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FRESHWATER ECOSYSTEMS: CURRENT CHALLENGES

Methane Emission From the Surface of the Mozhaisk Valley-Type Reservoir

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Abstract—This article deals with spatio-temporal changes in methane emission from the surface of the Mozhaisk reservoir. Seasonal changes in methane content and flux were revealed for different morphological areas of the reservoir, based on field observation data obtained in 2015–2018. In the low-flow Mozhaisk reservoir, the methane content in the boundary and bottom layers of the deep-water areas at the end of the summer stratification period may differ by three orders of magnitude. According to results from measuring with floating chambers in the central area of the reservoir from early June to the end of the period of direct stratification (August–September) the total methane flux increased from less than 1 to 16 mgC-CH_4/(m^2/hr). Time-coincident measurements with floating chambers of two types revealed characteristic values of the methane flux components and their change over the sampling period. It was found that at the period of stratification the diffusive flux predominates with the mean values 0.2 mgC-CH_4/(m^2/hr). A further increase in the total methane flux is associated with an increase of its bubble component. According to calculations, the diffusive flux reaches its maximum values in late summer in the shallow zone of the reservoir. It is established that a significant increase of the values of the total methane flux is observed when the upper boundary of the oxygen-free zone reaches the lower boundary of the epilimnion. The methane flux density reaches its largest values prior to destruction of the direct stratification. Comparison of field measurements with literature data showed that the magnitude of emission from reservoirs with a slow water exchange in the temperate zone can be underestimated in the evaluation of global methane emission.

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Keywords: reservoir, hydrological regime, water exchange, methane content, dissolved oxygen, floating chambers, oxygen-free conditions.

INTRODUCTION

Assessment of greenhouse gas emissions from different anthropogenic sources, which also include reservoirs, is of current relevance. According to various estimates, the total area of the artificial reservoirs is 205–250 thou km^2, excluding the regulated lakes (an increase in their area with a rise of the level cased by the construction of the dam on the receiving river can be neglected in this case). The intensity of greenhouse gas emissions depends on morphometric parameters of reservoirs: larger amounts of methane enters the atmosphere from shallow parts of the water body than from deep-water areas, because of lesser oxidation in the water layer of a lesser thickness [1] as well as because of the geoecological conditions of their location (natural zone, landscape conditions on the catchment, hydrological regime, their age, etc. [2]). In reservoirs, methane is the product of anaerobic decomposition of organic matter arriving from the catchment and produced in the water body. A rise of water temperature intensifies the activity of microorganisms, and methane emission from reservoirs depends on this indicator [3]. In the temperate belt, the methane flux from reservoirs varies from 0.1 to 108.5 mgCH_4/(m^2/day) and in the subtropical belt it varies from 10 to 1140 mgCH_4/

(m^2/day) [4]. The spread of the values indicates that the climate is not a dominant factor determining the methane flux. In low latitudes, however, the values of the methane flux are much smaller than in high latitudes. The technique of assessing the global methane emission from the reservoir surface is provided in [4] using, as the basis, the Global Lakes and Wetlands Database (GLWD) [5]. Noteworthy is the large spread of values of the methane flux from the reservoirs of the boreal and tropical zones, which might be accounted for by a shortage of expedition-based field data [6]. As is recommended in [1, p. 20], "At least a monthly monitoring of key parameters and GHG fluxes is likely to be required to cover the seasonal variability and provide robust mass balance measurements…". In this case, however, some estimates were made on the basis of irregular expedition-based observations. Noteworthy is also an insufficient knowledge of the greenhouses gas emission for reservoirs of Russia [7], more than 70% of which are categorized morphologically as the valley-type reservoirs. The objective of this paper is to assess spatio-temporal variability in the methane flux from the surface of a low-flow valley-type reservoir and the mean annual values of the flux as deduced from measurements.

OBJECTS AND METHODS

The object of investigation is the Mozhaisk reservoir (Fig. 1) that has been thoroughly studied in the hydrological and hydrochemical context; it is located in the upper reaches of the Moskva river. It is a morphometrically simple, low-flow valley-type reservoir with no intense dynamical mixing, and with the water exchange coefficient of 1.15 year^{-1}. In the summer and winter, it shows a thermal stratification [8]. The volume of the water mass with the absence of oxygen and its lifetime are associated ith synoptic conditions of each year and with the level regime of the reservoir. The reservoir has an asymmetric longitudinal profile with an increase in the maximum depth of the areas in the drowned channel of the Moskva river, from 5–7 m in the upper reaches to 20–23 m at the dam. The depth of the drowned floodplain increases from 2–3 to 10–12 m, respectively.

