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EXPERIMENTAL ARTICLES

Biogeochemical Processes of Methane Cycle in the Soils, Bogs, and Lakes of Western Siberia

V. F. Gal'chenko*, [1], L. E. Dulov*, B. Cramer, N. I. Konova***, and S. V. Barysheva*****

**Institute of Microbiology, Russian Academy of Sciences, pl. 60-letiya Oktyabrya 7, k. 2, Moscow, 117811 Russia*

***Federal Institute for Geosciences and Natural Resources, Hannover, Germany*

****All-Russia Research Institute of Geosystems, Moscow, Russia*

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Abstract—The biogeochemical processes of methane production and oxidation were studied in the upper horizons of tundra and taiga soils and raised bogs and lake bottom sediments near the Tarko-Sale gas field in western Siberia. Both in dry and water-logged soils, the total methane concentration (in soil particles and gaseous phase) was an order of magnitude higher than in the soil gaseous phase alone (22 and 1.1 nl/cm^3, respectively). In bogs and lake bottom sediments methane concentration was as high as 11 μl/cm^3. Acetate was the major precursor of the newly formed methane. The rate of aceticlastic methanogenesis reached 55 ng C/(cm^3 day), whereas that of autotrophic methanogenesis was an order of magnitude lower. The most active methane production and oxidation were observed in bogs and lake sediments, where the $\delta^{13}C$ values of CO_2 were inversely related to the intensity of bacterial methane oxidation. Methane diffusing from bogs and lake bottom sediments showed $\delta^{13}C$ values ranging from –78 to –47‰, whereas the $\delta^{13}C$ value of carbon dioxide ranged from –18 to –1‰. In these ecosystems, methane emission comprised from 3 to 206 mg CH_4/(m^2 day). Conversely, the dry and water-logged soils of the tundra and taiga took up atmospheric methane at a rate varying from 0.3 to 5.3 mg CH_4/(m^2 day). Methane consumption in soils was of biological nature. This was confirmed by the radioisotopic method and chamber experiments, in which weighting of methane carbon was observed (the $\delta^{13}C$ value changed from –51 to –41‰).

Key words: methane oxidation, methane production, bacterial CO_2 assimilation, carbon isotopic composition, tundra, boreal ecosystems.

Methane is one of the most important greenhouse gases, whose concentration increases by 1% yearly [1]. About 80% of the methane entering the atmosphere is formed in the course of modern methanogenesis [2]. Marine and lake ecosystems contribute little methane to the atmosphere because methanotrophs are a powerful bacterial filter that prevents methane flux [3]. Terrestrial water-logged ecosystems are believed to be the major sources of atmospheric methane [4], whose emission is temperature-controlled and depends on the degree of flooding, amount of the organic matter, vegetation, and the processes of methanogesis and methane oxidation [5–8]. In different ecosystems, these factors differ in their importance. Because of a lack of information, none of the mechanisms suggested can be claimed today as the main one controlling methane cycling in terrestrial ecosystems and the methane flux between the soil and the atmosphere [7–9].

The boreal and subarctic water-logged landscapes of western Siberia are considered to be a major source of atmospheric methane [2]. Moreover, the large natural gas fields located here may contribute, via methane diffusion, to the methane flux into the atmosphere. However, the scarce biogeochemical and microbiological data obtained for this area are inconclusive to adequately estimate the contribution of the buried and newly formed methane to the global budget of atmospheric methane [10, 11].

In this study, we aimed at evaluating the intensity and distribution of bacterial methanogenesis and methane oxidation in various boreal ecosystems of western Siberia.

MATERIALS AND METHODS

Our studies were performed from July 25 through August 9, 1995 in the territory of both the western (TS) and eastern (ETS) Tarko-Sale gas fields (Tarko-Sale, Tyumen oblast; 64°47′–65°11′ N, 76°58′–78°10′ E). This territory includes extremely diverse ecosystems. These ecosystems are soils, bogs, and lakes of the southern dwarf shrub, lichen, and forest tundra, and open forests of the northern taiga. We have classified the ecosystems studied into five groups (Table 1).

Dry soils had no surface aquiferous horizons. The upper layer was 2- to 7-cm-thick dry litter with the content of organic matter (OM) ranging from 34 to 43%;

[1] Corresponding author; e-mail: valgalch@inmi.da.ru

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beneath, there were podzolic horizons (OM < 1%). The TS5 and ETS9 stations were situated in tundra and forest tundra, respectively, on illuvial-ferrous sandy podzolic soils completely covered with lichen (*Cladonia, Cetraria*). The TS18, TS20, ETS3, and ETS18 stations were situated in the mixed forests (*Pinus silvestris, P. sibirica, Larix sibirica, Betula pubescens*) of high river floodplains, where soils were sandy and slightly podzolic, or in meadows with alluvial detritus covered with thin grass. The TS8 station was situated on the outskirts of a mixed forest with alluvial-gley soil and green moss on the surface.

Water-logged soils contain nearsurface aquiferous horizons. The upper 30 to 60 cm (OM, 40–46%) were peat horizons, and gleyed horizons or frozen lake clay (OM < 1%) were beneath. The TS1 and ETS13 stations were situated in the dwarf-shrub tundra covered mostly with marsh tea (*Ledum palustre*), blueberry (*Vaccinium uliginosum*), whortleberry (*V. vitis-idea*) and *Andromeda polifolia*. The soils were frozen peat with the upper five to seven centimeters consisting of lichen and moss waste. The TS6 station occupied a similar plot 50 cm from the lake shore; however, it contained no frozen horizons. The TS11 station was situated on a sphagnous peat bog with dwarf birch (*Betula nana*) thickets.

Bogs. These were raised bogs filled with water and covered with various mosses, mostly sphagnum (*Sphagnum*) contaminated with sedge (*Carex*) and cotton grass (*Eriophorum*). Half-decayed moss and peat with a sandy underlayer were beneath. The vegetation and degree of flooding of the surface horizon varied.

