

Original Research Paper

# Methane Emissions by Reed Formations on the Azov Sea Coast

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**Abstract:** Mapping of reed zones including both single-species formations and mixed formations of reeds and cattails has been done to assess methane emissions produced by reed formations growing on the coast and adjacent areas of the Azov Sea. In particular zones full-scale experiments have been carried out in order to measure methane emissions above common reed (*Phragmites australis* (Cav.) Trin. ex Steud.) and lake reed (*Scirpus lacustris* L.) areas, which have formed the basis for calculation of methane concentration produced by reed formations of the Azov Sea. Methane fluxes above the common reed and lake reed bushings range respectively from 1.73 to 5.85 mg/m<sup>2</sup> h and from 1.14 to 2.34 mg/m<sup>2</sup> h and are on average in 12-22 times higher than in open water areas. The total area of the Azov Sea coast and its surroundings with reed formations is 967.4 km<sup>2</sup> or 2.5% of the sea area with open water surface. The total amount of methane emissions from these formations is estimated to be 80 thousand m<sup>3</sup> per day or 34.5% of the total methane emissions from the open water surface of the sea. At the same time 84% of these data fall on a single system of estuaries and the lakes between the Kuban River and Primorsko-Akhtarsk town.

**Keywords:** Coastal Water Plants, *Phragmites australis*, *Scirpus Lacustris*, Methane Emissions in the Atmosphere

## Introduction

Vegetation plays an important role in methane cycle processes in aquatic ecosystems (Gar'kusha and Fedorov, 2016). In addition to the fact that aquatic plants can be a source of organic substances after their die-back, the decomposition of which can produce great amount of methane, living plants can have a significant impact on methanogenesis, the level of methane concentration and the methane flux rate. Analysis of the living plants that have an impact on the methane cycle processes and gas exchange at the interfaces "bottom sediments-water-atmosphere" has shown (Carmichael *et al.*, 2014; Gar'kusha and Fedorov, 2016) that:

Firstly, plants discharge solutions and accessible organic compounds into the soils where they grow, among which root excretions (*root exudates*) are the most abundant (Nguyen, 2003). The exudates easily decompose; they are recycled fast and provide various microorganisms with carbon compounds, including microorganisms that are precursors of methanogenic archaea (Kankaala and Bergström, 2004; Chanton *et al.*, 2008; Megonigal and Guenther, 2008). Moreover, root excretions force microorganisms to grow and, consequently, contribute to

decomposition of previously buried organic material and the release of nutrients into the plant rhizosphere (Juutinen, 2004; Saarnio *et al.*, 2004).

Secondly, wetland vascular plants provide indirect transportation of methane from soils (bottom sediments, peat, soils) (Tang *et al.*, 2010; Carmichael *et al.*, 2014) into the atmosphere through aerenchyma, which forms a continuous air space inside the plant. This makes it possible to avoid oxidation of a significant amount of methane in the system "bottom sediments – water". Aerenchyma of wetland plants is also a pipeline for oxygen, which allows this gas to diffuse through the roots into the rhizosphere and adjacent bottom sediments and, as a result, to stimulate methane oxidizing bacteria in them (Colmer, 2003; Fritz *et al.*, 2011; Iguchi *et al.*, 2015; Gar'kusha and Fedorov, 2016). Despite the fact that oxygen, carried to the rhizosphere, makes methane oxidation more intensive, aquatic vegetation increases methane fluxes, if compare it to the areas with an open (*vegetation-free*) water surface (Juutinen, 2004). This is due to the fact, that the plants carry methane much faster than it diffuses along the concentration gradient in the system "bottom sediments-water-atmosphere". However, in extreme cases methane oxidation by rhizosphere oxygen can make methane stop to emit (Fritz *et al.*, 2011).

Methane is carried to the environment by plant organs (*roots, stems, leaves*) located both under and above water (Gar'kusha and Fedorov, 2016). Since the diffusion coefficient of methane in air is significantly higher than in water (by 4 orders more (Tang *et al.*, 2010)), it is clear that the more a plant grows out of water, the more intensively methane will be carried to the atmosphere and, accordingly, there will be less diffusion in water. In general, methane emissions vary considerably depending on the composition of the plant community (Ding *et al.*, 2004; 2005; Bhullar *et al.*, 2014; Fedorov *et al.*, 2015; Gar'kusha and Fedorov, 2016). It has also been established (Bansal *et al.*, 2015), that floating vegetation, which is not anchored to the sea bottom, carries very little amount of methane, because it does not have either aerenchyma or a communication channel with bottom sediments—the main source of methane in water reservoirs (Fedorov *et al.*, 2007). Thus, coastal aquatic plants with aerenchyma attached to the ground and with only their lower parts submerged into water will be characterized by the greatest ability to emit methane (Gar'kusha and Fedorov, 2016).

