bubbles detected by echo sounding varied from 19 to 30.6 cm s^{-1} (Fig. 2b).

According to the literature data (Shestopalov et al., 2008), the studied part of the Laspi Bay is characterized by submarine discharge of freshwater. The mechanisms of inflow of bubble and dissolved may be associated with submarine discharge (Whiticar, 2002). However, CTD probing did not reveal any evidence of desalination of water in the area.

Microbiological analysis of the area of active gas emission revealed no active microbial processes associated with gas discharge. Visual examination of the sandy sediment with periodic bubble emission revealed no indication of microbial growth (biofilms, filaments, biofouling, etc.), which was reported previously (Lysenko and Shik, 2013). Since the sediments were well-washed sands with a low OM content and retained almost no gas, measurement of MO and SR rates in the sediments collected from the methane seepage area did not provide reliable data on the native methane and sulfate concentrations. Calculation of the real rates of methane oxidation and sulfate reduction was therefore impossible. However, even using the minimal methane concentration measured in the sediments retrieved on board (0.76–0.86 μmol dm^{-1}) the calculated MO rate in the upper 15 cm of sandy sediments varied from 0.2 to 0.3 μmol dm^{-3} day^{-1}. These values were almost an order of magnitude higher than MO rate measured previously in the sediments of an active jet in the Sevastopol Bay (Pimenov et al., 2013). SR was not detected in the upper horizons (0–10 cm), while at the depth of 10–20 cm the rate of this process did not exceed 1.1 μmol dm^{-3} day^{-1} (Table 2). Methane in the Laspi Bay jets was found to be enriched with the heavy isotope ^{13}C (–35.3‰), which is within the range characterizing methane of thermogenic origin.

