

Methane Emission from Flooded Soils of Rice Paddies in Rostov Oblast

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Received January 19, 2023; revised April 10, 2023; accepted April 11, 2023

Abstract—The methane fluxes to the atmosphere from the rice fields in the Rostov oblast (south of the European Russia) are analyzed using the results of field chamber measurements. In addition to the measurements of methane fluxes at the stages of rice seedlings and full ripeness, the concentrations of methane and hydrogen sulfide, Eh, pH, density, and moisture content are determined in water and different horizons of flooded paddy soils. The methane flux to the atmosphere from a rice paddy varies in the range of 0.195–0.531 mg CH₄/(m² h) and is on the average 2.1-fold higher at the stage of full ripeness as compared with the stage of seedlings. The rate of the methane flux to the atmosphere from the surface of dry soils separating rice paddies is on the average 4.9–12.1-fold lower as compared with the flux from the paddies, varying from 0.034 to 0.045 mg CH₄/(m² h). After flooding the rice paddies, the Eh values decrease in the soils isolated by a water layer and, as a consequence, the methane concentration in soils increases as well as its fluxes to the atmosphere. According to our assessment, the total methane emission from the rice fields in the Rostov oblast approximately reaches 1.253 t/day of 150 t/year, which accounts for 0.4–1.5% of the total methane emission from the soils of the Rostov oblast.

Keywords: paddy soils, greenhouse gases, anaerobic gases, hydrogen sulfide, emission

DOI: 10.1134/S106422932360094X

INTRODUCTION

The global climate change caused by an increase in the content of greenhouse gases (CO₂, CH₄, N₂O, and water vapor) in the atmosphere is currently one of the relevant ecological challenges [8, 34, 35]. Although the methane concentrations in the atmosphere are rather low, this greenhouse gas is the second in importance after carbon dioxide because of its high capacity for absorbing long wave radiation [42].

A large part of the atmospheric methane is of a bacterial (biogenic) origin and is completely controlled by the fluxes from the earth’s surface [29, 43]. The total methane emission to the atmosphere is estimated at 500–600 Tg/yr with annual variations in the sinks and sources [45]. Rice fields (paddies), being a kind of intermediate (between terrestrial and aquatic) types of technogenic landscape [41], are among the main anthropogenic sources of current biogenic methane in the atmosphere. The methane emission from 1 m² of rice paddies frequently exceeds the analogous characteristics of the bogs of the same latitudes. This fact is explainable with a lower degree of methane oxidation within rice paddies because it is released into the atmosphere through rice stems avoiding the influence of methane-oxidizing bacteria [2, 44].

The Intergovernmental Panel on Climate Change estimates the annual release of methane from rice fields at 20 to 100 Tg [34], which accounts for 3–20% of the total global emissions of all natural and anthropogenic sources. These volumes of methane emission are based on the field measurements of its fluxes from the rice fields of the United States, Spain, Italy, China, India, Australia, Japan, and Thailand. Note that in the mid-1980s, a team of the Lomonosov Moscow State University performed a few sessions of field chamber measurements of methane emission to the atmosphere from the flooded soils intended for rice growing in the territory of the former Soviet Union (south of Odessa oblast) [11, 12].

The available estimates of the total methane emission from the rice fields of the former Soviet Union [1, 13] and modern Russia [6, 19, 20] were calculated using the averaged values of 20 and 40 g CH₄/(m² year). These values were recorded by the field measurements of methane fluxes from the rice paddies worldwide, situated in humid tropics and subtropics [22, 33, 37]. According to the estimates [6], the total annual methane emission from the rice fields of Russia amounts to 0.1 million tons and of the former Soviet Union, varies from 0.14 [1] to 0.25 [13] million tons. Note that the contribution of Russian rice fields to the total methane

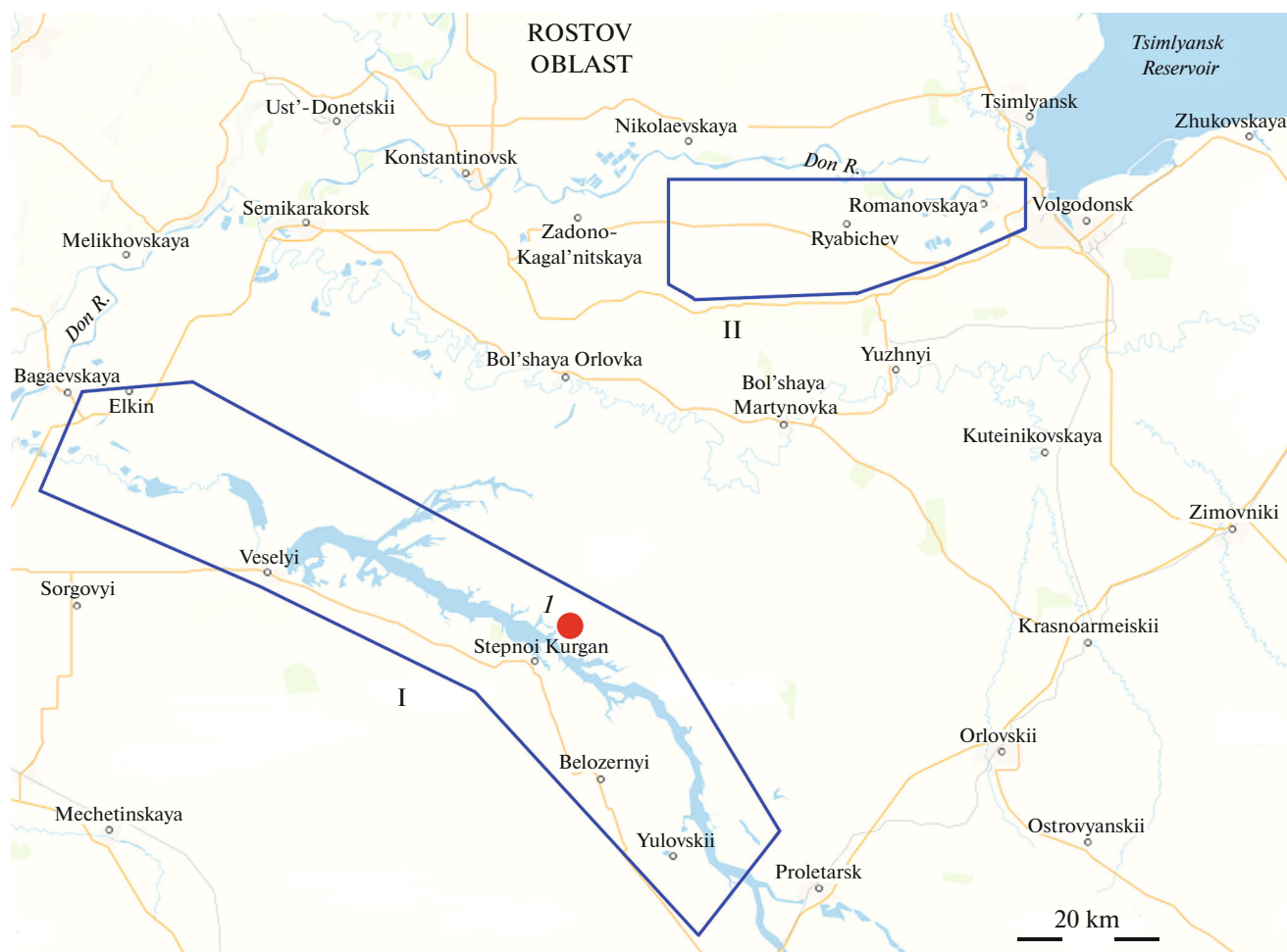


Fig. 1. Location map of rice growing area (I and II) in the Rostov oblast. Red dot (*I*) denotes the site of field measurements of the methane fluxes from rice paddy.

release in the agrarian sector of Russia on the average does not exceed 2.5% [19].