The measurements of the values of the methane flux by the method of floating chambers were made during 2015–2018 in the central part of the water body at the period of open water 4 to 13 times per season. On a regular basis, water samples were also collected from the surface and near-bottom horizons on raid vertical IV (see Fig. 1) in Krasnovidovo Ples (Bay) (10–20 times per season), and periodical hydrological-hydrochemical surveys were carried out along the longitudinal axis of the reservoir (from 5 to 10 stations 3–5 times per season) [9]. Samples were collected during the surveys at the stations located above the drowned channel (see Fig. 1), which are distinguished by the nature of ground and by the rate of oxygen consumption [10].

The method of phase-equilibrium degassing was used to determine methane content in water and air samples [11]. The resulting gas phase (the volume of a water and air sample was 40 and 20 mL, respectively, and the time of shaking was 3 min) was transferred for subsequent analysis to glass bottles for laboratory investigations [12, 13]. The methane concentration was determined with double and triple replication by means of gas chromatograph Kristall 5000.2 (ZAO Chromatec, Yoshkar-Ola, Russia) with the plasma ionization detector.

The methane flux was measured with the floating chambers following the methodology described in [13]. The exposure time varied from 40 to 60 min. Water temperature and water-dissolved oxygen were determined simultaneously with the YSI ProODO (Xylem Incorporated, USA) probe, with the measurement error of 0.1 mg/L and 0.2 °C, respectively, for dissolved oxygen and water temperature. To calculate the diffusive methane flux used data on the

Fig. 1. Schematic map of the Mozhaisk reservoir, and location of hydrological survey stations above the drowned channel of the Moskva river
I–V – stations. *1* – sampling points; *2* – installation point of the floating chamber; *3* – settlements; *4* – drowned channel network.

wind velocity from automated meteostation Davis Instruments (Davis Instruments Corporation, USA) installed on the buoyancy platform of station IV at the height of 2 m above the water surface. In the case of gaps of observations, use was made of data from the meteostation of the city of Mozhaisk located 5 km south-east of the dam. The diffusive methane flux into the atmosphere was calculated by the (Thin Boundary Layer, [1]) method from the difference of the methane concentration between the boundary and near-water layers using a parameterization of the exchange coefficient according to [14].

RESULTS AND DISCUSSION

First and foremost, noteworthy are the differences in the hydrological regime of the reservoir during the years under investigation, which was determined by weather characteristics (Fig. 2). In 2015 and 2017, the beginning of the period of formation of a direct stratification was cool and windy: the mean wind velocities reached 5–6 m/s and, on some days, 7–8 m/s, and no abrupt chages in air temperature vaiation were observed at the end of spring (see Fig. 2, *a*, *b*). Because of the synoptic situation, the wind mixing continued for a relatively long period and resuted in the formation of a less stable stratification that in 2016 and, especially, in 2018 when the difference of water emperature on the 0.5 and 10-m horizons reached essentially large values (see Fig. 2, *c*). These characteristics of the thermal regime were responsible for the density stratification of the water body and its oxygen regime in the hypolimnion which in a low-flow water body is dependent on the mixing conditions. In 2015 and 2017, the oxygen-free conditions in the central area of the reservoir, according to data of regular observations at raid vertial IV, occurred in the second 10-day period of June and the first 10-day period of July, respectively. In 2016 and 2018, the oxygen-free conditions persisted for a longer time: from the second 10-day period of June to the second 0-day period of Sentember, and fro the first 10-day period of June to the first 10-day period of October. But in this case the upper boundary of the oxygen-free zone reached 7–8 m in all periods but at diferent times depending on the mixing intensity. These characteristics of the hydrological regime influenced the mode of measurement of methane contents and emissions in the years covered by the observations.

