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TRANSFER OF FREE METHANE BY GAS BUBBLE STREAMS FROM ANAEROBIC TO AEROBIC WATERS OF THE BLACK SEA*

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"Breath of earth" in the form of methane gas bubble streams from a seabed (methane seeps, bubble emanations) is a planetary phenomenon that was noticed only at the end of the XX century. The study of this phenomenon, being an important link in processes of lithosphere, hydrosphere, atmosphere, and biosphere interaction, is relevant to date. In this work, methane fluxes were determined in the known area of intense methane occurrences of biogenic nature, geographically tied to Dnieper River paleochannel in the northwest of the Black Sea. Bubbling (free) methane flux from anaerobic to aerobic waters in the active methane seeps area of Dnieper River paleochannel in the depth range of 140–725 m is estimated averagely as $1.2 \cdot 10^3$ $m^3 \cdot km^{-2} \cdot year^{-1}$ (STP), or 2.8 % of bubbling methane emitted from a seabed. The value of the investigated flux was 4.2 % of the specific flux of bubbling methane to a water column on shelf depths (less than 140 m) in the same area. Methane flux estimate, obtained in this work, seems to be a significant environmental factor in conditions of strong stratification of Black Sea waters, where methane transfer by gas bubble streams is the main mechanism for introducing deep-water methane into biogeochemical cycles and carbon transformation processes of Black Sea aerobic zone.

Keywords: Black Sea, gas bubble streams, aerobic waters, anaerobic waters, methane fluxes

Methane studies in A. O. Kovalevsky Institute of Biology of the Southern Seas (hereinafter IBSS) began after the discovery of methane gas bubble streams in Black Sea hydrogen sulfide zone made by a team of researchers led by G. G. Polikarpov and V. N. Egorov in 1989 [4].

Later, Black Sea water area served as a testing ground for numerous interdisciplinary international studies related to the phenomenon of gas bubble streams. IBSS employees contributed to many works in priority research areas, including bubbling methane fluxes study.

It has been found that gas bubble stream discharge into the Black Sea is manifested in areas with different geomorphological characteristics: in paleochannels of the Danube, Dnieper – Kalanchak, Don – Kuban rivers; in the alluvial fan of Transcaucasian rivers; on the western continental slope with an adjacent shelf; and on the northwestern shelf [2]. The overwhelming number of methane seeps examined is classified as cold ones, *i. e.* seeps of biogenic origin [3]. Over 98 % of gas bubble streams were located

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above the boundary of gas hydrates stability zone (725 m for the Black Sea), which indicates the barrier effect of gas hydrates in bottom sediments. In Black Sea deep-water area, gas bubble streams are mainly associated with areas of active development of mud volcanism and diapirism. At the same time, gas bubble streams can reach sea surface only in Black Sea shallow water areas (in coastal areas; on the shelf; and at the top edge of continental slope at a depth of not more than 262 m) due to a high dissolution rate of methane, contained in bubbles [2].

The total content and vertical distribution of methane in Black Sea waters is generally considered to remain quasi-stationary, at least over a 30-year observation period, with a stable balance between methane discharge and consumption [7].

Previously, a direct calculation of rate and volume of bubbling methane discharge into Black Sea anoxic water column was carried out at IBSS in ten already studied and promising areas of active methane occurrences from three types of methane gas bubble streams existing in the Black Sea: methane seeps at anoxic depths down to 725 m; gas bubble streams, induced by a vertical heat flux, in gas hydrates stability zone; and mud volcanoes [1]. It has been found that among the considered sources of methane gas bubble streams, the largest contribution to Black Sea waters is made by methane seeps at anoxic depths down to 725 m. Contribution of other sources is orders of magnitude less. Moreover, the estimate of total emission of bubbling methane obtained is at least 2.5 times lower than corresponding estimates determined by biogeochemical methods. This work was aimed at obtaining the maximum estimate of bubbling methane discharge into Black Sea waters; therefore, some features of gas exchange of bubble flares with water, surrounding them, were not taken into account. In particular, the distributed flux of dissolved methane along gas flares in a water column was not considered. It was assumed that all bubbling methane from a seabed at depths of more than 140 m completely enters Black Sea anoxic waters in the dissolved form. In fact, some methane bubbles, emitted from a seabed, can cross the boundary between anaerobic and aerobic waters, when rising, and even reach sea surface, emitting free methane directly into the atmosphere.