Dry bogs. These stations were situated on high, temporarily dried out sphagnum bogs covered with sphagnum (*Sphagnum*), cotton grass (*Eriophorum*), cloudberry (*Rubus chamaemorus*), blueberry (*Vaccinium uliginosum*), and lichen. Sometimes, separate groves of dwarf birch (*Betula nana*), marsh tea (*Ledum palustre*), and sedge (*Carex*) were encountered. The upper 0–5 cm of soil were thickened brown peat passing into nearly black peat, which was more compact. Gray sand was found 20 cm deeper. A pit with a soil section was filled with water in an hour.

Mossy hillock examined the station ETS6 represented a specific ecosystem unique from the former ones. The upper 0–5 cm of the hillock was dry whitish sphagnum with a layer of gray-yellow half-decayed sphagnum was beneath. At a depth of 40–55 cm, dark brown peat was revealed with a gray sandy underlayer.

Lakes. Most lakes in the region examined were large but shallow water bodies (from one to three meters in depth) with peaty or sandy bottom. Dystrophic lakes with a high content of humus prevailed. They contained no fish or other mega- or mesofauna. The TS-S and ETS-S stations were situated in the littoral zones of these lakes.

Some lakes of the Tarko-Sale region had prominent specific features. Unlike most water bodies, which were dark brown or black on aerial photographs, these lakes were blue. Lake Yaganto, situated in the western Tarko-Sale region, is one of such lakes. It is an oligotrophic lake, probably of a recent thermokarst origin. Lake water and sediments were almost free of terrigenous humus, and well-washed sand constituted its bottom. A unique feature was the large amount of fish inhabiting this lake. Here, the BS-S1 and BS-S2 stations were situated on the littoral and in the center of the lake, respectively.

The redox potential and pH values were measured with a pH-150 portable potentiometer, and the temperature was measured with a thermoresistor thermometer. The oxygen content of the water was determined using an Aquamerck Kit (Merck) by the Winkler method.

Methane and hydrocarbon gas concentrations were estimated by the desorption method described previously [12–14]. For this purpose, we used Balch glass tubes 30 cm^3 in volume (Bellco Glass, United States) containing 5 g NaCl and 1 g KOH. The tubes were filled with water or ground samples (distilled water was added to dry samples), leaving 2–3 cm^3 for the gaseous phase. After immediate closing with a plug of gas-impermiable rubber (Bellco Glass, United States), the tubes were agitated thoroughly. In the laboratory, the gaseous phase was analyzed on a M-3700 chromatograph (AO Khromatograf, Russia) equipped with a flame-ionization detector. The column was 3 m long with a 3 mm inner diameter, the sorbent was Porapak Q 80/100 (Serva), the carrier gas was argon, the column temperature was 40°C, and the evaporator and detector temperature was 100°C.

In dry soils, the content of methane was determined by both the desorption and evacuation methods. In the latter case, a Schmidt tube was used to sample gas from a certain depth into a special evacuated vessel (100 cm^3) with an airtight stopcock. The methane concentration was determined as described above.

The total content of mineral carbon (C_{min}) was estimated by the desorption method as in the case with methane; however, 1 ml of H_3PO_4 was added instead of alkali. The content of CO_2 concentrated in the gaseous phase of the tube was measured under the same conditions as that of methane on a M-3700 chromatograph with a thermal conductivity detector. The content of H_2 was simultaneously measured on a column of the same size with MolSeive 5A sorbent (Supelco, United States). Concentrations of H_2, CH_4, and other hydrocarbon gases were calculated on the basis of chromatographic analyses and from the ratio between the sample and the gaseous phase in the tube.

Acetate was determined by gas–liquid chromatography with preliminary sample distillation and concentration [16]. For this purpose, the tubes in which the methane content had been determined were centrifuged (5 min, 4000*g*). The supernatant obtained was placed in a distiller with a direct condenser and, after the addition of H_3PO_4 up to pH < 2, it was boiled. A condensate volume exceeding that of the aliquot by ten times was