It is known that temperature is among the most important factors that control methane formation, concentration, and fluxes from the soils of rice paddies [3, 24, 36, 38, 44]. That is why, the assessment of methane emission based on the field measurements of its fluxes from rice fields in Russia situated in the temperate climate zone will somewhat differ from the above calculated values. The differences in rice-growing practices between the temperate zone and humid tropics–subtropics (for example, [44]) will also influence the annual methane emission from the rice fields of this county.

The goal of this work was to assess the rate of the methane flux to the atmosphere from the rice fields in the Rostov oblast according to the field measurements in one of the rice paddies of the OOO Energy Agricultural Enterprises (Valuyski and Proletarsk districts, Rostov oblast).

Specific features of rice growing in the Rostov oblast. According to the Southern Branch of the Center of Agroanalytics of 2020 [23], Rostov oblast is the third

among the Russian regions in rice sowing (14300 ha), after the Krasnodar region (117000 ha) and the Republic of Dagestan (20200 ha). Currently, the agricultural enterprises situated on the right and left banks of Manych Lake in the Martynovka, Volgodonsk, and Bagaevsk districts are involved in rice growing. The largest of them are the AO Tsimlyanskii (Martynovka district), OOO Manych-Agro (Bagaevskaya district), OOO Energy, OOO Primanychskii (both Proletarsk district), OOO Meliorator, and SPK Bol'shovskii (both Volgodonsk district). Thus, the Rostov oblast houses two blocks of rice growing [10]: the first (I) is situated on the right and left banks of the Veselovskii and Proletarsk artificial reservoirs, on the Western Manych River (between Proletarsk and Bagaevskaya) and the second (II), in the Don River floodplain (Fig. 1). The areas of rice fields in blocks I and II are slightly larger than 10000 and 4000 ha, respectively.

The Rostov oblast is the northernmost region of rice growing in Russia and worldwide; there, rice fields are formed as paddies flooded with rather thin layer of water for half year (spring–summer). Furrows are plowed in the fields to drive water during flooding.

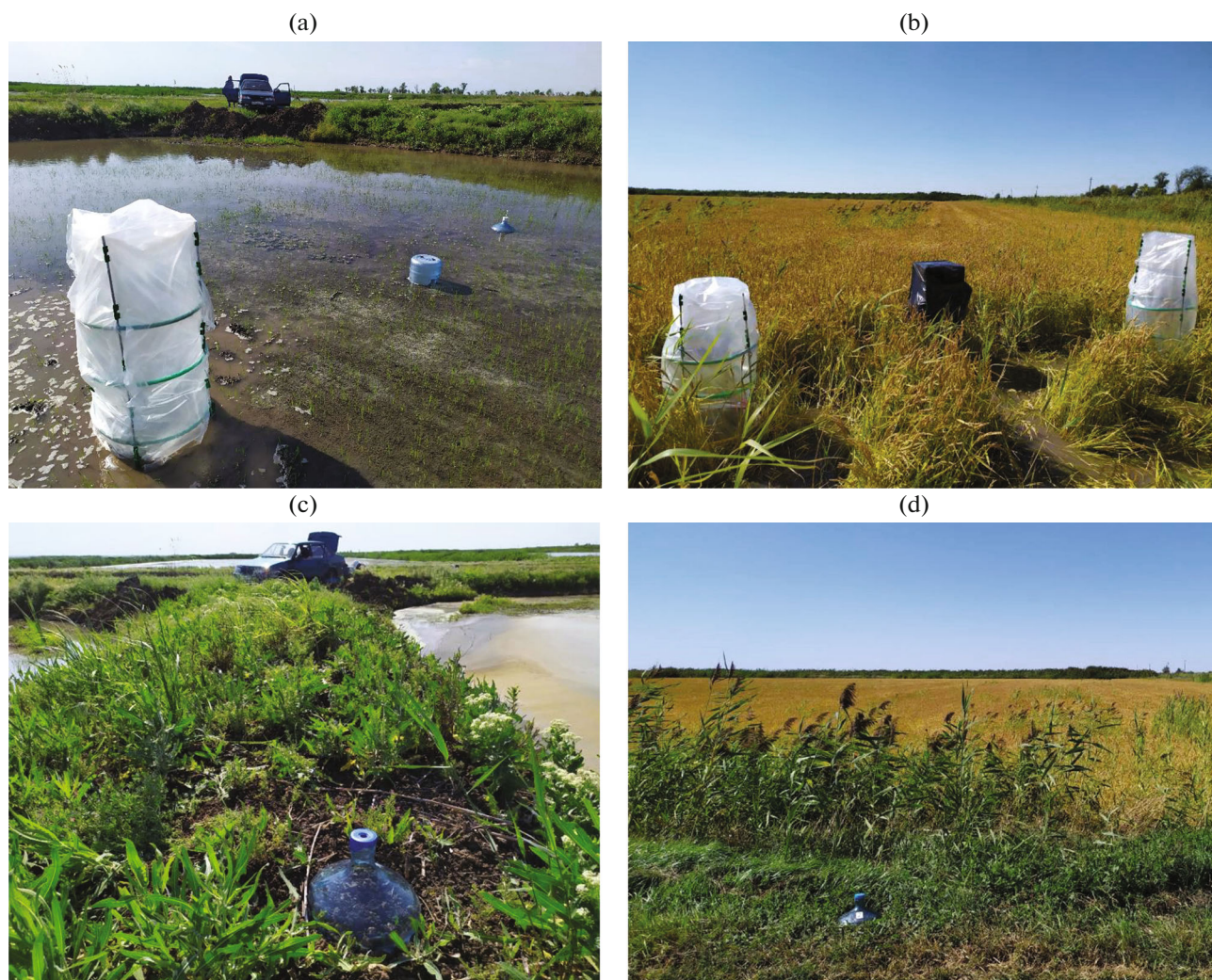


Fig. 2. Measurements of methane fluxes from rice paddy at the stage of (a) rice seedlings and (b) full ripeness and from the surface of the soils separating rice paddies in (c) May and (d) September 2021.

Note that the changes in the topography of the soil surface must not exceed 2 cm to provide a uniform water distribution and prevent wash-off of the seeds. The rice sowing is commenced when the soil temperature at a depth of 5 cm rises above 12–14°C. In the rice-growing zone of the Rostov oblast, these conditions are met by the end of April–beginning of May [10].

Short flooding is used in the Rostov oblast, that is, the initial water layer is created immediately after sowing except for the case of seed buried dressing. Water is discharged for the period of rice germination to restore the constant layer in paddies at the stage of seedlings with two–three leaves. Rice is harvested in the early–middle September. All activities on sowing, maintenance, and harvesting are mechanized.