The aim of this work is to study the significance of directed transfer of free methane by gas flares from anaerobic to aerobic waters.

MATERIAL AND METHODS

The study focuses on Dnieper River paleochannel area (Fig. 1) characterized as one of the most active areas of methane occurrences. This is the part of an extensive alluvial fan accumulating huge masses of organic material from the entire northwestern part of the Black Sea with adjacent rivers [6].

In this region, 902 seeps were recorded on a shelf area of 41.2 km^2 (sector A), and 1,295 seeps were recorded on a continental slope in the anoxic zone (sector B) over an area of 345 km^2 [5].

For each of the seeps detected, data on bubbling methane emission flux from a seabed Φ_0 (L·min^{-1} under normal conditions: standard temperature and pressure, STP) was obtained, as well as free methane fluxes into the atmosphere [5]. Summary of the data obtained in Dnieper River paleochannel area is given in Table 1.

As seen from Table 1, the isobath of 140 m was chosen as a boundary between sectors A and B, which approximately corresponds to the middle of a boundary layer between aerobic and anaerobic zones. Mainly, seeps, located below the upper boundary of pycnocline (140 m) and above the upper boundary of gas hydrates stability zone (725 m), emit bubbling methane into the anoxic water

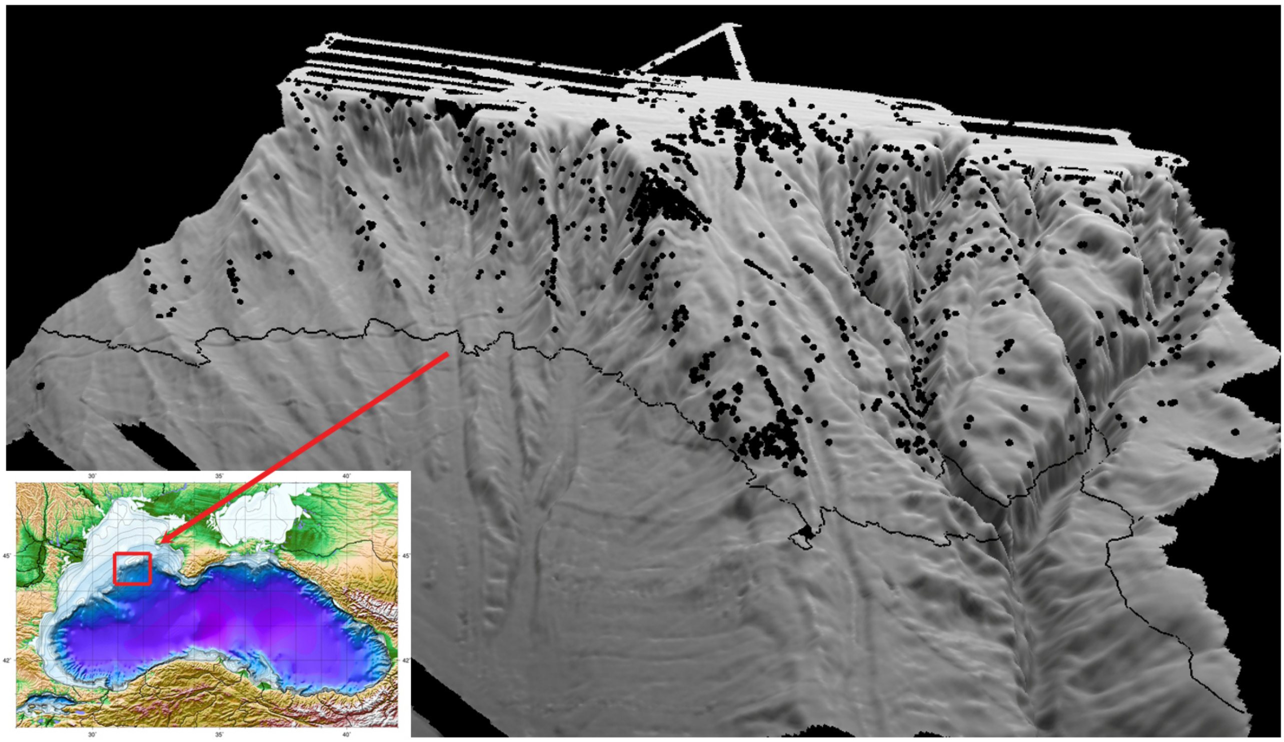

Fig. 1. Gas bubble streams (●) on a bathymetric map of a seabed in Dnieper River paleochannel area. The line is drawn along the isobath of 725 m. The inset shows location of Dnieper River paleochannel on the map of the Black Sea