Relatively recently, Keppler *et al.*, (2006) have revealed a new mechanism of methane formation in the aerobic plant phyllosphere. Although the process of the aerobic methane formation hasn't been studied thoroughly, interrelations between gas emissions by plants and ultraviolet radiation effect on vegetation and other physiological stresses (in particular, rapid temperature change or plant damage) revealed in numerous experiments show that it is a widespread process (McLeod *et al.*, 2008; Vigano *et al.*, 2008; 2009; Bruggemann *et al.*, 2009; Bruhn *et al.*, 2009; Messenger *et al.*, 2009; Qaderi and Reid, 2009; Nisbet *et al.*, 2009). The effect of ultraviolet radiation and other physiological stresses on plants initiate chemical reactions in them, forming active oxygen compounds; that results in some methane emissions from methyl groups of plant pectin (and even from vegetation cellulose and lignin) as a component of cell decomposition (Keppler *et al.*, 2008; Ghyczy *et al.*, 2008; Messenger *et al.*, 2009; Keppler *et al.*, 2009).

Thus, both the direct and indirect role of vegetation in formation of methane emitted into the atmosphere is currently in no doubt. According to estimates (EPA, 2010), total global methane emissions produced by vegetation range from 4 to 69 Tg/year. And according to more modern and detailed studies (Carmichael *et al.*, 2014), methane emissions by vegetation are estimated to be even higher i.e. from 32 to 143 Tg/year, which is 5-22% of its annual global emissions into the atmosphere by known natural and anthropogenic sources. At the same time, the methane emissions formed in aerobic in the plant phyllosphere make up about 25-42% of the total vegetation contribution, the rest coming from indirect transportation. As it can be seen from the previous

estimates there is a large degree of uncertainty, since, on the one hand, little attention has been paid to the studies of contribution of methane carried by vegetation; on the other hand, researchers have only recently found aerobic methane formation in the plant phyllosphere (Conrad, 2009; Schlesinger and Bernhardt, 2013; Carmichael *et al.*, 2014; Gar'kusha and Fedorov, 2016).

The Azov Sea is a semi-enclosed sea of the Atlantic Ocean basin in Eastern Europe with salinity of 1.0 to 14.5 and frequent hypoxia in the water. This is the shallowest sea in the world, being up to 13.5 meters deep. In its coastal zone and along the banks and especially in the river deltas and limans (Liman is a term used for shallow estuaries of the Black and Azov Seas. Liman can be both open and separated from the sea by a narrow strip of land), the common or southern reeds dominate (Gromov, 2012), represented by both pure (*single-species*) reed brushwoods and mixed reed brushings, or bulrush and cattails – plants having aerenchyma.

The purpose of this paper is to measure amount of methane emitted into the atmosphere, produced by southern reed formations, which grow in the coastal zone and along the shores of the Azov Sea, its bays and estuaries. In August 2016-2018, site mapping was done where these formations grow and also, with specially designed stationary storage chambers or traps, the field experiments were carried out to measure methane emissions produced by the southern reed (*Phragmites australis* (Cav.) Trin. ex Steud.) and lake reed (*Scirpus lacustris* L.) formations, that can be found in mixed associations of plants. Apart from estimation of methane emissions produced by the reed formations of the Azov Sea, methane emissions from the open water surface of the studied sea were measured, the previously obtained formula (Gar'kusha *et al.*, 2011; Fedorov *et al.*, 2015; Gar'kusha *et al.*, 2016), that approximates dependency between methane concentration in the surface layer of water and its flux in the atmosphere was used.

This paper could be a methodological background for similar research practices on other water bodies, which will contribute to more accurate measurements of methane emissions produced by vegetation at the regional and global levels and, consequently, reduce uncertainty in modeling future climate scenarios (Arneeth *et al.*, 2010; Kirschke *et al.*, 2013).