OBJECTS AND METHODS

The field measurements of the rate of methane flux to the atmosphere from the flooded soil of paddy 1 at

the stages of seedlings (two–three leaves) and full ripeness (before harvesting), as well as from the leved soils between the rice paddies (Fig. 2) were performed on May 28 and September 09, 2021. In addition to measuring methane fluxes, concentrations of methane and hydrogen sulfide ($\Sigma\text{H}_2\text{S}$), Eh, pH, soil density, and moisture content were determined in different horizons of the flooded soils (Tables 1 and 2). The water of rice paddies was assayed for temperature, concentration of salts, content of particulate matter, pH, and methane concentration. In September 2021, methane concentration was determined in the water of adjacent paddy 2 (47°01'34.64" N, 41°21'44.39" E), where rice was sown two weeks earlier. In addition, on June 11, 2022, methane and hydrogen sulfide concentrations and the above listed physicochemical characteristics were measured in the water and flooded soils of two paddies (Table 3), including paddy 1, in which the experiments on assessing the methane emission described here were conducted in 2021.

Table 1. Field data on rice paddy 1 at the stage of rice seedlings, May 28, 2021

Location of stationary chamber for trapping methane fluxes	Volume of air phase in trap, cm ³ /trap base area, m ²	Time of CH ₄ flux sampling/exposure	CH ₄ concentration, µL in 2 cm ³ of the air collected with syringe in trap*	Mean rate of CH ₄ flux, mg CH ₄ /(m ² h) / mg CH ₄ /(m ² day)	Water near traps		Soils near traps									
					temperature, °C / pH	CH ₄ concentration, µL/dm ³ /mineralization, mg/dm ³	sampling depth, cm	CH ₄ concentration, µg/g wet soil/ΣH ₂ S, mg/g wet soil	bulk density, g/cm ³ /moisture content, %	pH/Eh, mV						
Trap 1 in rice paddy	$\frac{3000}{539}$	$\frac{15:25}{0 \text{ min}}$	0.010 (1)	0	$\frac{31.0}{8.52}$	$\frac{0.87-1.28(2)}{1035}$	0-2	$\frac{0.065}{<0.005}$	$\frac{1.639}{30.0}$	$\frac{7.62}{168.6}$						
											$\frac{16:35}{70 \text{ min}}$	$\frac{0.022-0.025}{0.023(3)}$	$\frac{0.217}{5.208}$	$\frac{0.050}{<0.005}$	$\frac{1.442}{26.4}$	$\frac{7.52}{108.2}$
Trap 2 in rice paddy	$\frac{293422}{2206}$	$\frac{15:40}{0 \text{ min}}$	0.010 (1)	0	-	-	-	-	-	-						
											$\frac{17:30}{110 \text{ min}}$	$\frac{0.011(2)}{0.011(2)}$	$\frac{0.254}{6.096}$	$\frac{0.013-0.018(2)}{-}$	-	-
Trap 3 in leveed dark chestnut soils between rice paddies	$\frac{4000}{539}$	$\frac{17:10}{70 \text{ min}}$	$\frac{0.011-0.013(2)}{0.011-0.013(2)}$	$\frac{0.045}{1.080}$	-	-	0-2	-	-	-						

* In this column, numerator shows the detection limits; denominator, mean value; and the number of measurements is parenthesized.

Table 2. Field data on rice paddy 1 at the stage of full rice ripeness, September 9, 2021

Location of stationary chamber for trapping methane fluxes	Volume of air phase in trap, cm ³ /trap base area, cm ²	Time of CH ₄ flux sampling/exposure	CH ₄ concentration, µL in 2 cm ³ of the air collected with syringe in trap*	Mean rate of CH ₄ flux, mg CH ₄ /(m ² h) / mg CH ₄ /(m ² day)	Water near traps		Soils near traps																	
					temperature, °C / pH	CH ₄ concentration, µL/dm ³ / mineralization, mg/dm ³	sampling depth, cm	CH ₄ concentration, µg/g wet soil / ΣH ₂ S, mg/g wet soil	bulk density, g/cm ³ / moisture content, %	pH/Eh, mV														
Trap 1 in rice paddy	293 422 2206	12:50 0 min	0.010 (1)	0	19.0 7.43	1.07–4.52(6) 632	0–2	0.034 –	1.534 32.4	7.44 13.1														
											15:20 150 min	0.012 (2)	0.372 8.928	–	0.070 –	1.612 26.9	7.26 –114.4							
																		16:20 210 min	0.013–0.014 (2)	0.466 11.18	–	0.12 –	1.865 26.5	7.30 –101.0
											15:30 130 min	0.011 (2)	0.517 12.41	–	–	–	–							
																		16:30 190 min	0.012 (2)	0.531 12.74	–	–	–	–
12:15 0 min	0.008 (1)	0	–	0.026 –	1.264 17.9	6.58 246.7																		
							14:15 120 min	0.011–0.012 (2)	0.034 0.816	–	–	–	–											
16:15 240 min	0.016–0.018 (2)	0.044 1.056	–	–	–	–																		
							Trap 3 in leveled dark chestnut soils between rice pad- dies	3000 539	12:15 0 min	0.008 (1)	0	–	–	0–2	0.026 –	1.264 17.9	6.58 246.7							
14:15 120 min	0.011–0.012 (2)	0.034 0.816	–	–	–	–																		
							16:15 240 min	0.016–0.018 (2)	0.044 1.056	–	–	–	–											

* In this column, the range of variation; and the number of measurements (in parentheses) are presented.

In the main part of the rice field area, where the studied rice paddies are located, the soil cover is composed of dark chestnut solonchic soils.

Water and soils, including soils in rice paddies, were sampled to assay for methane using certified methods [16, 17] and additional technical procedures [3, 25]. Test pits were made in the soils separating the paddies to take 3-mL soil samples from the pit walls (0–2-cm layer) with a sampler. The flooded soils in rice paddies were first sampled with a plastic tube of special design (length, 500 mm and diameter, 45 mm) with sharp edge and fluoroplastic plunger. Then, 3 mL of soils were sampled from different horizons (down to 25 cm) of the extracted core and placed into standard glass vials with a total volume of 42 mL filled with water with preservation agent (HgCl_2) to the mark (fixed air volume, 5 mL). The vials are adapted to the headspace analysis and have screw plastic caps with the openings for needle as well as resin and fluoroplastic inserts for airtight sealing. After the sealing, the sample was vigorously shaken to homogenize the soil samples and avoid methane formation and oxidation in the vial. Concurrently with this special soil sampling, weighed samples of soil were collected and placed into weighed and numbered containers to determine soil density and moisture.

The methane concentration in soil and water samples was determined in a Chromatech-Crystal 5000.2 gas chromatograph with a headspace sampler and flame ionization detector [16, 17]. The mass fraction of sulfide sulfur ($\Sigma\text{H}_2\text{S}$) in flooded soils is measured according to the transformation of sulfides to hydrogen sulfide with hydrochloric acid and subsequent blow-off of hydrogen sulfide with high-purity nitrogen into sodium hydroxide solution and detection of sulfide ions by photometric technique with *N,N*-dimethyl-*p*-phenylenediamine [18].

The pH, Eh, and temperature values were measured with an Ekotest 2000 portable ionomer immediately after sampling. The degree of mineralization and content of particulate matter in the water of rice paddies were determined according to the standard protocols of the Federal Service for Hydrometeorology and Environmental Monitoring of the Russian Federation [21].