Table 1. Biogeochemical parameters of the ecosystems studied

Station	Horizon sampled		Content						Intensity of processes, ng C/(cm^3 day)						CH_4 emission, mg CH_4/(m^2 day)*
			nl/cm^3				μg/cm^3		methanogenesis		oxidation			CO_2 assimilation	
	name	cm	H_2	CH_4	C_2H_4	C_2H_6	acetate	C_{min}	autotrophic ($H_2 + CO_2$)	aceticlastic	$CH_4 \longrightarrow CO_2$	$CH_4 \longrightarrow C_{org}$	Acetate $\longrightarrow CO_2$		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
DRY SOILS															
TS5	A0	0–2	106	14.2	1.8	0.07	148	18.8	0	0	0	0	–	43	–4.90
	B1	45–50	85	3.2	0.2	0	33	30.0	0	0	0.016	0	–	29	
	B2	80–85	0	3.9	0.2	0	12	20.2	0	0.1	0.014	0	–	11	
TS8	A0	0–5	66	6.7	0.7	0.19	681	3.8	0	0	0.247	0.032	1782	0	–2.54
	B1	10–15	11	3.2	1.3	0	24	12.9	–	–	–	–	–	–	
	Bg	95–99	76	3.2	0.2	0	33	17.7	0	0.1	0.001	0.0006	147	0	
TS18	A0	0–3	107	4.0	0.9	0	110	59.0	0	0	0	0	152	0	–1.66
TS20	A0	0–3	71	–	–	–	312	23.8	0	0	0	0	64	23	–2.46
ETS3	Ad	0–5	144	21.9	0.4	0.08	167	15.1	0	0	0	0.002	448	132	–2.89
ETS9	A0	0–2	6	1.8	0.2	0	271	0.86	0	0	0.0026	0.0011	0	0.5	–2.02
ETS18	A0	0–2	131	5.2	2.7	0	208	20.5	0	0	0	0	0	7	–3.72
WATER-LOGGED SOILS															
TS1	O2	7–9	95	13.3	0.9	0.01	29	4.9	0	0.2	0.0014	0	18	0	–4.00
	O2	20–24	5	8.3	0.5	0	100	4.9	0	4.6	0.015	0.002	20	0	
	O2	30–32	7	9.4	2.0	0	66	14.3	0	8.9	0.016	0.002	73	14	
TS6	O1	5–10	4	2.4	0.4	0	15	3.4	0	0.1	0.012	0	753	6	2.93
	A0	35–40	2	94.0	1.4	0	21	1.7	0	–	–	–	–	15	
	G	55–60	0	4600	1.4	0	12	5.4	0	5.1	0.0001	0	4	14	
TS11	O1	0–10	13	1.3	0.8	0	346	5.3	0	55.3	0.014	0	863	12	–0.32
	O2	15–20	33	2.8	3.0	0.02	106	5.8	0	2.5	0	0	229	17	
	O2	25–30	11	2.7	1.9	0	40	12.7	0	14.6	0.0023	0.0003	180	33	
ETS13	O1	0–2	45	2.6	1.5	0	60	1.8	0.01	0.19	0.11	0	–	4	–0.56
BOGS															
TS3	Sph	0–2	0	39	0	0	9	1.3	0	0.2	0.012	0.002	22.6	9	33.60
	Sph-W	35–40	0	6200	0	0	15	3.4	0	3.0	2.3	0	90.5	0.4	
TS-B1	Sph	0–2	0	1020	0	0	10	1.7	0	0	0.296	0.12	45.0	6	
	Sph-W	35–40	0	9770	0	0	15	3.8	3.6	24.8	8.75	0	88.8	0.5	
TS-B2	Water	0–5	0	158	0	0	5	0.9	0	0	0.06	0.032	33.4	0.4	
	Sph-W	5–10	0	1920	0	0	26	5.5	0.1	4.7	2.18	0.78	38.1	43	
	Peat-W	40–45	0	3640	0	0	20	2.3	0	2.0	5.34	0	74.4	8	
TS-B3	Water	0–2	0	18	0	0	4	1.7	0.3	0.04	2.02	0	11.7	6	
	Sph-Peat	40–45	0	3870	0	0	17	4.3	4.6	0.1	23.7	27.0	62.7	0	
TS-B4	Sph-W	0–2	0	3040	0	0	7	1.7	0.2	0	0.69	0	45.7	19	
	Sph-Peat	35–40	0	8720	0	0	31	6.4	0	0	3.63	4.1	97.3	17	
TS15	Sph	0–2	0	2190	0	0	12	3.9	0	1.8	0.001	0.0005	21.5	0.2	75.00
	Sph-W	35–40	0	5340	0	0	25	9.3	0	0	0.002	0	58.1	4	

Table 1. (Contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
ETS-B	Water	0–2	0	3	0	0	8	1.1	0	0	1.3	1.0	36.5	7	
	Sph-W	35–40	0	1	0	0	7	1.3	0	0	0.002	0.001	450.0	1	
	Sand	50–55	0	2610	0.8	0.8	30	2.4	0.8	0	10.4	4.3	49.1	11	
ETS8	Sph-W	0–2	0	2	0	0	8	1.6	0	0	0.001	0.001	57.4	1	135.71
	Sph-Peat	35–40	0	4400	0.4	0	44	–	0.9	0	11.1	4.4	96.7	11	
DRY BOGS															
TS19	Peat	0–5	2	53	0.1	0	110	5.0	0	1.8	0.143	0.044	291	19	66.58
	Peat	30–35	0	3130	3.2	0.05	100	7.0	0	0	0.422	0	381	19	
ETS10	Peat	3–5	0	2400	0.9	0	96	1.6	0	0	10.7	0.8	214	15	38.20
	Peat	12–14	0	2400	2.2	0	53	4.5	0	0	0.21	1.69	115	5	
	Sand	20–25	0	3300	0.2	0.2	12	2.6	0	0	0.13	2.17	–	0	
ETS11	Sph-Peat	5–10	0	8530	1.5	0	148	1.6	0	0	65.6	11.3	365	8	37.14
	Sph-Peat	30–35	0	10940	1.4	0	52	1.6	0	0	18.8	3.5	243	0.6	
	Sand	55–60	0	8690	2.3	0	66	2.6	0.1	0	2.8	1.3	507	11	
LAKES															
TS-S	Water	0–5	0	2.2	0	0	3	0.6	0	0	0.002	0	58.5	0.2	
	Water	70–75	0	1.3	0	0	3	1.5	0	0	0.001	0	24.1	2.0	
	Sand-Peat	0–10	0	3040	5.5	0	25	3.2	2.8	0	0.15	0	4.7	10.9	
ETS-S	Water	0–5	0	0.2	0	0	3	0.5	0	0	0.001	0	18.3	0.7	
	Water	55–60	0	0.4	0	0	6	0.3	0	0	0.0003	0.0002	35.7	0	
	Sand-Peat	0–5	0	1.5	0	0	9	1.4	0	0.1	0.012	0	42.4	1.2	
	Sand-Peat	20–25	0	1780	0.4	0	19	2.6	0	1.2	1.15	0	48.9	3.3	
	Peat-Sand	30–35	24	1800	0.5	0	28	2.1	3.1	2.9	6.49	0.08	17.3	1.2	
BS-S1	Water	0–5	0	0.4	0	0	2	1.9	0	0	0	0.0002	23.5	0	
	Water	125	0	0.9	0	0	4	1.5	0	0	0.0004	0.0006	36.9	0.6	
	BM-Sand	0–2	0	6	0	0	–	–	0	0	0.022	0.23	–	2.7	
BS-S2	Water	55–60	0	1	0	0	8	0.3	0	0	0	0.001	82.0	0	3.50**
	Sand	0–5	0	4940	0	0	73	2.6	0	3.2	3.52	0	200.0	9.2	
	Sand	20–30	9	5130	0	0	40	8.0	0.1	0.4	0.138	0	61.8	1.7	
MOSS HILLOCK															
ETS6	Sph	0–5	6	2.7	0.1	0	128	2.8	0.3	0.2	0.0009	0.0002	661	13	–2.07
	Sph	35–40	9	1.9	0.1	0	46	1.0	0	0	0.0014	0.0004	235	1	
	Sand	55–60	19	3.8	1.5	0	95	7.9	0.3	0	0.075	0.0116	256	24	

Note: Sph is sphagnum; W is water; BM means bacterial mats.