## Materials and Methods

In preliminary investigation the space images of the Azov Sea 2016 (*Google Earth*) have been used in order to specify areas in the sea coastal zone and adjacent territories, presumably decoded as abundant in south reed formations. During subsequent site investigation activities on the Azov Sea coast in Rostov Region and Krasnodar Region in 2016, 2017 and 2018, the real

conditions of the areas were compared to the ones from presumably annotated space images. Practically, all of the reed bushings (more than 95%), decoded in preliminary investigation, were proved during site investigation activities. Besides, in many space images, due to a number of different factors (e.g., color, distance from the water's edge and the form of reed bushings), areas of the southern reeds and lake reeds were clearly distinguished.

During the 2016-2018 site investigation activities the space images of the Russian coastal areas of the Azov Sea were used in order to draw up schemes of growing reed formations according to the methods (Papchenkov, 2006). Projective cover was noted. In some areas which were most overrun with reeds and at spots full of plants, the reed formations were described. The height, a number of stems and the wet top plant biomass were calculated in mowed areas (0.5×0.5 m) and the site was mapped. All of these, as well as the interpretation of satellite images made it possible to map the habitat of the reed formations on the Azov Sea coast and to determine their location. The samples of water and sediments at the sites were collected to calculate methane concentrations.

Similar studies of the Ukrainian Azov Sea coast were not conducted by the authors due to its inaccessibility. However, research data on the species composition of the reed formations in these areas were provided (Gromov, 2012).

At the end of August 2017, in the Yeisky Liman coastal zone (100 m east of Nikolaevka village) the original storage chambers or traps, specially designed with plastic supporting plane and a metal rod, plastic hoops and a plastic film, were used (Fig. 1 and Table 1). Inside each of these storage trap chambers, a small battery-powered fan was installed in order to mix air and equalize methane concentrations in its volume. Experimental measurements of methane emissions over the lake reed formations (trap 1 with a base area of 2206 cm<sup>2</sup> and an air volume in the trap of 293422 cm<sup>3</sup>) and the southern reed formations (trap 2 with a base area of 908 cm<sup>2</sup> and an air volume of 136188 cm<sup>3</sup>) were carried out. The accumulation period lasted from 250 to 330 min for traps 1 and 2, respectively. Air samples of 2.5 mL in volume, taken at intervals of 60 to 120 min from the traps with a syringe (through a plastic film), were introduced into 42 mL standard glass bottles, which were filled up with distilled water and a preservative to the marked point (fixed air volume was 5 mL). The bottles could be used for subsequent vapor-phase analysis; they had screw-on plastic caps with holes for needle to enter, with rubber and fluoroplastic liners to seal them. In such a case each sampling was performed three times (parallel samples). Also, in all three cases, immediately after the traps had been put, blank samples were taken. The amount of methane concentration was calculated according to the certified analysis methods (Gar'kusha and

Fedorov, 2014; Gar'kusha *et al.*, 2016) with a Chromatek-Crystal 5000.2 gas chromatograph which had an equilibrium vapor dispenser using a flame ionization detector. The methane concentration was calculated according to amount of change in methane concentration in the air phase of the trap chambers during the exposure.

In addition, methane fluxes were measured by the similar method in areas with free water surface using trap 3 (a base area is 201 cm<sup>2</sup> and an air volume in the trap is 1250 cm<sup>3</sup>), which had a slightly different design described in the papers (Fedorov *et al.*, 2007; Gar'kusha *et al.*, 2011; Fedorov *et al.*, 2015; Gar'kusha *et al.*, 2016) and located in several dozens of meters from the studied coastal vegetation. While gas fluxes in areas with aquatic vegetation and a free water surface, near the traps were measured, samples from the surface water layer and from the 0-2 cm- bottom sediment horizon to calculate methane concentrations were taken. For traps 1 and 2 of the southern reed and lake reed bushings covered with traps, the height, a number of shoots and their dry top biomass were calculated.

Sampling of water and bottom sediments and then methane concentration data were taken according to certified analysis methods (Fedorov *et al.*, 2007; Gar'kusha *et al.*, 2016) with the help of a gas chromatograph "Khromatek-Crystal 5000.2" which has a metering device of equilibrium steam.