Table 1. Parameters of bubbling methane emission in Dnieper River paleochannel area

Parameter	Sector A: depths 60–140 m	Sector B: depths 140–725 m
Acoustic coverage, km^2	41	346
Seeps number	902	1295
Total initial methane flux Φ_0, $\cdot 10^6$ $m^3 \cdot year^{-1}$ (STP)	1.2	15.6
Spatial density of methane emission flux Φ_p, $\cdot 10^3$ $m^3 \cdot km^{-2} \cdot year^{-1}$ (STP)	29.5	45.1
Total methane flux into the atmosphere Φ_a, $\cdot 10^5$ $m^3 \cdot year^{-1}$ (STP)	3.1	0.1

column of the Black Sea. Gas bubble streams of the oxic zone emit a significant part of free methane into the atmosphere, while methane, dissolved as gas bubbles rise, is more likely to migrate to sea surface than overcome the density gradient in pycnocline layer and penetrate the anaerobic zone with a higher concentration of dissolved methane.

To assess the evolution of methane concentration in gas bubble streams of seeps in the anaerobic zone when moving away from gas emission source, we used the approach described earlier in [5]. It involves using the model of gas exchange between methane seeps bubbles and seawater, surrounding them. This model is based on a system of differential equations that take into account, inter alia, the effect of van der Waals forces on gas exchange between bubbles and a water column; the adsorption of surfactants, contained in water, by bubbles; and the appearance of the Marangoni effect reducing gas bubbles rising speed and weakening mass transfer of substances through shells of these bubbles.

Initial sizes of methane bubbles of gas bubble streams were determined using statistical data obtained by measuring bubbles target strength. Size range was divided into size classes with a step of 2 mm, and frequency of occurrence of each class in the sample was determined. Initial methane fluxes of gas bubbles, *i. e.* vertically directed flux of methane contained in the rising bubble at the moment it emerges from a seabed, Φ_0 were determined by volume and rise rate of bubble at the moment it emerges from a seabed. Then, bubble model was run for each size class.

The following parameters were recorded at the model output: time t, sec; bubble rise depth h, m; bubble diameter d, mm; gas content in a bubble m, µmol. The depth of methane seep was 140 m and deeper. It was assumed that gas composition of bubbles includes highly and sparingly soluble gases (CH_4, N_2, He, and Ar). Initial methane content, *i. e.* at the moment a bubble emerges from a seabed, was set at no less than 99 %, the same as in [5].

Model calculation was stopped either when a bubble reached sea surface or when its diameter decreased to 0.001 mm, which was interpreted as a complete dissolution of gas contained in the bubble. For each size class of bubbles according to modeling data, vertical profiles of methane content m(h) and dissolved methane flux into a water column $f_w(h)$ were calculated:

$$f_w(h) = \bar{v}_h \frac{m(h+\Delta h) - m(h)}{\Delta h} \,, \tag{1}$$

where $\bar{v}_h$ is average bubble rise rate in a sector (h + Δh, h).

Methane content in average bubble of gas flare M(h) and methane flux into a water column $F_w(h)$ from a seabed to the horizon of 140 m were determined by summing over size classes of bubbles with weights proportional to their frequency distribution.

The use of $F_w(h)$ profiles made it possible to estimate integral methane fluxes from local gas bubble seeps into a water column in the range from localization depth of methane seep to the horizon of 140 m Φ_{140+}:

$$\Phi_{140+} = \int_{H_0}^{140} F_w(h) \cdot dh \,. \tag{2}$$

The obtained graph of Φ_{140+}/Φ_0 ratio depending on localization depth of methane seep emission (Fig. 2) was approximated by a simple function:

$$Y = 100\left(1 - e^{(150.0 - X)\cdot 37^{-1}}\right), \tag{3}$$

where X is depth, m.