* Chamber measurements.

** Mean of two repeated measurements (±0.35) on adjacent plots.

made alkaline by the addition of KOH to reach a pH of 8–9 and evaporated at 60°C until dry. The precipitate was dissolved in 0.5 ml of a 10% H_3PO_4 solution and the acetate concentration was determined as it was for methane at a column temperature of 170°C and at evaporator and detector temperatures of 230°C.

The radioisotopic method was used to evaluate the intensity of bacterial processes [12–14]. Soil samples (7 cm^3) were placed into glass tubes, which were airtight and closed with plugs of butyl rubber. Water was sampled into Balch glass tubes of 30 cm^3 in volume. Samples were supplemented with 100 µl of aqueous solutions of U-^{14}C-cellulose (0.05 MBq; 20 MBq/mg NEN, United States), $NaH^{14}CO_3$ (0.25 MBq; 0.8 GBq/mmol), $^{14}CH_3COONa$ (0.15 MBq; 1.6 GBq/mmol), $^{14}CH_4$ (0.08 MBq; 1.2 GBq/mmol), $^{14}CH_3OH$ (0.05 MBq; 0.13 GBq/mmol), or $^{14}CH_3NH_2$ (0.08 MBq; 1.6 GBq/mmol) (V/O Izotop, Russia). The sample

incubation for 72–96 h at an in situ temperature was followed by fixation with 2 ml of 1N KOH solution or with 2 ml of 80% solution of H_3PO_4 in the case where $^{14}CH_3NH_2$ had been used as the labeled substrate.

Isolation of the ^{14}C-products formed was carried out with a special device by the method described in [12–15]. For extraction of gaseous components, the samples were placed in flasks with a reflux condenser, heated to 80–90°C, and blown with air. The radioactive methane released was burned to CO_2 in an oven over a catalyst (silica gel impregnated with $CoCl_2$) and trapped with a 10% solution of 2-phenylethylamine (Koch-Light, United Kingdom) in the toluol-containing scintillation liquid ZhS-106 (Joint-stock company Monokristall, Ukraine). When methane was distilled from the samples containing ^{14}C-acetate and ^{14}C-methanol, acetone was added to a concentration of 10% to reduce the evaporation of these substances. After methane removal, concentrated H_3PO_4 was fractionally added to the flasks and $^{14}CO_2$ was driven off with an air flow. Carbon dioxide was trapped with a 10% solution of 2-phenylethylamine in ZhS-106. The samples containing ^{14}C-methylamine were treated using two successive traps with a solution of 2-phenylethylamine: $^{14}CO_2$ was trapped by the trap ahead of the oven with the catalyst, whereas $^{14}CH_4$ oxidized to $^{14}CO_2$ was trapped by another trap after the oven with the catalyst. In samples supplemented with ^{14}C-methane and ^{14}C-carbonate, ^{14}C-incorporation into organic compounds was determined after removal of volatile products. For this purpose, we used the method of wet combustion of organic matter to $^{14}CO_2$ in the presence of $K_2S_3O_8$ (15g/150ml) at 100–105°C. Radioactivity was determined on a RackBeta 1219 scintillation counter (LKB, Sweden).

The intensity of the processes was calculated from the formula: $I = rC/Rt$, where I is the intensity of a process (ng C/(cm^3 day)); r is the activity of the radioisotopic compounds added (cpm); and C is the concentration of substrate (ng C/cm^3); R is the activity of the radio labeled substrate introduced (cpm); t is the incubation time (days). During ^{14}C-substrate degradation, the respiration index was calculated as the ratio of the $^{14}CO_2$ formed to the sum of $^{14}CO_2$ and $^{14}CH_4$.

Methane flux from the ecosystems studied was determined using Plexiglas chambers 30 cm in height and 50 cm in diameter. The chamber content was sampled with evacuated tubes (100 cm^3) with airtight stopcocks in the same manner as methane was sampled with a Schmidt tube. The stable isotope compositions of methane and CO_2 carbon was determined by IR-mass-spectrometry [17, 18].

For the correlation analysis, STATISTICA 4.3 was used (Moscow Economic and Statistic Institute).

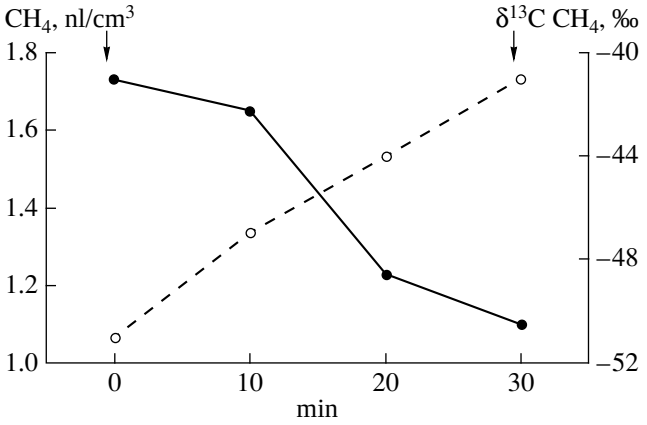

Fig. 1. Changes in the concentration and $\delta^{13}C$ value of methane determined in a static chamber (TS16 chamber, dry soil) during a short-term experiment.

RESULTS

Physicochemical Parameters

The soil surface temperature depended on the air temperature and varied from 10 to 30°C. In the near-surface horizons (5–10 cm), it decreased to 4–10°C and then remained almost unchanged down to a depth of 100 cm. Bog and lake temperatures were virtually the same (13–24°C) through the entire vertical profile studied. Acid pH values were characteristic of all of the ecosystems studied (usually, 3.8–4.8). Lower pH were determined in wetland soils (3–3.7); the pH of dry soils and of an oligotrophic lake was 5–6.4. The soil redox potential (Eh) ranged from +310 to +490 mV and reached +190 mV in the lower horizons of the bogs and lake sediments. No oxygen was detected here, whereas in the upper horizons, the oxygen concentration was 5–9 mg/l.