To calculate the methane emissions in the atmosphere which came from the open water surface of the Azov Sea, its bays and estuaries, as well as the deltas of large rivers flowing into it, the formula, obtained by the authors earlier from some experimental data, was used (Fedorov *et al.*, 2007; Gar'kusha *et al.*, 2011; Fedorov *et al.*, 2015; Gar'kusha *et al.*, 2016). This formula, as mentioned above, approximates dependency of methane concentration in the surface layer of water and its flux into the atmosphere and is as follows (Gar'kusha *et al.*, 2016):

$$\lg F_{\text{CH}_4} = 0.8763 \cdot \lg C_{\text{CH}_4} + 3.7384 \quad (1)$$

( $r = 0.72; n = 65; P < 0.01$ ),

Where:

$\lg F_{\text{CH}_4}$  = The logarithm of methane flux from water into the atmosphere, nl/m<sup>2</sup> day

$\lg C_{\text{CH}_4}$  = Logarithm of methane concentrations in water, nl/dm<sup>3</sup>

This formula proved to be versatile and adequate as exemplified by various bodies of water of Rostov Region (such rivers as the Don, the Temernik, the Dead Donets and the Taganrogsky Bay) (Fedorov *et al.*, 2007), wetland landscapes of Pskov Region (Fedorov *et al.*, 2015) and the wastewater treatment plant of the Rostov aeration station (Gar'kusha *et al.*, 2011).



**Fig. 1:** Photos of accumulative chambers or traps installed to measure methane fluxes in the lake reed bushings (1), the southern reed bushings (2) and on pure water (3) in the coastal zone of the Yeisky Liman

**Table 1:** The methane fluxes measurements in the Yeisky Liman of the Azov Sea, August 2017

The location of the trap (stationary camera) used for calculation of methane fluxes	Coordinates, north latitude and east longitude	Water near the traps		CH <sub>4</sub> fluxes from water into the atmosphere			Bottom sediments		
		T, °C/pH	CH <sub>4</sub> , µl/dm <sup>3</sup>	Sampling time for flow CH <sub>4</sub> / Exposure	The content of CH <sub>4</sub> , µl in 2.5 mL of air, selected by a syringe in the trap	The flow rate of CH <sub>4</sub> , mg/m <sup>2</sup> h	CH <sub>4</sub> , µg/gin.o.	Moisture content%/ Density, g/cm <sup>3</sup>	Visual bervation, description
Trap number 1. Set over lake reed bushings; water layer up to 0,15 m	46°43,370' 38°34,799'	25 8,52	2,80	9 h 50 min	< 0,001 (3) *	0	0,24	34,15 2,67	Fine brown silt
				0 min (blank sample)					
				11 h 54 min	0,008-0,013	1,44-2,34			
				124 min	0,010 (3)	1,80 (3)			
				13 h 25 min	0,011-0,017	1,14-1,77			
				215 min	0,014 (3)	1,46 (3)			
				15 h 17 min	0,020-0,034	1,37-2,32			
Trap number 2. Set over the reed bushings; water layer up to 0,05 m	46°43,398' 38°34,827'	26 -	-	11 h 15 min	< 0,001 (2)	0	0,14	27,30 1,95	Fine brown silt
				0 min (blank sample)					
				12 h 11 min	0,007-0,013	3,15-5,85			
				56 min	0,009 (3)	4,05 (3)			
				13 h 32 min	0,014-0,019	2,57-3,49			
				137 min	0,016 (3)	2,94 (3)			
				15 h 23 min	0,017-0,028	1,73-2,84			
Trap number 3. Set over in areas with free water surface; depth up to 0,6 m	46°43,201' 38°34,497'	22 8,64	6,0-7,18 6,5 (3)	8 h 30 min	< 0,001 (3)	0	0,25	30,05 2,11	Dark gray soft silty-pelitic silt with small sandy fragments (up to 3%)
				0 min (blank sample)					
				11 h 43 min	0,010-0,019	0,05-0,10			
				193 min	0,014 (3)	0,08 (3)			
				13 h 05 min	0,008-0,023	0,10-0,29			
				82 min	0,015 (3)	0,19 (3)			

Note. \* Here and in table 2 a numerator shows limits of change; a denominator is mean value; a number of measurements is in brackets

The Azov Sea water surface, its bays, estuaries, river deltas, as well as identifiable reed formations were measured with Google (2016) satellite images and the

“polygon” software tool that allows one to provide accurate data of the areas of contoured space images of any shape and complexity.