The emission of methane from the surface of rice paddies and leveed soils was determined directly by measuring the rate of methane flux using a chamber technique with the help of stationary accumulation chamber traps [4, 25, 32] of different sizes and designs.

Two chamber traps were placed in rice paddy 1 to measure the methane fluxes at the stage of rice seedlings (May 2021), namely, small trap 1 with an air phase volume of 3000 cm³ and a base area of 539 cm² and a large trap 2 with the air volume of 293422 cm³ and a base area of 2206 cm². The exposure time of the traps in an accumulation mode was 70 to 120 min. The accumulation chamber placed between the large and small traps (Fig. 2a) and the chamber trap with black polyethylene film (Fig. 2b) were used in the experiment to determine CO₂ fluxes, not considered in this paper.

When the methane fluxes were measured at the stage of full rice ripeness (September 2021), two large chamber traps were placed in the rice paddy 2: trap 1 with an air phase volume of 293422 cm³ and a base area of 2206 cm² and trap 2 with an air volume of 353000 cm³ and a base area of 2206 cm². The exposure time of the traps in an accumulation mode was 130 to 210 min.

In both measurement intervals, small accumulation chamber traps 3 with an air phase volume of 3000 and 4000 cm³ and a base area of 539 cm² were placed between rice paddies to measure the methane fluxes from the surface of leveed soils (Figs. 2c, 2d). The exposure time of these traps in an accumulation mode was 70 and 120–240 min in May and September, respectively.

The used small traps (with an air phase volume of 3000 and 4000 cm³) are plastic polycarbonate containers with an open base and airtight cap with a special opening for sampling the gas phase. Before measurements, the traps were placed onto soil surface (including the flooded soils in rice paddies) burying them to a depth of 1.2–2.3 cm; in this process, the cap was opened for 10–15 min to remove the methane that can be released from soil while burying the trap. Then the trap was closed and 2-mL samples were taken with a syringe through the special opening at certain time intervals and transferred to standard glass vials for headspace analysis.

The accumulation chamber traps of a larger size were constructed of plastic pillars with a metal rod, plastic rings, and polyethylene covering film (thickness, 60 μm). To mix the air and level the methane concentrations within large traps, a small battery-operated blower fan was mounted at the lower part of one of the pillars. The 2-mL air samples collected from traps with a syringe (through polyethylene film) with the above-indicated periodicity were placed into the standard glass vials for headspace analysis filled with water and supplemented with preserving agent (HgCl_2). After a sampling event, the prick in the polyethylene film was sealed with an airtight scotch tape.

In all cases, a control sample was taken (exposure, 0 min) immediately after mounting the traps. Note that each sampling was performed in several replicates (parallel samples). Methane concentration in gas mixture of a standard vial was determined using headspace analysis as described in [17]. The flux (F) of methane (mg CH₄/(m² h)) was calculated as

$$F = (CV_1 \times 10\,000 \times 0.0007 / (V_2ST)) \times 60,$$

where C is the difference between methane concentrations in 2 cm³ of the air sampled with a syringe in trap after time T and in the control sample, μL; V_1 is the volume of air phase in trap, cm³; V_2 is the volume of air phase sampled with syringe in trap, cm³; S , base area (inlet), cm²; T , time of trap exposure, min; 10000, coefficient for recalculation to m², cm²/m²; 0.0007, coefficient for recalculation of μL to mg; and 60, coefficient for recalculation to hours, min/h.

Table 3. Field data on rice paddies 1 and 3 at the stage of rice seedlings, June 11, 2022

Location of stationary sampling chamber	Coordinates of sampling points	Water in rice paddies		Flooded soils of rice paddies			
		temperature, °C/pH	CH ₄ concentration, μL/dm ³ / mineralization, mg/dm ³	sampling depth, cm	CH ₄ concentration, μg/g wet soil / ΣH ₂ S, mg/g wet soil	bulk density, g/cm ³ / moisture content, %	pH/Eh, mV
Rice paddy 1	47°01'34.62" N, 41°21'22.39" E	29.0	1.64–5.54 (2)	0–2	0.115	1.405	7.19
		8.01	648	2–5	0.211	37.0	–10.8
Rice paddy 3, point 3-1	47°02'25.55" N, 41°17'07.86" E	28.0	3.02–3.93 (2)	2–5	0.025	1.800	7.29
		8.22	6723	5–10	<0.005	31.6	–12.8
Rice paddy 3, point 3-2, (100 m to northeast from point 3-1)	47°02'27.51" N, 41°17'05.60" E	–	1.75	0–2	0.030	1.849	7.34
		–	–	2–5	<0.005	31.2	132.1
		–	–	0–2	0.052	1.606	7.29
		–	–	5–10	<0.005	27.0	158.8
		–	–	0–2	0.083	2.090	7.27
		–	–	2–5	<0.005	25.3	–1.0
		–	–	0–2	0.028	1.235	6.91
		–	–	2–5	0.006	31.1	28.4
		–	–	2–5	0.021	1.849	7.03
		–	–	5–10	<0.005	29.0	73.8
		–	–	10–15	0.044	1.834	7.07
		–	–	20–25	<0.005	27.4	75.5
		–	–	10–15	0.014	1.857	7.19
		–	–	20–25	<0.005	22.0	62.7
		–	–	20–25	0.063	1.819	7.08
		–	–	–	<0.005	22.2	75.4

RESULTS AND DISCUSSION

During the field measurements of the methane fluxes in rice paddy 1 at the stage of seedlings (late May 2021), the concentration of methane in paddy water (water layer to 8–10 cm) near the traps amounted to 0.87–1.28 $\mu\text{L}/\text{dm}^3$ (two samples); water pH, 8.52; water temperature, at 15:30, 31°C; content of particulate matter, 31.3 mg/dm^3 ; and mineralization, 1035 mg/dm^3 .

The methane concentration one year later in the water of this rice paddy at the stage of seedlings (early June 2022) amounted to 1.64–5.54 $\mu\text{L}/\text{dm}^3$ (two samples); water pH, 8.01; water temperature at 13:30, 29°C; and mineralization, 648 mg/dm^3 .

In the same period (early June 2022), the concentration of methane in the water of rice paddy 3, situated at a considerable distance from the rice paddy 1 (at the other side of the rice field), varied in the range of 1.75–3.93 $\mu\text{L}/\text{dm}^3$ (average, 288 $\mu\text{L}/\text{dm}^3$; three samples); water pH, 8.22; water temperature, at 12:00, 28°C; and mineralization, 6723 mg/dm^3 . Note that immediately after rice sowing, a larger amount of nitrogen fertilizers was applied over the entire area of rice paddy 3, which most likely explains a high degree of mineralization of its water. In addition, numerous gas bubbles with a diameter of up to 5–6 mm periodically emitting from soils and entering the atmosphere were observed on the surface of flooded soils in a considerable part of paddy 3, especially, near point 3-2, where the largest amount of nitrogen fertilizers were applied. However, any putrid, sulfide, or any other smells were absent. A burning match held close to the water surface over the bubbles rising from the bottom caused no flame. Along with low concentrations of methane and hydrogen sulfide in water and bottom sediments of a rice paddy, this suggests a non-methane and non-hydrogen sulfide composition of gas bubbles. Application of large amounts of nitrogen fertilizers most likely activated nitrification processes with the oxidation of nitrogen ammonium and formation of nitrates in the aerobic water layer and on the soil surface [9]. Under the transient conditions between aerobic and weakly anaerobic situations, observed in the 0–2-cm layer of flooded soils (point 3.2, Eh = 28.4 mV), the denitrification processes were most likely intensified with the formation of both molecular nitrogen (N_2) and gaseous nitrogen monoxide and dioxide (NO and N_2O) [7, 9], which are the greenhouse gases released from paddy fields next in their significance after methane [27].