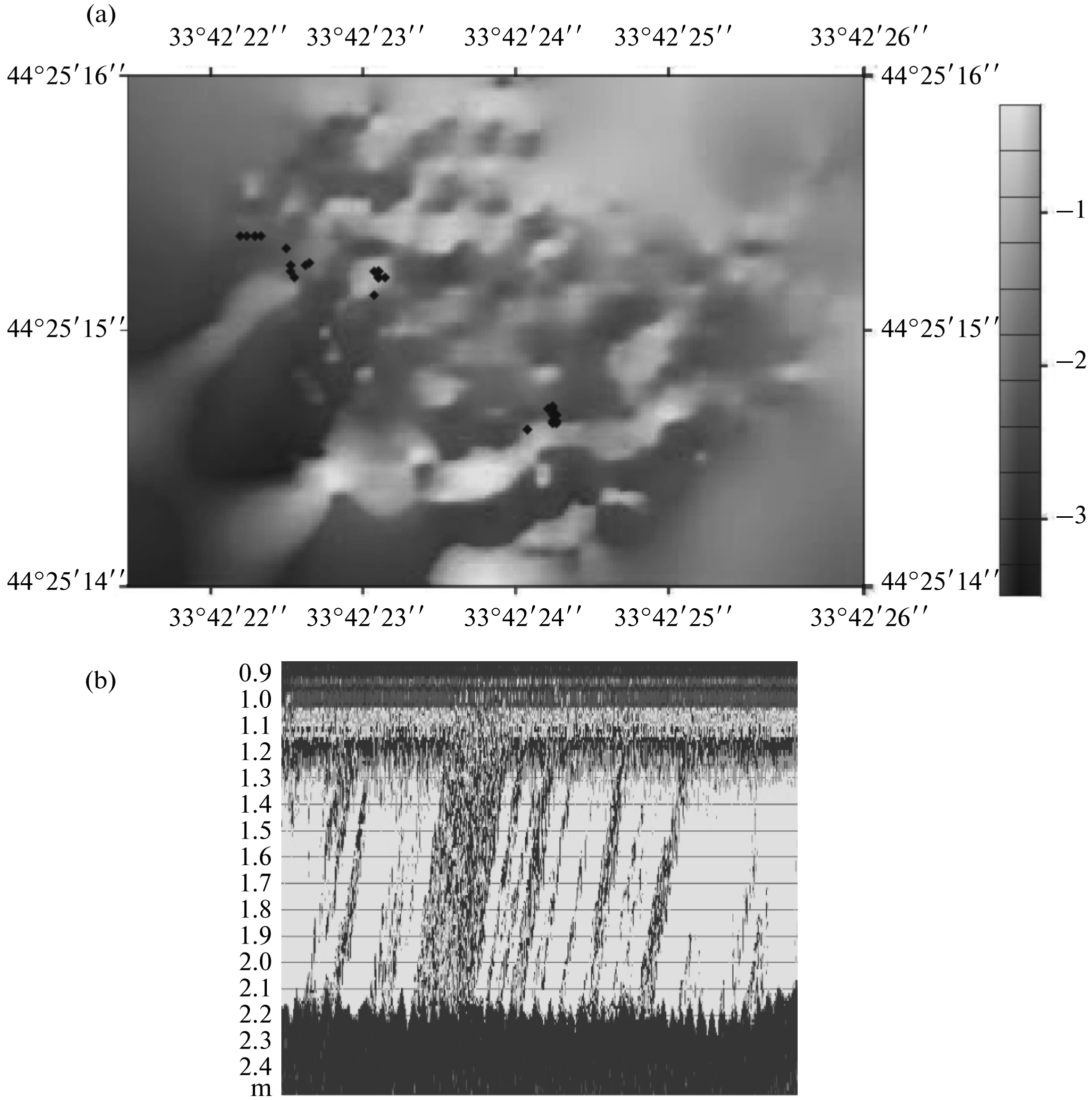

Fig. 2. Bathymetric map of the studied area in the Laspi Bay, with black diamonds indicating the sites of bubble emission detected by hydroacoustic mapping on September 11, 2014 (a) and an echogram of surfacing methane bubbles at the point 44°25.257 N, 33°42.372 E (b).

The presence of methane homologs in the gas also indicated its deep origin (Table 1).

The area of bubble gas emission in the Khersones Bay, which was revealed by our observations in July–October 2014, was visually similar to the Laspi Bay one. The bottom sediments in the discharge area were also sands with no indication of reduced conditions. Throughout the observation period, gas flow in this area was considerably less intent than in the Laspi Bay. Photo and video imaging in September–October revealed, however, the presence of bacterial biofilms in the area of bubble gas emission. Their formation is probably directly associated with gas seepage and may act as an indicator of the areas of gas discharge (Fig. 3a).

Microscopy of bacterial growths (Fig. 3b) revealed the microbial community morphologically similar to "*Thiodendron*" (Dubinina et al., 1993), predominated by thin curved filaments (~0.5 μm in diameter) and spirochete-like cells, constituted the basis of Khersones Bay bacterial mats. The sediment below the biofilm (collected by a diver) had a smell of sulfide, low Eh (–210 mV), and exhibited high SR rates (Table 2), ranging from 240 to 460 μmol dm^{-3} day^{-1}. Methane oxidation rate was considerably lower than in the Laspi Bay (below 0.03 μmol dm^{-3} day^{-1}). The isotopic composition of methane was considerably lighter (–60.4‰), indicating a considerable share of methane of modern microbial origin in the gas bubbles discharged in this bay (Table 1).

Table 2. Physicochemical parameters and the rates of microbial processes in the sediments of the areas of Crimean shallow-water seeps discharge

Polygon	Horizon, cm	Eh, mV	CH_4, μmol dm^{-3}	SO_4^{2-}, mM	C_{org}, %	SR, μmol dm^{-3} day^{-1}	MO, μmol dm^{-3} day^{-1}
Laspi Bay	0–5	+250	0.76	16.82	1.53	0	0.21
	5–10	+110	0.86	16.97	1.36	0	0.32
	10–15	+100	0.81	17.7	1.38	1.12	0.21
	15–20	+90	0.83	17.3	–	0.1	0.02
Kazach'ya Bay	0–2	+120	0.54	16.85	0.71	0.28	0.03
	2–7	–90	0.71	17.3	0.46	0.46	0.02
	10–15	–110	1.02	17.9	0.88	0.24	0.02
Khersones Bay	0–4	–80	174	14.6	2.67	256	34
	6–8	–150	814	1.92	3.15	31	30
	11–13	–200	962	2.57	3.45	158	21
	14–16	–180	957	0.83	3.74	60	8.9