## Results and Discussion

According to the research, the reed bushings, representing both pure and mixed formations of the southern reeds, are 100 meters wide in some areas directly on the Azov Sea coast. Among the pure reed bushings there are local areas (up to 2-3% of the total mapped area) (*Scirpetum purum*) including the southeastern coast being dominated by bulrush or lake reeds (*Scirpus lacustris* L.); on the northern coast three-edged reeds (*Scirpus triqueter* L.) prevail ((Gromov, 2012) and the present studies). In the mixed southern reed associations the most frequent, but not dominant ones (up to 15-25% of the total area of the site) are lake reeds (or bulrush) and three-edged reeds, broad-leaved cattails (*Typha latifolia* L.) and narrow-leaved cattails (*Typha angustifolia* L.) (The latter dominate among the cattails). At the same time, reed bushings occupy deeper (usually up to 0.5 m) and distant places from the water edge and reeds and cattails grow both in the water and on the shore. Reeds and cattails are up to 2-3 m high, bulrush is up to 1.5 m high. The measured top wet biomass of the southern reeds varies within 2.6-4.5 kg/m<sup>2</sup>, the one of lake reeds (bulrush) is 1.5-3 kg/m<sup>2</sup>.

In shallow waters of the vast system of estuaries and lakes between the Kuban River and Primorsko-Akhtarsk town, reed roots usually grow up to 1.5 m deep. Being thick spaces of pure bushings, reeds cover up to 70-90%; the weight of air-dry mass is about 2.97 kg/m<sup>2</sup>, the stems are 3-4 m high and 1.1-1.3 cm thick. Reeds and cattails are widespread here (up to 20%), narrow-leaved cattails being predominant. As salinity of water bodies increases, the depth of reed roots decreases to 0.1-0.6 m, the stem becomes thinner, the height decreases to 1.4-3.0 m and the productivity drops to 1.2-2.0 kg/m<sup>2</sup>. Reed bushings are sparse at the water edge. There is no vegetation in highly saline areas and when they dry out, salty spots appear.

Calculations show (Fig. 2 and Table 2), that the total area of the Azov Sea coast and adjacent territories, overrun with reed bushings, is 967.4 km<sup>2</sup> or 2.5% of the sea with open water surface. At the same time, 84% of this value falls on a single system of estuaries and lakes between the Kuban River and Primorsko-Akhtarsk town. Among other regions, which are considerably overrun with reed formations, one can pick up the sea edge of the Don River delta (bushings area is 50 km<sup>2</sup>), the Akhtarsky Liman (31.6 km<sup>2</sup>), the Akhtanizovsky Liman (19.3 km<sup>2</sup>), connected to the Azov Sea by the narrow Peresypsky Strait, the Taganrogsky Bay with the Yeysky Liman and the Miussky Liman (14.5 km<sup>2</sup>), the Yasensky Bay (12.2 km<sup>2</sup>), the Beysugsky Liman (12.0 km<sup>2</sup>), connected to the Azov Sea by the narrow Yasensky Strait, a system of lakes and estuaries at the mouth of the Byrd River (10.6 km<sup>2</sup>), the straits and the channels connecting the Azov Sea with Lake Sivash (4.4 km<sup>2</sup>).

If one does not take into account the system of estuaries and lakes between the Kuban River and

Primorsko-Akhtarsk town, the river deltas, as well as the estuaries, which are separated from the sea by bays and connected with the sea only through narrow straits (the Akhtanizovsky Liman, the Beysugsky Liman, the Miussky Liman), the area of the Azov Sea, overrun with reed formations is 56.7 km<sup>2</sup>. These reed bushings are located in the coastal zone of the Akhtarsky Liman, the Yasensky and Taganrogsky bays with the Yeisky Liman.

The reed formations of the southern and northern coasts of the Taganrogsky Bay (excluding the sea edge of the Don River delta, the Yeisky Liman and Miussky Liman) cover 0.7 km<sup>2</sup> and 7.7 km<sup>2</sup>, respectively, with the vastest zones of reed bushings being concentrated in the eastern part of the Taganrogsky Bay, waters of which are fresher.