During the field measurements of the methane fluxes in rice paddy 1 at the stage of full ripeness (September 2021), the concentration of methane in water (layer to 8–10 cm) near the traps amounted to 1.07–4.52 $\mu\text{L}/\text{dm}^3$ (mean, 2.56 $\mu\text{L}/\text{dm}^3$; six samples); water pH, 7.43; water temperature, at 13:00, 19°C; and mineralization, 632 mg/dm^3 . The concentration of methane in the water of adjacent rice paddy 2, where the rice

ripeness was higher, amounted to 4.62–11.4 $\mu\text{L}/\text{dm}^3$ (two samples). In general, the mean methane concentration in water of rice paddies over all samples collected in 2021–2022 (13 samples) was 2.57 $\mu\text{L}/\text{dm}^3$, being by one order of magnitude lower as compared with the average methane concentration in the Don River lower reaches, amounting to 44.9 $\mu\text{L}/\text{dm}^3$ [26].

In May 2021, the concentration of methane in the upper 10-cm horizon of flooded soils in rice paddy 1 varied in the range of 0.050–0.065 $\mu\text{g}/\text{g}$ wet soil (mean, 0.058 $\mu\text{g}/\text{g}$ wet soil) with the maximum concentrations in the surface layer (0–2 cm). In September, the methane concentration in flooded soils of this rice paddy considerably increased in the 5–10-cm layer and varied along the sampled core from 0.034 to 1.44 $\mu\text{g}/\text{g}$ wet soil (mean, 0.34 $\mu\text{g}/\text{g}$ wet soil). On the other hand, pH and Eh values along the sampled core of wet soils in September decreased: pH, from 7.47–7.62 (May) to 7.26–7.44 (September) and Eh, from 6.4–168.6 mV (May) to –114.4...+13.1 mV (September).

In June 2022, the concentration of methane in the upper 5-cm layer of flooded soils in the rice paddy 1, with its weakly reducing conditions (Eh = –12.8...–10.8 mV) and neutral pH (7.19–7.29), amounted to 0.025–0.115 $\mu\text{g}/\text{g}$ wet soil with the maximum values in the surface 0–2-cm layer, as in May 2021. The concentration of hydrogen sulfide maximal over the observation period (0.211 mg/g wet soil) and 37% moisture content of flooded soils were recorded in this layer.

The concentration of methane in the flooded soils of rice paddy 3 in June 2022 varied in the range of 0.014–0.083 $\mu\text{g}/\text{g}$ (mean, 0.042 $\mu\text{g}/\text{g}$; eight samples) with the highest values in the lower horizons. The Eh values changed from –1.0 to +158.8 mV and pH, from 6.91 to 7.34. The concentration of hydrogen sulfide was below the detection level (<0.005 mg/g) except for one sample with the minimum pH values and one of the lowest Eh values in this observation period.

In general, the concentration of methane in the flooded soils of rice paddies in all samples collected during the study (2021–2022, 17 samples) varied in the range of 0.014–1.44 $\mu\text{g}/\text{g}$ (mean, 0.136 $\mu\text{g}/\text{g}$ and median, 0.052 $\mu\text{g}/\text{g}$). These concentrations (omitting the outlier of 1.44 $\mu\text{g}/\text{g}$) are very low for aquatic objects [26]. Presumably, this is determined by relatively high Eh values, which, along with the content of readily decomposable organic matter [3, 26, 11], are an important factor that controls the methane formation by methanogenic archaea in both the bottom sediments in water bodies, water flows [26] and soils [3, 23, 43], including the flooded soils of rice paddies [31, 46]. For example, the critical soil Eh value for the activation of methane formation according to experimental data [46] is approximately –150 to –160 mV; note that the dependence of methane formation on soil Eh in the range of –230 to –150 mV is inverse exponential [46]. A considerable increase in the rate of methane flux from flooded soils was observed when the soil redox potential was below –100 mV [31]. Note that aerobic

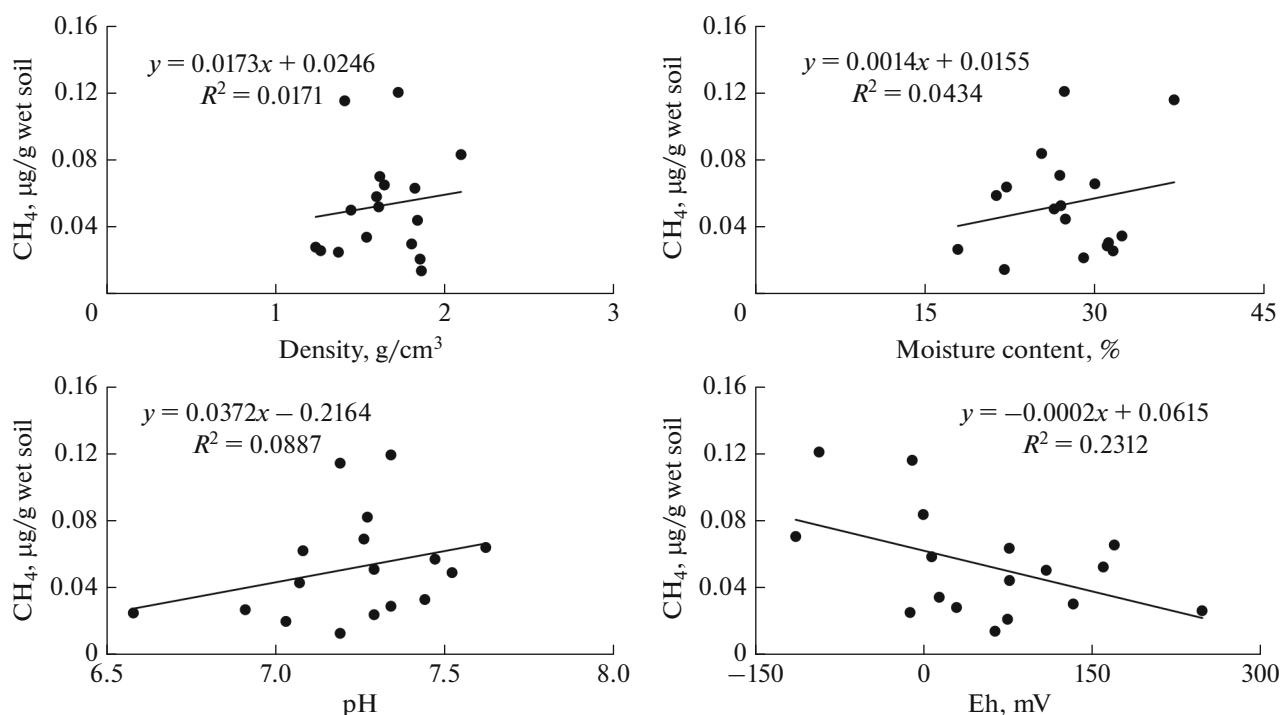


Fig. 3. Dependence of methane concentrations on physicochemical characteristics of the flooded and dry soils. An abnormal methane concentration (1.44 µg/g wet soil), untypical of the remaining data array, is discharged from the constructed plots.

conditions do not kill but only inhibit methanogens, ubiquitous in soils [38], allowing them to maintain their population in dried rice paddies in a state of low activity [28] and rapidly increase their abundance and methane production with the formation of anaerobic conditions [38].