Gas jets in the western branch of Kazach'ya Bay were originally detected in September 2014 and have been observed till mid-October. The site of bubble gas emission was located at 1.5-m depth, 10 m from the shore line (Fig. 1). Abundant vegetation of the gas seepage area was predominated by mixed *Zostera* sp.–*Cystoseira* sp. communities. The bottom sediments at the gas jet site were black sludgy sands, unlike the sediments at the sites without bubble emission. The sediments of the gas seepage area had high methane content, which reached 174 μmol dm^{-3} in the uppermost horizon (0–4 cm) and increased with depth to 814–960 μmol dm^{-3}. The sediments had a smell of sulfide; the oxidized layer was almost absent, and Eh varied from –100 to –250 mV. SR rate in the sediments varied from 30 to 260 μmol dm^{-3} day^{-1}, with the highest values revealed in the upper sediments (0–4 cm) and in the 10–15-cm layer (260 and 158 μmol dm^{-3} day^{-1}, respectively) (Table 2). Apart from high SR rates, high rates of methane oxidation (up to 34 μmol dm^{-3} day^{-1}) were revealed in the Kazach'ya Bay sediments. The isotopic composition of methane ($\delta^{13}C$) was –56.3‰ (Table 2).

DISCUSSION

Our results indicate that the Laspi Bay gas jets are probably of deep origin. Low thickness of Quaternary deposits consisting of sand and pebbles, low OM content, and low rates of microbial processes indicate the absence of association between the upper sediment layers and gas emissions. Mid-Jurassic carboniferous rocks may be considered as a possible source of degassing. For bubble methane, $\delta^{13}C$ was –33.34‰, which is typical of the gas of thermogenic origin. It should be noted that the Laspi Bay gas is isotopically considerably heavier than that from other shallow-water jets of European seas.

Mercury release associated with gas jet seepage sites is considered an indication of thermogenic nature of methane bubbles (Shnyukov et al., 1992). Elevated mercury concentrations have been repeatedly observed in Black Sea deep-water areas (depths from 100 to 2000 m) above the sites of gas emission (Kostova et al., 2006). In the Laspi Bay water, however, mercury concentrations above the gas jet site and at the background station (500 m to the south) differed insignificantly (63 and 91 ng L^{-1}, respectively).

Paleozoic or deeper (Proterozoic and Archaean) rocks, or even mantle formations may be the source of gas in Laspi Bay. Abiotic origin of the gas may be assessed using the Anderson–Shultz–Flory (ASF) distribution (Etiope and Sherwood Lollar, 2013). The ASF model represents molecular mass distribution of *n*-alkanes and other hydrocarbons obtained by radical polymerization and linear polycondensation (Glebov and Kliger, 1994). ACF distribution for the Laspi Bay gas is shown on Fig. 4.

Thermogenic gas was shown to have the correlation coefficient $R^2 < 0.9$, while $R^2 > 0.99$ usually characterized quasi-pure abiotic gas, and the intermediate values correspond to the mixtures of thermogenic and abiotic gas (Etiope and Sherwood Lollar, 2013). The R^2 values were determined for the gas from the Laspi Bay jet, which contained methane, ethane, and propane (Table 1, Fig. 4). Considering the relative nature of this method and the absence of butane from the bubble gas, the value $R^2 = 0.98$ may indicate admixtures of abiotic gas in the Laspi Bay jet gas emissions.

Several hours of high-resolution video imaging revealed predominance of pulsing gas emissions. Video imaging of the Laspi Bay gas emission site