Formula (3) allowed estimating Φ_{140+} values for each of 1,295 methane seeps from Table 1 according to previously determined values of their initial flux:

$$\Phi_{140+} = Y \cdot \Phi_0 \,. \tag{4}$$

Then, flux of methane, transferred by rising bubbles of methane seeps outside Black Sea anaerobic zone, was estimated by the ratio as follows:

$$\Phi_{140-} = \Phi_0 - \Phi_{140+} \,. \tag{5}$$

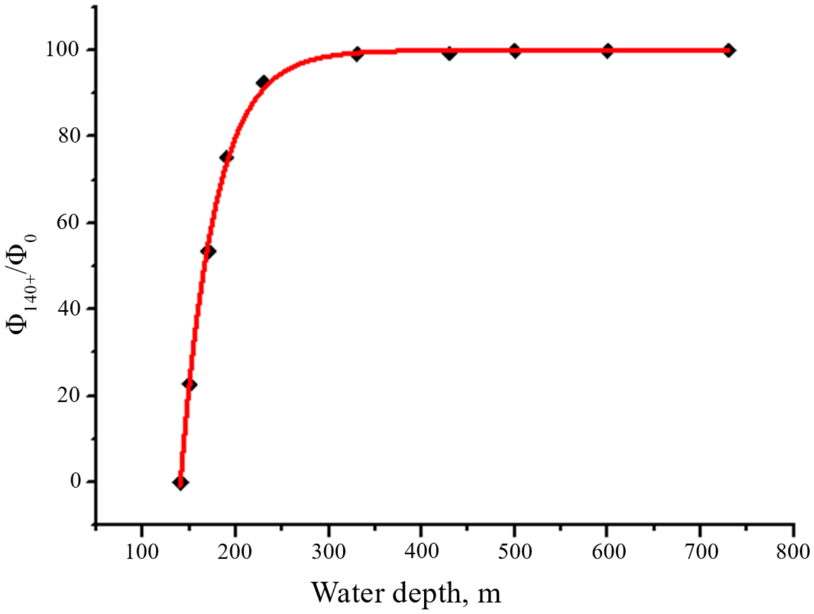

Fig. 2. Dependence of Φ_{140+}/Φ_0 ratio value on localization depth of methane seep emission (♦). Red line is an approximating curve

RESULTS AND DISCUSSION

Fig. 3A presents a histogram of frequency of occurrence of gas bubble streams, transferring free methane by rising bubbles above the horizon of 140 m, in Dnieper River paleochannel area.