In general, the distribution of reed formations is controlled mainly by the depth and salinity of waters, as well as the content of nutrients (mainly nitrogen and phosphorus compounds) (Gromov, 2012). In this regard, the areas, overrun with reeds most, are typical for fresh and poorly salted, shallow water areas and usually coincide with river confluence zones, which are suppliers of biogenic components.

The methane concentration in the Azov Sea and its water bodies varies within 0.7-94.5 µl/dm<sup>3</sup> (average is 3.1 µl/dm<sup>3</sup>) (Table 2). Minimum methane concentrations are typical for open sea areas, which are long distance from the coast. The maximum ones are for the zone where the Don River flows into the Taganrogsky Bay (Gar'kusha *et al.*, 2016), as well as for shallow, well-heated estuaries, separated from the Azov Sea by bay bars and which are connected with the sea only through narrow channels (the Akhtanizovsky Liman and the Miussky Liman). The measured methane concentration significantly exceeds its equivalent concentrations (Gar'kusha *et al.*, 2016), which indicates that methane comes from water into the atmosphere.

The calculations made according to the formula (1), which approximates the dependence between the methane concentration in the surface water layer and its flow into the atmosphere, showed that methane emissions from the water surface of the Azov Sea, including all adjacent water bodies, are 242.6 thousand m<sup>3</sup>/day (Table 2). At the same time, 56.4% of this value fall to the open areas of the Azov Sea directly, 28.3% belongs to the Taganrog Bay with the Yeisky Liman, 11.9% is for the system of estuaries, lakes, rivers and canals between the Kuban River and Primorsko-Akhtarsk town.

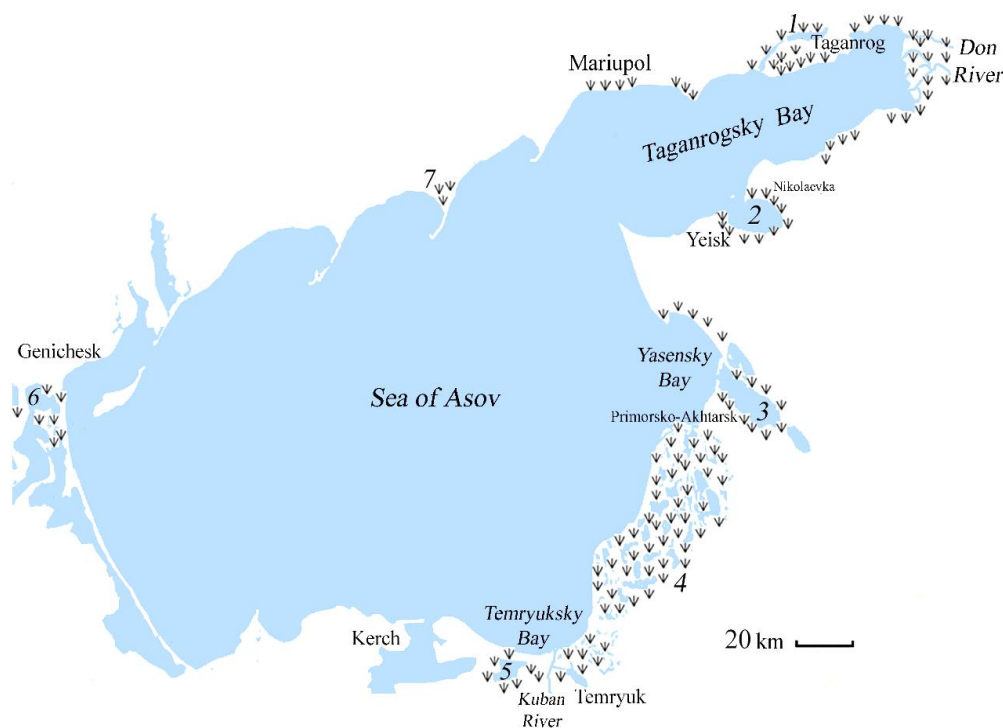
According to the experimental measurements (Table 1), methane fluxes over the southern reed formations varied within 1.73-5.85 mg/m<sup>2</sup> per h and were, on average, 2 times higher than their flows over the lake reed formations (or bulrush) i.e., 1.14-2.34 mg/m<sup>2</sup> per h. The obtained measurements are a little bit less than the methane emission indices in the boggy area (the USA) where broad-leaved cattails grow (16.04 mg/m<sup>2</sup> h)