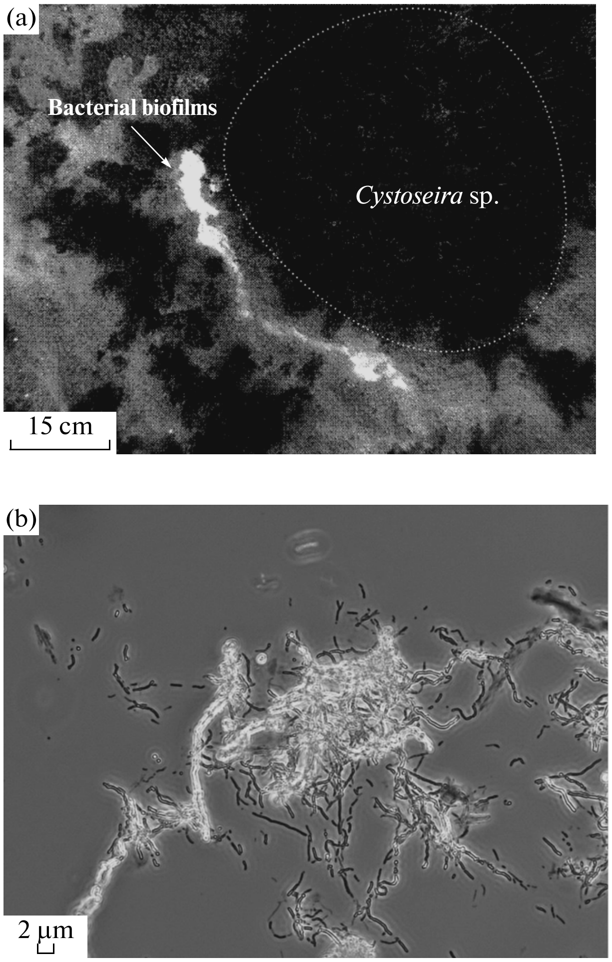

Fig. 3. Underwater photograph of a bacterial biofilm at the site of gas jets in the Khersones Bay (a) and phase contrast image of the biofilm (b).

showed the gas exits in the sand acting as release valves: a certain volume of gas is accumulated in subsurface sand, with visible evolution of the jet "crater," which is followed by gas release into the water column. At some discharge site, the bubbles of a uniform size rose constantly at the same frequency. These discharge sites were located in the rock massif or at the sand–rock interface (Fig. 5).

The presence of an anticlinal structure, with its wings composed of mid-Jurassic rocks and core of older formations of the Tauric series, is an important factor favoring local gas accumulation. Gas jets at the Mocha Island are probably of a similar nature (Jessen et al., 2011). The wings and the bend of the Laspi Bay anticlinal saddle are dislocated by numerous fractures creating the zones of enhanced permeability. This feature differentiates it from a classical structural gas- and oil-bearing trap and makes it doubtful that large (industrial-scale) volumes of gas may be accumulated due to its multidirectional leakages.

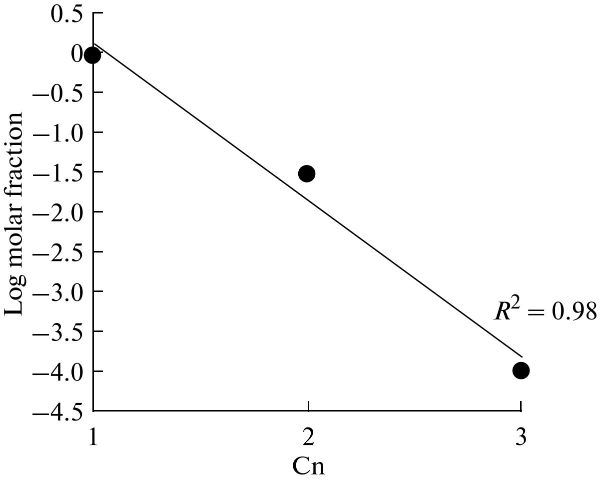

Fig. 4. Anderson–Shulz–Flori distribution coefficient (R^2) for the Laspi Bay seep gas.

The gas emission process in the Kazach'ya Bay is fundamentally different. Similar to the numerous gas jets in the Sevastopol Bay (Malakhova et al., 2013), this jet depends directly on the modern processes of OM decomposition in the bottom sediments. This was indicated by high SR and MO rates in the upper sediment layers. The isotopic composition of bubbled methane ($\delta^{13}C$) was –56.3‰. A similar $\delta^{13}C$ value (–56.7‰) was observed previously for methane from the heavily contaminated Martynov Bay (Pimenov et al., 2013). This isotopic composition may be caused by high rates of MO, which result in preferential consumption of the isotopically light ^{12}C methane or by the high rate of microbial methanogenesis on C1 and C2 organic compounds, the products of active OM degradation.