The untypical (abnormal) value of methane concentration (1.44 µg/g) recorded in the 5–10-cm layer of flooded soils in rice paddy 1 in September 2021 is explainable with intensive methanogenic processes in this layer determined, along with anaerobic conditions (Eh = –101.0 mV), by locally increased amounts of readily decomposable organic matter represented by both semidecomposed plant residues (stems, roots, and so on) and the organic compounds released by rice roots (root exudates) [2, 39].

In the leveed soils between rice paddies, methane concentrations increase from 0.013–0.018 µg/g wet soil in May to 0.026 µg/g wet soil in September 2021. In general, the methane concentration in leveed soils fits within the background concentrations characteristic of automorphic soils of the East European Plain [15]. The pH values (6.58) in leveed soils measured in September are appreciably lower as compared with the flooded soils, complying with the data on the increase in pH in the soils after flooding [40]. The Eh value in dry soils amounted to 246.7 mV, being considerably higher as compared with the flooded soils of rice paddies.

Analysis of the correlations between methane concentration and the studied physicochemical characteristics of soils for the overall data array (Fig. 3)

demonstrates a statistically significant feedback between the methane concentrations and Eh values ($r = -0.48$, $P < 0.01$). This confirms that Eh is an important factor that controls methane formation. Less pronounced and statistically insignificant direct correlations ($P > 0.05$) of methane concentrations with pH ($r = 0.30$), moisture content ($r = 0.21$), and soil density ($r = 0.13$) are also observable.

Experimental measurements show that the amount of methane emitted from rice paddy 1 varies in the seedling stage from 0.195 to 0.254 mg CH₄/(m² h) with a mean of 0.222 mg CH₄/(m² h) and in the stage of full ripeness, from 0.372 to 0.531 mg CH₄/(m² h) with a mean of 0.472 mg CH₄/(m² h). Consequently, the mean rate of methane flux in the stage of full ripeness was 2.1-fold higher as compared with the seedling stage (May). In turn, the rate of methane flux to the atmosphere from the surface of the soils separating rice paddies was on the average 4.9-fold lower in May and 12.1-fold lower in September as compared with the rate of its flux from rice paddies and amounted to 0.045 and 0.034–0.044 0.045 mg CH₄/(m² h), respectively, in May and September.

Analysis of publications ([40, 44] and references herein) and the above reported data, including the correlations, suggests that the oxidation processes that determine the minimum methane concentrations and its fluxes to the atmosphere are prevalent in the soils before flooding of paddies. After flooding, the soils isolated by a layer of water lose oxygen, which results in a decrease in the redox potential (Eh values), acti-

vation of methanogenesis, and, as a consequence, an increase in the concentration of methane in the flooded soils of rice paddies and its subsequent transfer from their surface to the atmosphere. Note that the time interval between the soil flooding and beginning of methanogenesis in different soils varies depending on soil structure and physicochemical properties; as a rule, this takes several days or weeks after flooding [40, 44].

Three mechanisms underlying the transfer of the methane formed in flooded soils to the atmosphere are known [5, 44], namely, diffusion through water layer, evolution within gas bubbles, and passive transport through the air channels in rice aerenchyma. It is believed that a larger part of methane (about 90%) enters the atmosphere via the passive transport in aerenchyma because this route allows a considerable part of methane to avoid oxidation in the soil–water system [44]. The methane bubbles formed when the pore space of flooded soil is supersaturated with methane and forcing their way to the soil surface are usually minor contributors to the transfer of methane to the atmosphere and this contribution decreases with the plant growth [30]. In the experiments described here, any bubbling was unobservable because of low methane concentrations in soils, which rules out any considerable contribution of this mechanism to the determined rate of methane flux. However, the gas transfer in the beginning of the season and in the presence of large amounts of organic matter in soils or the application as fertilizers may be an important mechanism of the methane transport to the atmosphere [30]. As for the diffusion of methane through the superjacent water layer, it is regarded as insignificant (1–2%) because the diffusion of gases through water is considerably slower as compared with the transport via the air channels of plant aerenchyma [44].

The formation of hydrogen sulfide is in general untypical of the examined rice paddies; however, single cases of appreciable $\Sigma\text{H}_2\text{S}$ concentrations (0.211 mg/g wet soil) in the 0–2-cm layer of flooded soils with a reducing situation suggests the sulfate reduction process in the upper soil layers of some plots.

The *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* [40] consolidates a large volume of information on the variation in methane emission fluxes from rice fields experimentally measured in different countries. Summing up these data demonstrates that the methane fluxes from paddy fields change from 0.02 to 99 mg $\text{CH}_4/(\text{m}^2 \text{ h})$ and considerably vary not only during the growing season, but also within a day [40]. A considerable variation range (approximately 5000-fold) is determined by strong differences of several factors controlling the rates of methane formation and emission in both space and time. In addition to climate, these factors include the types and texture of soil, its physicochemical characteristics (Eh, pH, and content of labile organic substances), rice cultivar and growth stage, flooding regime, and volume of applied organic and mineral fertilizers [40, 44, 47]. The experimentally measured

values of flux rates for the flooded chestnut soils of rice paddies in the Rostov oblast, varying in the range of 0.195–0.531 mg $\text{CH}_4/(\text{m}^2 \text{ h})$ with a mean of 0.365 mg $\text{CH}_4/(\text{m}^2 \text{ h})$, fit into the above variation range but are close to its lower limit. Note that the measured values of methane emission from the rice paddies of the Rostov oblast are in general by one order of magnitude lower as compared with its emission from the flooded soils in the rice fields of the Odessa oblast. The latter fluxes range from 0.11 to 5.9 mg $\text{CH}_4/(\text{m}^2 \text{ h})$ for southern chernozem and from 4.0 to 8.3 mg $\text{CH}_4/(\text{m}^2 \text{ h})$ for meadow–bog (gley) soils [11, 12]. Possible main causes of a lower methane emission are the differences in rice growing practices, soils, and climate of the Rostov oblast as northernmost region of rice growing in the world.

To calculate the total methane emission to the atmosphere from rice paddies of the Rostov oblast, let us use the mean rate of methane fluxes from the paddy surface, amounting to 0.365 mg $\text{CH}_4/(\text{m}^2 \text{ h})$ and the data on the area occupied by rice fields in the Rostov oblast in 2020, amounting to 14300 ha (or 143 million m^2) [23]. As is mentioned above, short flooding is used in the Rostov oblast, that is, the initial water layer is created immediately after emergence of seedlings (end of May) and is retained to the beginning of full rice ripeness (beginning of September).