Near the stations examined, the atmospheric methane concentration was 1.7 nl/cm^3 at a height of 2.5 m above the soil surface. In the gaseous phase of dry soils, it varied within a range of 0.6–1.1 nl/cm^3 at a depth of 10 cm. However, as determined by the desorption method, the total content of methane in these soils was an order of magnitude higher, from 1.8 to 21.9 nl/cm^3 (Table 1). The bulk of methane is obviously adsorbed by soil particles rather than concentrated in the soil gaseous phase. Methane concentrations in water-logged soils were similar, except for the TS6 coastal station, where they increased with depth to 4600 nl/cm^3. The maximal methane concentration was determined in the lower horizons of bogs (including dry bogs) and lake bottom sediments (from 1780 to 10940 nl/cm^3). Gas samples taken from these horizons contained 25 to 80% methane. In lake water, the methane concentration was lower than in the atmosphere.

In addition to methane, C_2–C_5 hydrocarbons, mainly ethylene and ethane, were revealed in soils, dry bogs, and lake bottom sediments (up to 5.5 and

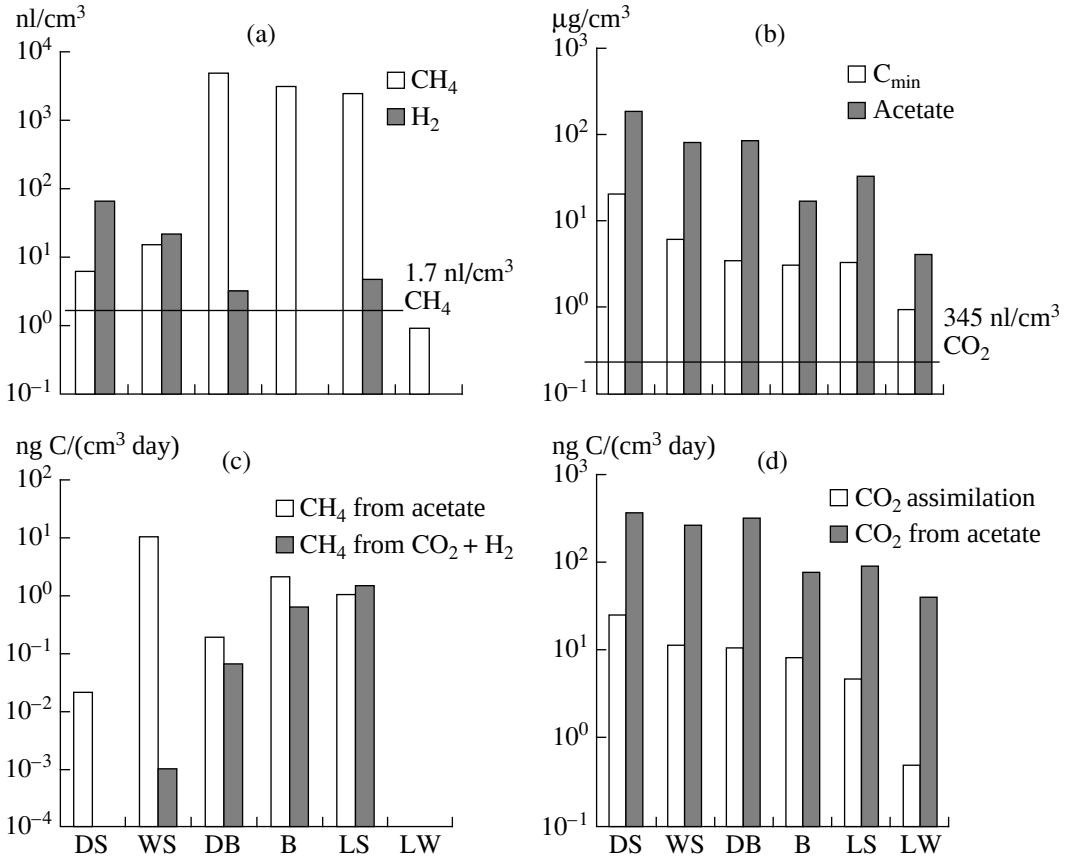

Fig. 2. Mean values of compound concentrations and process intensities in ecosystems. (a) Methane and hydrogen concentrations; (b) mineral carbon, C_{min}, and acetate concentrations; (c) intensity of methanogenesis from acetate and $CO_2 + H_2$; (d) intensity of dark CO_2 assimilation and acetate oxidation to CO_2. DS, dry soils; WS, water-logged soils; DB, dry bogs; B, bogs; LS, lake sediments; LW, lake water. In Fig. 2a and 2b, concentrations of methane and CO_2 in the air are indicated.

0.8 nl/cm^3, respectively). In these ecosystems, hydrogen was also detected, and maximal concentrations of hydrogen (up to 144 nl/cm^3) were determined in the humus horizons of dry soils. In lake bottom sediments, the content of H_2 reached 9–24 nl/cm^3; no hydrogen was revealed in bogs.

The content of mineral carbon, C_{min}, ranged from 0.3 to 59 μg/cm^3. The maximal values were determined in dry soils despite the great variations observed here. In bogs, including dry ones, and in lake sediments, mineral carbon concentrations ranged from 0.9 to 14.3 μg/cm^3. C_{min} concentrations increased with depth, especially when passing from peat into mineralized horizons. Gas samples taken from these horizons contained from 1 to 8% CO_2. Minimal C_{min} values were characteristic of the lake water: 0.3–3.6 μg/cm^3.

The maximal acetate concentrations were determined in the surface horizons of dry soils (110–681 μg/cm^3); in subsurface and bottom horizons, they were an order of magnitude lower. A similar acetate distribution was revealed in water-logged soils and dry bogs. Conversely, acetate concentration increased with depth (up to 15–73 μg/cm^3) in common bogs and lake bottom sediments. In surface horizons, it ranged from 5 to 12 μg/cm^3. Minimal acetate concentrations were determined in lake water: 2–6 μg/cm^3.