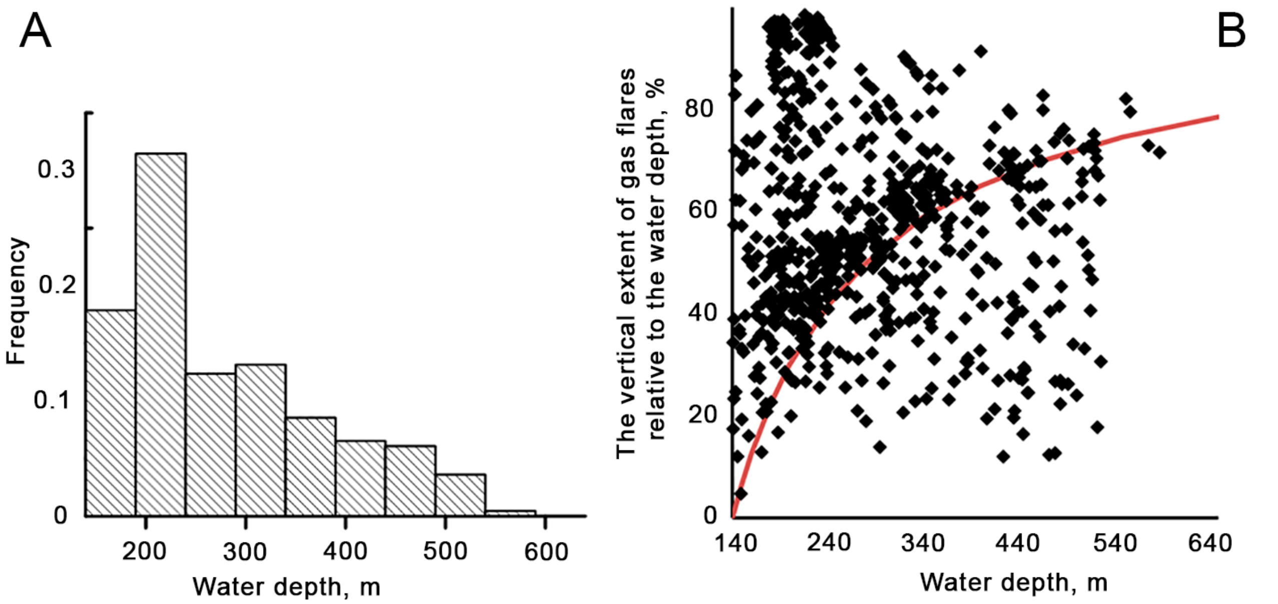

Fig. 3. A – histogram of frequency of occurrence in Dnieper River paleochannel area of gas bubble streams, transferring free methane above the horizon of 140 m; B – vertical extent of gas flares relative to water depth (♦) and graph of relative heights of hypothetical flares, reaching strictly the horizon of 140 m [(D – 140)/D × 100], where D is water depth (red line)

As shown in Fig. 3A, free methane transfer from the anaerobic zone is provided in Dnieper River paleochannel area both by seeps, emitting methane into the atmosphere (localized above a depth of 262 m), and seeps, located much deeper (up to 590 m). The validity of this statement is confirmed by Fig. 3B, showing data on the height of gas flares at sites of gas bubble emissions from a seabed in Dnieper River paleochannel area. The data are stored in IBSS marine research database, containing, inter alia, electronic echograms of seeps, as well as heights of registered gas flares throughout the Black Sea [2]. For clarity, the curve of the function $[(D - 140)/D \times 100]$ is plotted in Fig. 3B. This allows comparing flares rising above the horizon of 140 m (all dots on Fig. 3B above the red line) with flares not reaching this horizon (all dots below the red line). It is quite obviously seen from Fig. 3B that a significant number of seeps, located on a seabed in a depth range of 140–600 m, form gas flares of height being sufficient to transfer free methane outside the anoxic zone. It is interesting that this factor had not been previously investigated. Meanwhile, the total estimate of methane flux from all seeps outside the anoxic zone, calculated by formula (5) (Table 1, sector B), was 824 $L \cdot min^{-1}$, or $4.3 \cdot 10^5$ $m^3 \cdot year^{-1}$ (approximately 2.8 % of the initial flux). At the same time, emission of free methane into the atmosphere from seeps in this area is only $0.1 \cdot 10^5$ $m^3 \cdot year^{-1}$ (2.3 % of the emission of bubbling methane to the aerobic zone in sector B).

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ПЕРЕНОС СВОБОДНОГО МЕТАНА СТРУЙНЫМИ ГАЗОВЫДЕЛЕНИЯМИ ИЗ АНАЭРОБНЫХ В АЭРОБНЫЕ ВОДЫ ЧЁРНОГО МОРЯ*

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«Дыхание недр» в форме метановых струйных газовыделений из морского дна (метановые сипы, или пузырьковые эманации) — явление планетарного масштаба, на которое обратили внимание лишь в конце XX столетия. Изучение этого явления как важного звена процессов взаимодействия литосферы, гидросферы, атмосферы и биосферы не потеряло своей актуальности до настоящего времени. В данной работе определены потоки метана в известном районе интенсивных метанопроявлений биогенной природы, географически привязанных к палеоруслу р. Днепр в северо-западной части Чёрного моря. Впервые оценено, что поток струйного (свободного) метана из анаэробных в аэробные воды на участке активных метановых газовыделений в районе палеорусла р. Днепр в диапазоне глубин 140–725 м составляет (в среднем по участку) $1{,}2 \cdot 10^3$ $м^3 \cdot км^{-2} \cdot год^{-1}$ (STP), или 2,8 % от выделившегося из дна струйного метана. Величина исследованного потока — 4,2 % от удельного потока струйного метана в водный столб на шельфовом участке (глуби́ны менее 140 м) в этом же районе. Полученная в работе оценка потока метана — значимый экологический фактор в условиях стратификации вод Чёрного моря, где перенос метана струйными газовыделениями является основным механизмом внесения глубоководного метана в биогеохимические циклы и процессы трансформации углерода аэробной зоны Чёрного моря.

Ключевые слова: Чёрное море, струйные газовыделения, аэробные воды, анаэробные воды, потоки метана

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