(Knapp and Yavitt, 1992) and are comparable to its emissions over reed brushings in the reservoir located in the floodplain of the Yamuna River (2.6-6.4 mg/m<sup>2</sup> h) (Bansal *et al.*, 2015), as well as over reed brushwoods in the tidal swamp located in the Min River Delta (2.08-5.13 mg/m<sup>2</sup> h) (Tong *et al.*, 2010). In open water surface areas the methane flux varied 0.05-0.29 mg/m<sup>2</sup> per h, which is on average 12-22 times lower than over the vegetation studied in this paper. The high emissions of the studied gas produced by reed brushings, despite relatively low concentrations of methane in water and the upper 0-2 cm layer of sediments in the area where they grow, is probably due to the additional transportation of methane by the root systems and plant stems from lower sediment horizons, usually containing higher methane concentrations (Fedorov *et al.*, 2007).

Trap 1 contained 50 green reed stalks which were 20 to 120 cm long; their diameter at the bottom was 0.6 to 1.7 cm, with 15 dry stalks. Trap 2 had 25 green reed stalks, 110 to 180 cm long and with a diameter 0.7 to 1.0 cm, without dry stalks. The top biomass of reed and bulrush, respectively, in traps 1 and 2 was 0.6 and 0.75 kg. If calculate the measured methane fluxes over lake reed brushings and southern reed formations regarding the number of stems that are in traps 1 and 2 during the exposure, then each stem of these plants, respectively, will account for an average 0.034 and 0.126 mg/h of

methane released. That is, the southern reed stem is in 3.7 times more efficient in terms of transporting methane than the lake reed stem. When calculate the weight of top biomass, methane emissions produced by lake reed and bulrush formations are on average 2.7 and 4.2 mg/h per 1 kg of stems, respectively.

If the methane emission rate from the surface of the coastal areas overrun with reeds (104.6 km<sup>2</sup>), including the sea's bays and estuaries (except for the sea edge of the Don Delta and the system of estuaries and lakes located between the Kuban River and Primorsko-Akhtarsk town) is its average flux over the reed brushings of the southern reed and bulrush as 2.41 mg/m<sup>2</sup> per h (or 57.9 mg/m<sup>2</sup> per day), then the total methane emissions produced by reed formations will be only 8.7 thousand m<sup>3</sup> per day or 4.1% of the total methane emissions produced by the open water surface of the Azov Sea (Table 2). If the entire area of the Azov Sea (967.4 km<sup>2</sup>), overrun with reed formations, including the sea edge of the Don Delta and the system of estuaries and lakes between r. Kuban and Primorsko-Akhtarsk town is taken into account when measurements are done, the total methane emissions produced by reed formations will be 80 thousand m<sup>3</sup> (56 thousand kg) per day or 34.5% of the total methane emissions produced by the open water surface of the sea.



**Fig. 2:** Sketch map of the southern reed formations on the Azov Sea coast and adjacent areas: 1-the Miussky Liman; 2-the Yeysky Liman; 3-the Beysugsky Liman; 4-a system of estuaries and lakes between the Kuban River and Primorsko-Akhtarsk town; 5-the Akhtanizovskiy Liman; 6-channels and straits connecting the Azov Sea with Lake Sivash; 7-a system of lakes and estuaries at the mouth of the Berd River

**Table 2:** The open areas of the Azov Sea and the areas covered with reed bushings and methane emissions into the atmosphere