The seasonal nature of gas emission is also an indication of the biogenic nature of the Kazac'ya Bay jet. Thus, the bubble flow was much more intense in September than in October. In the highly eutrophic bay with limited water exchange, massive algal death and their microbial degradation, accompanied by abundant production of biogenic gases in anoxic zones of the sediment, occurs by mid-summer. The previously studied MartynovBay jet exhibited a similar seasonal dynamics (Egorov et al., 2012). Gas movement between the gas and water phases follows Henry's law, according to which the concentration of dissolved gas is equal to the partial pressure of the gas multiplied by its solubility (the Henry's constant, which is inversely proportional to temperature). Elevated temperatures during the warm season result in decreased gas solubility, causing its transition from the dissolved phase to the gaseous one. The gas phase pressure in the sediments of the coastal areas depends both on the atmospheric and hydrostatic pressure and on the rates of gas production and elimination. Decreased atmospheric pressure (and a decrease in the water level in the tidal

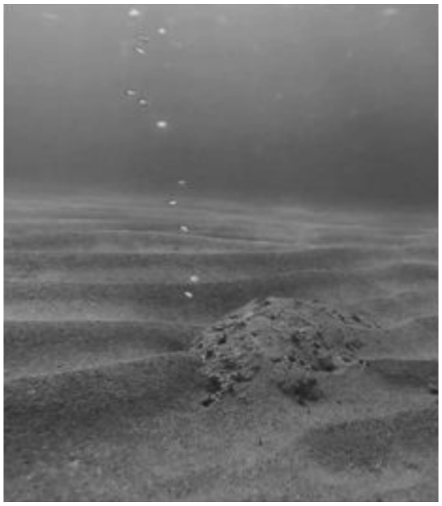

Fig. 5. Gas bubbles emerging from the sand in Laspi Bay, underwater photograph.

zones) results in decreased pressure in the depth and therefore to an increased volume of the gas phase due to bubble expansion and gas exolution. Thus, seasonal and synoptic variations in temperature and atmospheric pressure have a direct effect on the rages of gas discharge from shallow-water biogenic jets.

The Khersones Bay jet was also a source of mostly biogenic gas. The isotopic composition of methane bubbles was considerably lighter (–60.4‰) than in the Laspi and Kazach'ya bays (Table 1). This is an indication of a considerable share of modern microbial methane in the gas bubbles discharged in this bay. Since the investigated upper sandy horizons of the sediments had low methane content, which indirectly indicated no noticeable methanogenic activity, the horizon from which isotopically light microbial methane is discharged remains to be determined.

The area of gas seepage in the Khersones Bay contained characteristic microbial biofilms, which were predominated by spirochete-like filamentous organisms, similar to the "*Thiodendron*" microbial community. Such bacterial mats are widespread in the areas of constant sulfide inflow, such as Kamchatka thermal sulfur springs, sediments of the highly productive littoral zone where active sulfate reduction occurs, etc. According to our preliminary data, bacterial biofilms develop on the Khersones Bay sediments by the end of summer, when easily digestible OM is accumulated and the rates of destruction processes peak. Formation of such microbial growths is accompanied by sulfide release in a stable flow, which is necessary for development of the "*Thiodendron*"-type community. Hydrogen sulfide may also be present in gas seepage as an admixture, activating anaerobic processes in the sandy sediments of the methane discharge zone.

Generalization of the results obtained at the present stage of research makes it possible to suggest the existence of different reservoirs feeding the jet gas emissions of the Laspi Bay ant the Heracles Peninsula. Analysis of the component and isotopic composition of the Laspi Bay bubble gas indicates its deep genesis, with carboniferous rocks being, in our opinion, the most probable source of degassing. Additional isotopic data ($\delta^{13}C$-C_2H_6, δ^2H, $^3He/^4He$), and complete analysis of the bubble gas composition will make it possible to identify the Laspi Bay source of deep gas. The gas in the Kazach'ya and Khersones bays is polygenetic, with the prevalence of a microbial component, as was confirmed by the $\delta^{13}C$-CH_4 data. While in the Kazach'ya Bay the gas is produced in the upper sediment layers, gas-bearing sediments of the Khersones Bay are probably located in the sediments below the upper layers. Further research on the coastal jet gas emissions will determine the possible presence of hydrogen sulfide among the jet gases and to identify the structure of the microbial community developing at the discharge sites of Crimean shallow-water jets using molecular genetic techniques.

ACKNOWLEDGMENTS

The work was supported by the Russian Foundation for Basic Research, project no. 14-04-90400-Ukr-a.

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Translated by P. Sigalevich