Intensity of Biogeochemical Processes

The most active methanogenesis was revealed in bottom horizons of bogs and lake sediments (the autotrophic process, 4.6–5.2 ng C/(cm^3 day); the aceticlastic one, 3.2–24.8 ng C/(cm^3 day)). No methanogenesis occurred in the surface horizons of these ecosystems, as well as in most other ecosystems. An exception was water-logged soils, where aceticlastic methanogenesis occurred in all horizons; its intensity ranged from 0.1 to 55 ng C/(cm^3 day).

Carbon dioxide was the main product of bacterial methane oxidation; no more than 5–8% of carbon was converted into organic substance. In bogs and lake sediments, the intensity of methane oxidation was maximal, and ranging from 6.6 to 77 ng C/(cm^3 day), whereas in soils and lake water, the rate of this process did not exceed 0.28 and 0.002 ng C/(cm^3 day), respectively.

Dark CO_2 assimilation ranged from 0 to 132 ng C/(cm^3 day) in soils, bogs, and lake bottom

sediments. In lake water, it did not exceed 2 ng C/cm^3 per day. The rate of acetate oxidation to CO_2 varied from 0 to 1782 ng C/(cm^3 day). Note that the maximal and minimal values of this process were determined in dry soils. In lake water, the rate of acetate oxidation was no more than 82 ng C/(cm^3 day). In other ecosystems, it ranged from 216 to 863 ng C/(cm^3 day).

An uptake of atmospheric methane by soils, both dry and water-logged, was determined by the chamber method, ranging from 0.3 to 5.3 mg CH_4/(m^2 day) (Table 1). Note that the rate of CH_4 uptake depended neither on soil type nor on vegetation type. In other ecosystems, methane emission into the atmosphere varied from 3 to 206 mg CH_4/(m^2 day). Minimal CH_4 emission was characteristic of the lake littorals, and the maximal values were determined in bogs. The results of chamber experiments, including those obtained from stations not listed in Table 1, will be published later in more detail.

Stable Isotopic Composition of Carbon

Atmospheric methane sampled at a height of 2.5 m over the land surface showed $\delta^{13}C$ values of –47…–46‰. In the surface air of dry and water-logged soils, methane carbon became heavier with time, from –51 to –41 and to –44‰, respectively (Fig. 1), as determined by the chamber method. In bottom horizon gas stores of both bogs and lake sediments, the $\delta^{13}C$ values of methane ranged from –72 to –61‰, whereas in the upper horizons and surface air of these ecosystems, this parameter ranged from –78 to –47‰.

The carbon isotopic composition of the atmospheric CO_2 varied within a narrow range of $\delta^{13}C$ values, from –7 to –6‰. In the air above the soil and in the bottom horizon gaseous phase of bogs and lake bottom sediments, a wider range of values were observed, from –18 to –1‰. In the air above the soil, the chamber method revealed a range of CO_2 $\delta^{13}C$ values of –16 to –1‰. In dry soils, the values were in the range from –16 to –12‰. A value of –25‰ was determined for the organic matter of lake bottom sediments.

DISCUSSION

We have examined almost all ecosystems intrinsic to the area examined except for the rivers and human habitats. Therefore, the results obtained characterize, to a considerable extent, the biogeochemical processes of the methane cycle in this territory.

We have studied only the upper horizons of ecosystems where aerobic degradation of the organic matter prevails. In most cases, acetate, which was used to analyze heterotrophic processes, was actively oxidized to CO_2 with a respiration index of approximately one during the process. The concentration of acetate correlated positively with the intensity of its oxidation ($r = 0.70$; $p < 0.05$; $n = 65$), which suggests that this process may be substrate-limited. High acetate concentration and the presence of hydrogen in the upper horizons indicate that anaerobic degradation of the organic compounds occurs here along with aerobic oxidation. Both products are likely formed during the fermentation of organic compounds, which is confirmed by the positive correlation between their concentrations ($r = 0.45$; $p < 0.05$; $n = 65$).

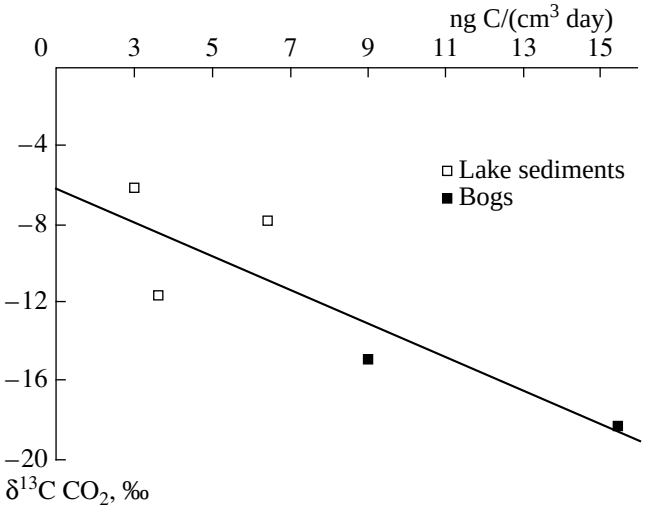

Fig. 3. Correlation between the $\delta^{13}C$ values of CO_2 in bottom horizons of bogs and lake sediments and the intensities of methane oxidation.

Note that the acetate concentrations revealed in our work are a rare phenomenon, although natural ecosystems with acetate concentrations as high as hundreds of micrograms per cm^3 have previously been described [19]. The high acetate concentrations, as well as high hydrogen concentrations, that we recorded in some samples, may be explained by the tough preliminary treatment of the samples, which resulted in the desorption of acetate and H_2 from the organomineral particles, as it occurred, according to our data, with methane in dry soils.