According to the calculations, the total emission of methane from rice fields in the Rostov oblast amounts to 1.253 t/day (or 1800 m^3/day). Assuming that the period of methane emission from the rice fields in the Rostov oblast is on the average 120 days over a year (May to September), the annual emission is approximately 150 t (or 214000 m^3) or 0.4–1.5% of the annual methane emission from the soils of the Rostov oblast (9675–40663 t/year [4]). Presumably, this volume of the total methane emission to the atmosphere from the surface of rice paddies in the Rostov oblast is somewhat undervalued because it lacks the results of field measurements of the methane fluxes during the tillering and flowering stages, characteristic of which are the maximum seasonal rates of methane emission [47].

Recalculation of this average value, 0.365 mg $\text{CH}_4/(\text{m}^2 \text{ h})$, for the total area of rice paddies in Russia (approximately 200000 ha [19, 20]) estimates the daily methane emission from the rice fields of this country at 17.5 t and the annual emission at approximately 2100 t (or 0.0021 million tons). This value accounts for only 2.1% of the earlier calculated estimate (0.1 million tons [6]) based on the averaged values according to the measurements in the rice fields situated in other climatic zones of the world.

CONCLUSIONS

In the period of studies, the methane emission from the surface of flooded soils of rice paddies varied in the range of 0.195–0.531 mg $\text{CH}_4/(\text{m}^2 \text{ h})$ and was

on the average 2.1-fold higher at the stage of full ripeness as compared with the stage of seedlings. The rate of methane flux to the atmosphere from the surface of leveed soils, separating rice paddies, was on the average 4.9–12.1-fold lower as compared with the flux from rice paddies, varying in the range of 0.034–0.045 mg CH₄/(m² h). Oxidation processes are prevalent in the soils before flooding of the rice paddies; these processes determine low methane concentrations there as well as low fluxes to the atmosphere. After flooding of rice paddies, the soils isolated by water layer lose oxygen, which results in a decrease in the redox potential (Eh values), activation of methanogenesis, and, as a consequence, increase in the concentrations of methane in the flooded soils of rice paddies and methane fluxes to the atmosphere from their surface. According to approximate estimates, the total emission of methane from the rice fields of the Rostov oblast amounts to 1.253 t/day or 150 t/year, accounting for 0.4–1.5% of the annual methane emission by the soil in the Rostov oblast. The rates of methane fluxes from the rice fields of the Rostov oblast calculated basing on field measurements are helpful for the institutions in southern Russia involved in the inventories of greenhouse gases in agrarian area.

FUNDING

The work was supported by the Russian Science Foundation (grant no. 22-27-00671, <https://rscf.ru/project/22-27-00671/> to Southern Federal University).

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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REFERENCES

1. N. M. Bazhin, "Methane in the environment: an analytical review," in *Ecology. Series of Analytical Reviews of World Literature. Series Ecology* (Gos. Publ. Nauchno-Tekh. Bibl. Sib. Otd. Ross. Akad. Nauk, Novosibirsk, 2010), vol. 93. <https://elibrary.ru/item.asp?id=12992797>. Cited October 27, 2022.
2. D. N. Gar'kusha and Yu. A. Fedorov, "Effect of plants on processes of methane cycle in bottom deposits and soil rhizosphere," *Contemp. Probl. Ecol.* **9** (6), 771–782 (2016).
3. D. N. Gar'kusha, Yu. A. Fedorov, and N. S. Tambieva, "Methane in soils of different geographical zones of Russia," *Izv. Ross. Akad. Nauk, Ser. Geogr.*, No. 3, 47–55 (2018). <https://doi.org/10.7868/S2587556618030068>
4. D. N. Gar'kusha, Yu. A. Fedorov, R. G. Trubnik, and M. L. Krukier, "Concentration and emission of methane in different types of soils in Rostov oblast," *Voprosy Stepevedeniya*, No. 4, 13–24 (2022).
5. A. N. Gennadiev, Yu. I. Pikovskii, A. S. Tsibart, and M. A. Smirnova, "Hydrocarbons in soils: origin, composition, and behavior (review)," *Eurasian Soil Sci.* **48** (10), 1076–1089 (2015).
6. Yu. A. Izrael', I. M. Nazarov, A. I. Nakhutin, A. F. Yakovlev, and M. L. Gitarskii, "Russia's contribution to changes in the concentration of greenhouse gases in the atmosphere," *Meteorol. Gidrol.*, No. 5, 17–27 (2002).
7. V. N. Kudiyarov, "Nitrous oxide emission from fertilized soils: an analytical review," *Eurasian Soil Sci.* **53** (10), 1396–1407 (2020).
8. V. N. Kudiyarov, V. A. Demkin, D. A. Gilichinskii, S. V. Goryachkin, and V. A. Rozhkov, "Global climate changes and the soil cover," *Eurasian Soil Sci.* **42** (9), 953–966 (2009).
9. I. N. Kurganova, V. O. Lopes de Gerensh, R. Vell, N. Loftfil'd, and X. Flessa, "Gaseous losses and transformation of mineral nitrogen in arable burozem soil depending on humidity," *Agrokhimiya*, No. 10, 5–13 (2007).
10. V. V. Makarov and M. V. Sereda, "Peculiarities of agricultural technology of rice cultivation in Rostov oblast," *Nauchn. Zh. Kuban. Gos. Agrar. Univ.*, No. 79, 1–10 (2012).
11. O. I. Min'ko, S. V. Kasparov, and Ya. M. Ammosova, "Gaseous substances—metabolic products of microbial cenoses of waterlogged soils," *Zh. Obshch. Biol.* **48** (2), 182–193 (1987).
12. O. I. Min'ko, S. V. Kasparov, Ya. M. Ammosova, and N. G. Zborishchuk, "Formation of gaseous hydrocarbons by irrigated soils," *Biol. Nauki*, No. 1, 106–112 (1989).
13. I. M. Nazarov, A. I. Fridman, Sh. D. Fridman, et al., "Anthropogenic methane emissions in the CIS and Baltic countries," *Meteorol. Gidrol.*, No. 11, 15–20 (1992).
14. O. A. Oleinik, "Ameliorative state of lands of rice irrigation systems of Rostov oblast," *Nauchn. Zh. Ross. Nauchno-Issled. Inst. Probl. Melior.*, No. 4, 1–19 (2011).
15. Yu. I. Pikovskii, M. A. Smirnova, A. N. Gennadiev, Yu. A. Zavgorodnyaya, A. P. Zhidkin, R. G. Kovach, and T. S. Koshovskii, "Parameters of the native hydrocarbon status of soils in different bioclimatic zones," *Eurasian Soil Sci.* **52** (11), 1333–1346 (2019).
16. RD 52.24.511-2013. Mass Fraction of Methane in Bottom Sediments. Measurement Technique by Gas Chromatographic Method using Equilibrium Vapor Analysis (Rosgidromet, GU "Gidrokhimicheskii Institut", Rostov-on-Don, 2013).
17. RD 52.24.512-2012. Volume Concentration of Methane in Waters. Measurement Technique by Gas Chromatographic Method using Equilibrium Vapor Analysis (Rosgidromet, GU "Gidrokhimicheskii Institut", Rostov-on-Don, 2012).