Water areas of the Azov Sea and adjacent areas	Water area, km <sup>2</sup>		CH <sub>4</sub> content in the water column, μl/dm <sup>3</sup>	CH <sub>4</sub> emission into the atmosphere from water, m <sup>3</sup> /day	
	From an open water surface	Covered with reed formations		From open water surface (calculated by the formula (1))	Covered with reed formations
Sea edge of the Don River delta	23,0	50,0	2,2-91,2 39,9 (14)	1355	4136
Taganrogsky Bay without the Yeisky Liman and the Miussky Liman	5289,3	8,4	6,8 *	66104	695
The Miussky Liman	65,2	1,6	7,4-40,5 17,9 (5)	1903	132
The Yeisky Liman	239,4	4,5	2,8-7,2 5,5 (4)	2484	372
The Yasensky Bay	184,4	12,2	0,7-1,6 1,1 (4)	467	1009
The Beysugsky Liman	268,8	12,0	1,0-2,4 1,6 (4)	945	993
The Akhtarsky Liman	31,1	31,6	1,2-2,2 1,7 (5)	115	2614
The system of estuaries, lakes, rivers and canals between the Kuban River and Primorsko-Akhtarsk town	564,7	812,8	7,2-77,8 33,9 (12)	28842	67230
The Akhtanizovsky Liman	91,8	19,3	10,2-94,5 28,0 (9)	3965	1596
Bays and the straits connecting the Azov Sea with Lake Sivash (near Genichesk)	13,0	4,4	6,8 **	163	364
The system of lakes and estuaries at the mouth of the Berd River	0,5	10,6	6,8 **	6	877
The Azov Sea without the sea edge of the Don River delta and the system of estuaries, lakes, rivers and canals between the Kuban River and Primorsko-Akhtarsk town	38175,3	104,6	2,7 *	212367	8652
<i>The Azov Sea totally with adjacent areas</i>	38763,0	967,4	3,1	242564 ***	80018 ***

Notes. \*-according to (Gar'kusha *et al.*, 2016); \*\*-the average concentrations of CH<sub>4</sub> in the water of these objects are assumed to be equal to its concentrations in the water of the Taganrogsky Bay, \*\*\*-the calculation of the total values of CH<sub>4</sub> emissions was carried out by summing the values of methane emissions from particular regions of the Azov Sea and adjacent areas.

## Conclusion

The Azov sea coast is dominated by reed formations of both pure (single-species) southern reed bushings and mixed associations in which the southern reeds, bulrush, three-edged reeds, broad-leaved and narrow-leaved cattails grow all together. The total area of the sea coast and adjacent territories, overrun with reed formations, is 967.4 km<sup>2</sup> or 2.5% of the area of the sea with open water surface. At the same time 84% of this value falls on a single system of estuaries and lakes between the Kuban River and Primorsko-Akhtarsk town. The area, covered with red formations only on the Azov Sea coast is 56.7 km<sup>2</sup>. These reed bushings are found in the coastal zone of the Akhtarsky Liman, the Yasensky and Taganrogsky bays.

Experimentally measured methane fluxes over the southern and lake reed formations vary, respectively, in the range from 1.73 to 5.85 mg/m<sup>2</sup> per h and from 1.14 to 2.34 mg/m<sup>2</sup> per h and on average 12-22 times higher

than in the water surface areas with no vegetation. At the same time, the southern reed stem is 3.7 times more efficient in carrying methane than the bulrush stem.

The total amount of methane emissions from areas, overrun with reed formations (104.6 km<sup>2</sup>), including its bays and estuaries, including separated ones from the sea (except the system of estuaries and lakes between the Kuban River and Primorsko-Akhtarsk town of and the sea edge of the Don Delta), is 8.7 thousand m<sup>3</sup> per day or 4.1% of the total methane emissions, produced by the open water surface of the Sea of Azov. However, if one takes into account the huge areas of reed formations, belonging to the system of estuaries and lakes between the Kuban River and Primorsko-Akhtarsk town of, as well as to the sea edge of the Don Delta, the total methane emissions of the reed formations are estimated to be 80 thousand m<sup>3</sup> (56 thousand kg) per day or 34.5% of its total emissions by the open water surface of the Azov Sea.

Further research activities should be aimed at studying seasonal dynamics of methane emissions by reed formations growing on the coast and adjacent areas of the Azov Sea to assess the annual methane emissions produced by these plants. The important trend could evaluation of contribution of individual plant species (cattail, reed and bulrush) to the total methane emissions, included the reed formations. An important subject area for future research is also the assessment of vegetation contribution to the total methane emissions, carried to the atmosphere indirectly and the methane fluxes formed in the aerobic plants phyllosphere.

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## Author's Contribution

**Dmitry Nikolaevich Gar'kusha:** The head of the research project, who designed the research plan and organized the study, coordinated the data analysis and contributed to the writing of the manuscript.

**Viktor Vladimirovich Sukhorukov:** Participated in all experiments, collected the field data and contributed to the writing of the manuscript.

## Ethics

This article is original and contains material that hasn't been published before. The corresponding author confirms that all the other authors have read and approved the manuscript and no ethical issues have been involved.

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