In the ecosystems studied, the content of methane varied within a range of five orders of magnitude (Fig. 2a). In the upper horizons, methanogenesis of low intensity was only periodically detected and, therefore, it cannot be responsible for the high content of methane in the environment. In most cases, aceticlastic methanogenesis prevailed (Fig. 2c), which is undoubtedly associated with the high content of acetate (Fig. 2b). However, no correlation between these parameters was found, because the bulk of the acetate was oxidized through aerobic processes.

Autotrophic methanogenesis was from one to three orders of magnitude lower in intensity than the aceticlastic process (Fig. 2c). In most cases, hydrogen is the limiting factor in autotrophic methanogenesis in natural ecosystems. However, in the ecosystems we examined, it was not of crucial importance. Hydrogen was detected in half of the samples studied, but an inverse correlation was observed between its concentration and

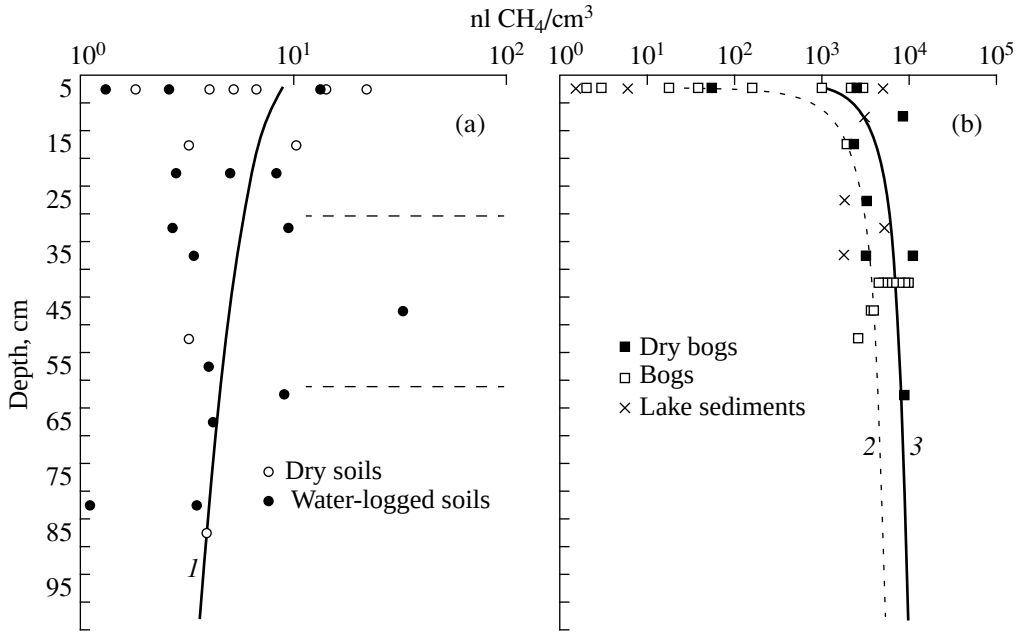

Fig. 4. Vertical profile of methane concentrations in (a) soils and in (b) bog and lake sediments. Trend lines are indicated: (*1*) that common for dry and water-logged soils and those for bog and lake sediments with (*2*) loose and (*3*) compact horizons. Horizontal lines indicate the depth range for the upper boundary of water-bearing horizons in water-logged soils.

the methane content ($r = –0.29$; $p < 0.05$; $n = 65$). The deficiency of mineral carbon is a more probable limiting factor in autotrophic methanogenesis in the ecosystems studied. Low pH prevents carbonate accumulation in these ecosystems. Because of this, the average concentrations of mineral carbon, including insoluble compounds unavailable for microorganisms, are only one to two oders of magnitude higher than the atmospheric CO_2 concentration (Fig. 2b). In this situation, the autotrophic methanogens and microorganisms involved in other biogeochemical processes probably compete in carbon dioxide consumption. Bacterial dark CO_2 assimilation, characterized by one to four orders of magnitude higher intensity than that of autotrophic methanogenesis, may be one of such competitive processes (Fig. 2d). However, we failed to reveal any correlation between the intensities of the processes discussed.

Methane can also be formed from methanol and methylamine, although the contribution of these substrates to methanogenesis was previously found to be insignificant in lake sediments and peatland soils [20, 21]. We also performed experiments with ^{14}C-methanol, ^{14}C-methylamine, and ^{14}C-U-cellulose in the ecosystems examined. Because of the lack of data concerning the concentrations of these compounds in the environments studied, we were unable to calculate the intensities of the processes. Nevertheless, all three substrates were readily oxidized to $^{14}CO_2$, with a respiration index of approximately one during their degradation. Thus, the high methane concentrations detected under the conditions of low-intensity methanogenesis cannot be explained by the fact that some substrates were not taken into sufficient account as the methane precursors.

The spatial distribution of methane concentrations in the ecosystems studied probably depends on the location of their anaerobic zones. In bogs and lake sediments, anaerobiosis increases with depth. Accordingly, the concentrations of methane, acetate, and carbon dioxide also increase with depth, as well as the intensities of bacterial processes. Sidorov *et al.* have established that a sharp increase in the intensity of methanogenesis occurs at the interface of peat and mineralized horizons [22]. We have also observed this phenomenon. Nevertheless, the main part of methane is probably formed in deeper horizons, which have more anaerobic conditions.

Methane produced within the deep horizons of bogs and lake sediments diffuses to the surface, where it undergoes bacterial oxidation. As determined by radioisotopic methods, this process was most intense at the boundary between the aerobic and anaerobic zones, where the methane concentration is maximal. This is also confirmed by a direct correlation between methane oxidation intensity and lightening of stable isotopic composition of CO_2 determined in the deepest horizons of the bogs and lakes examined (Fig. 3).