18. RD 52.24.525-2011. Mass Fraction of Sulfide Sulfur in Bottom Sediments. Method for Performing Measurements by the Photometric Method with N,N-Dimethyl-p-Phenylenediamine (Rosgidromet, GU "Gidrokhimicheskii Institut", Rostov-on-Don, 2011).
19. A. A. Romanovskaya, "Emissions of methane and nitrous oxide in the agricultural sector of Russia," *Meteorol. Gidrol.*, No. 2, 87–97 (2008).
20. A. A. Romanovskaya, V. N. Korotkov, N. S. Smirnov, R. T. Karaban', and A. A. Trunov, "Estimation of the contribution of land use to anthropogenic greenhouse gas emissions in Russia during 2000–2011," *Meteorol. Gidrol.*, No. 3, 5–18 (2014).
21. Guidelines for Chemical Analysis of Land Surface Waters. Ed. by L. V. Boevaya (NOK, Rostov-on-Don, 2009), Part 1.
22. Guidelines for National Greenhouse Gas Inventories. IPCC National Greenhouse Gas Inventory Program (IPCC, Hayama, 2006). chrome-extension://efaidnbmnnnibpcajpcglclefindmkaj/https://www.ungsp.org/sites/default/files/documentos/ghg_booklet_russian_final.pdf. Cited October 27, 2022.
23. From 2017 to 2020, rice yield in the Rostov region increased by 23% (Tsentr Agroanalitiki, 2021). <https://specagro.ru/news/202106/v-rostovskoy-oblasti-aktivno-razvivaetsya-proizvodstvo-risa>. Cited October 27, 2022.
24. Yu. A. Fedorov, V. V. Sukhorukov, and R. G. Trubnik, "Analytical review: greenhouse gas emissions and absorption by soils. Ecological problems," *Antropogennaya Transformatsiya Prirodnoi Sredy* **7** (1), 6–35 (2021). <https://doi.org/10.17072/2410-8553-2021-1-6-34>
25. Yu. A. Fedorov and D. N. Gar'kusha, "Emission of methane by soils of the steppe zone of the Rostov region," *Izv. Russ. Geogr. O-va* **142** (2), 45–52 (2010).
26. Yu. A. Fedorov, N. S. Tambieva, D. N. Gar'kusha, and V. O. Khoroshevskaya, *Methane in Water Ecosystems* (ZAO Rostizdat, Rostov-on-Don, 2007) [in Russian].
27. H. Akiyama and K. Yagi, "Direct N₂O emissions from rice paddy fields: summary of available data," *Global Biogeochem. Cycles* **19**, GB1005 (2005). <https://doi.org/10.1029/2004GB002378>
28. R. Conrad, "Control of microbial methane production in wetland rice fields," *Nutr. Cycling Agroecosyst.* **64**, 59–69 (2002). <https://doi.org/10.1023/A:1021178713988>
29. R. Conrad, "The global methane cycle: recent advances in understanding the microbial processes involved," *Environ. Microbiol. Rep.* **1**, 285–292 (2009). <https://doi.org/10.1111/j.1758-2229.2009.00038.x>
30. H. A. C. Denier van der Gon and H. U. Neue, "Influence of organic matter incorporation on the methane emission from a wetland rice field," *Global Biogeochem. Cycles* **9**, 11–22 (1995).
31. Y. K. Gaihre, R. Wassmann, and G. Villegas-Pangga, "Impact of elevated temperatures on greenhouse gas emissions in rice systems: interaction with straw incorporation studied in a growth chamber experiment," *Plant Soil* **373**, 857–875 (2013). <https://doi.org/10.1007/s11104-013-1852-4>
32. D. N. Gar'kusha and V. V. Sukhorukov, "Methane emissions by reed formations on the Azov Sea coast," *OnLine J. Biol. Sci.* **19**, 286–295 (2019). <https://doi.org/10.3844/ojbsci.2019.286.295>
33. Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. IPC-IGES-OECD-IEA (Japan, 2000). <https://www.ipcc-nggip.iges.or.jp/public/gp/english>.
34. IPCC Climate Change 1996, "Scientific and technical analysis of impacts, adaptations and mitigation," in *Contribution of Working Group II to the Second Assessment Report of the Intergovernmental Panel on Climate Change* (Cambridge Univ. Press, London, 1996).
35. IPCC Climate Change 2014, "Synthesis report," in *Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* (Geneva, 2014).
36. M. A. Khalil and M. J. Shearer, "Decreasing emissions of methane from rice agriculture," *Int. Congr. Ser.* **1293**, 33–41 (2006). <https://doi.org/10.1016/j.ics.2006.03.003>
37. E. Matthews, I. Fung, and J. Lerner, "Methane emission from rice cultivation: geographic and seasonal distribution of cultivated areas and emission," *Global Biogeochem. Cycles* **5**, 3–24 (1991). <https://pubs.giss.nasa.gov/abs/ma03400p.html>. Cited October 27, 2022.
38. L. Nazaries, J. C. Murrell, P. Millard, L. Baggs, and B. K. Singh, "Methane, microbes and models: fundamental understanding of the soil methane cycle for future predictions," *Environ. Microbiol.* **15**, 2395–2417 (2013). <https://doi.org/10.1111/1462-2920.12149>
39. C. Nguyen, "Rhizodeposition of organic C by plants: mechanisms and controls," in *Sustainable Agriculture* (Springer, Dordrecht, 2009), pp. 97–123. https://doi.org/10.1007/978-90-481-2666-8_9
40. *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories: Reference Manual. Workbook*, Vol. 2: *Module 4: Agriculture*, pp. 1–20. <https://www.ipcc-nggip.iges.or.jp/public/gl/invs5c.html>.
41. M. Saunio, A. R. Stavert, B. Poulter, P. Bousquet, J. G. Canadell, et al., "The global methane budget 2000–2017," *Earth Syst. Sci.* **12**, 1561–1623 (2020). <https://doi.org/10.5194/essd-12-1561-2020>
42. J. H. Seinfeld, "Insights on global warming," *AIChE J.* **57**, 3259–3284 (2011). <https://doi.org/10.1002/aic.12780>
43. N. Serrano-Silva, Y. Sarria-Guzman, L. Dendooven, and M. Luna-Guido, "Methanogenesis and methanotrophy in soil: a review," *Pedosphere* **24**, 291–307 (2014). [https://doi.org/10.1016/S1002-0160\(14\)60016-3](https://doi.org/10.1016/S1002-0160(14)60016-3)
44. A. D. Smartt, K. R. Brye, and R. J. Norman, "Methane emissions from rice production in the United States: a review of controlling factors and summary of research," in *Greenhouse Gases* (In-Tech, London, 2016), Ch. 8, pp. 179–207. <https://doi.org/10.5772/62025>
45. A. J. Wallenius, P. Martins Dalcin, C. P. Slomp, and M. S. M. Jetten, "Anthropogenic and environmental constraints on the microbial methane cycle in coastal Sediments," *Front. Microbiol.* **12**, p. 631621 (2021). <https://doi.org/10.3389/fmicb.2021.631621>
46. Z. P. Wang, R. D. Delaune, W. H. Jr. Patrick, and P. H. Masscheleyn, "Soil redox and pH effects on methane production in a flooded rice soil," *Soil Sci. Soc. Am. J.* **57**, 382–385 (2009). <https://doi.org/10.2136/sssaj1993.03615995005700020016x>
47. Z.-Y. Wang, Y.-C. Xu, Z. Li, Y.-X. Guo, R. Wassmann, H. U. Nene, R. S. Lantin, and L. V. Buendia, "Methane emission from irrigated rice fields and its control," *Acta Agron. Sin.* **27**, 757–768 (2001).

Translated by G. Chirikova