The stable isotopic composition of methane is also altered in the course of biological methane oxidation. In the surface horizons, the residual methane was from 4 to 18‰ heavier than in the underlying layers. Nevertheless, we failed to reveal a usual CO_2 carbon lightening in the surface horizons of bogs and lake sediments. Under conditions of mineral carbon deficiency, the

Table 2. Mean values of biogeochemical parameters in the ecosystems studied

Ecosystem	CH_4	H_2	Acetate	CH_4 production	CH_4 oxidation	CO_2 assimilation	CH_4 emission
	nl/cm^3		μg/cm^3	ng C/(cm^3 day)			mg C/(m^2 day)
Dry soils	8	82	197	0.01	0.015	27	–2.9
Water-logged soils	395	25	76	7.7	0.03	10	–0.5
Bogs	3545	0	18	3.2	10	8	+81.4
Dry bogs	4560	0.3	83	0.3	13	11	+47.3
Lake sediments	2319	3	25	1.8	1.2	5	ND
Moss hillock	3	11	90	0.27	0.003	13	–2.1
Bog water	60	0	6	0.1	1.5	5	ND
Lake water	1	0	5	0	0.001	0.4	+3.5

$\delta^{13}C$ value of CO_2 is most probably determined by the ratio between methane formation and consumption. In the upper horizons of the ecosystems studied, along with methane oxidation, the source of carbon dioxide was the heterotrophic degradation of the organic matter, which was accompanied by intense CO_2 consumption via the dark assimilation pathway. Thus, in the surface horizons of bogs and lake sediments, the final $\delta^{13}C$ value of CO_2 was determined by several oppositely directed processes.

Unlike the bog and lake sediment structure, soil aerobic and anaerobic horizons are not clearly distinguishable. In soil ecosystems, the content of methane correlated with that of the organic matter ($r = 0.86$; $p < 0.05$; $n = 26$). Maximum methane concentrations were often recorded in the upper humus or peat horizons, even though these horizons are oxidized (Fig. 4a). Here, methane formation is only possible within the organomineral conglomerates with a layer of aerobic microorganisms covering their surface and protecting the inner space from oxygen penetration. Similar conglomerates were previously found in tundra ecosystems [23].

Hydrogen and acetate, which are intermediate products in the anaerobic degradation of organic compounds, accumulate in soils, probably due to the specific microzonal structure of the latter. The presence of hydrogen and acetate in soils characterized by a relatively low methane concentration suggests an imbalance of the processes brought about by primary and secondary anaerobes. Methanogen activity is probably inhibited to a greater extent by conglomerate-penetrating oxygen than that of anaerobic microorganisms, both hydrolytic and fermentative. Under these conditions, hydrogen and acetate formed through the fermentation of the organic compounds are incompletely utilized and accumulate in the medium.

In dry and water-logged soils, methane concentration is low not only because of the low methane production, but also because of active methane oxidation. The uptake of methane in soils is of biological nature, which is confirmed by both radioisotopic and chamber experiments. Bacterial methane oxidation in a chamber resulted in a decrease in the methane concentration (from 1.5- to 3-fold as compared to the air methane concentration) and a synchronous weighting of the methane carbon (Fig. 1).

Methane oxidation in bogs and lake sediments was most active. Nevertheless, methane diffusing from deep horizons was not completely utilized by methanotrophic bacteria; all bogs and lake sediments serve as sources of atmospheric methane (Table 1). In these ecosystems, the emission intensity most probably depends on the organic-matter stores and the degree of flooding. The maximal methane emission was observed in bogs with thick water-filled peat horizons. When the surface horizons dry up, methane oxidation intensity increases, and methane emission becomes lower. Moss hillock (station ETS6) is an extreme variant of a dried bog; there, similarly to dry soils, methane uptake from the atmosphere was recorded. Lake bottom sediments, which contain mostly sands, are far short of organic matter stores as compared to bogs and their methane emission is minimal (Table 1).

The ground density seems to be another factor affecting the methane flux from deep horizons to the surface. A decrease in methane concentration was most pronounced in the surface horizons with loose ground (Fig. 4b). In the more compact horizons, methane concentration remained almost unchanged up to the very surface. In bogs and lake sediments, the compact ground of the surface horizons is likely amenable to methane accumulation rather than to its emission into the atmosphere, which is confirmed by an inverse correlation between methane concentration in upper horizons and the intensity of its emission ($r = –0.43$; $n = 6$). However, the scarce data so far available are still inconclusive.

As can be seen from Table 2, the calculations of the methane flux based on the intensities of methanogenesis and methane oxidation on the one hand and on the results of chamber measurements on the other hand produced inconsistent results. This can probably be explained by the fact that the intensity of methanogenesis at depths below 50–100 cm was not sufficiently accounted in the radioisotopic experiments. In addi-

tion, it is difficult to obtain representative samples from ecosystems with extremely diverse microzonality and layering. However, we believe that the chamber measurements and radioisotopic and gas-chromatographic measurements complement each other and give insight into the biogeochemical processes in the microbial communities of the ecosystems studied.

In our study, we also tried to assess the possibility of methane diffusion from the gas field into the atmosphere. This phenomenon can be most easily revealed in dry soils with minimal modern biological methanogenesis. The presence of C_2–C_3 hydrocarbons in the upper soil horizons and the isotopic carbon composition of the surface methane (–51…–47‰), which is similar to the geological one (–55…–45‰), seemed to indicate that diffusion is possible. However, in the subsurface and deeper soil horizons, the content of all hydrocarbons, including methane, decreased dramatically, which suggests that they were not diffusing from the deep layers of the gas field to the surface. Moreover, direct measurements indicate with certainty that dry soils serve as sinks for atmospheric methane. Hence, if even a proportion of the gas-field methane reaches the upper horizons of the terrestrial core, it is completely oxidized here by the soil methanotrophs. Stable isotopic composition of the soil methane carbon is likely determined by the ratio between modern methanogenesis and methane oxidation. The similarity found between the isotopic composition of geological and soil methane is most probably accidental.

Our study suggests that modern biological methane (but not buried methane) is emitted from the natural ecosystems of western Siberia. Bogs and, to a smaller degree, lakes, are the main sources of modern methane. Considerable areas of tundra and taiga characterized by dry and water-logged soils serve as sinks for atmospheric methane. Thus, the contribution of the Russian tundra and forest tundra to the global methane flux in the atmosphere requires further comprehensive biogeochemical and microbiological analyses.

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