According to the results of the installation of the floating chamber in the central area of the reservoir at station IV at the beginning of the period of measurements (in June), the value of the total (diffusive and bubble) flux does not exceed 3 mgC-CH_4/(m^2/hr). At the end of the period of summer stratification, a significant increase in the methane flux was observed (to 16 mgC-CH_4/(m^2/hr) in 2017 and 2018 with the longest observation series when the oxygen-free zone in the near-bottom horizons reached the largest volume as well as when the water temperature gradient in the water column decreased. More than 90% of the total flux prior to destruction of the stratification corresponds to the bubble flux which was determined from the difference of the total and diffusive flux. At the beginning of the period of autumn mixing, the values

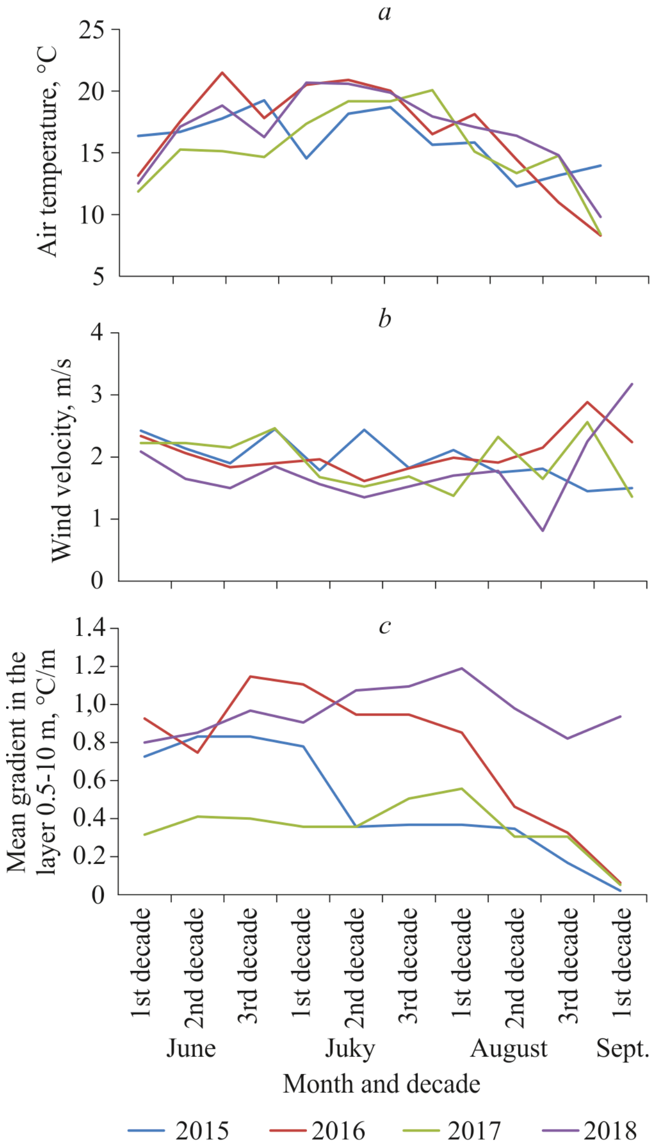

Fig. 2. Variation of 10-day averaged values of air temperature (°C) (a), wind velocity (m/s) (*b*) and mean gradient of water temperature in the 0.5–10 m layer (°C/m) (*c*) in 2015–2018.
Years: *1* – 2015, *2* – 2016, *3* – 2017, *4* – 2018.

of the methane flux decreased by an order of magnitude (to 3 mgC-CH_4/(m^2/hr) during the first 10-day period of September 2017)). In 2018, sampling was discontinued until destruction of the direct stratification because of an accident on the ship.

In 2016 and 2018, the values of the methane flux for the period after the onset of the stratification assume smaller values when compared with the corresponding periods of 2017 (4–16 mgC-CH_4/(m^2/hr): 3.5–5.5 mgC-CH_4/(m^2/hr) in 2016, and 1.2–6.5 mgC-CH_4/(m^2/hr) in 2018. This is due to the difference in the thermal and oxygen regimes of the water body during those years: in 2017, a stable stratification arose later because of weather conditions, while the near-bottom water temperature at the end of August reached 16.5 °C, and the vertical water temperature distribution was uniform, with the maximum gradient not exceeding 0.5 °C/m; therefore, a cooling of the surface water layers in cyclonic weather at the end of August led to a deep mixing, and to an increase in methane content in the boundary layer and its flow into the atmosphere. In 2016 and 2018, the near-bottom horizon is isolated by a density stratification, and before the period of autumn cooling its temperature rose to a mere 14 and 12 °C, respectively.

A significant increase of the values of the methane flux (to 16 mgC-CH4/(m^2/hr)) was observed on Sept. 2, 2017 and Sept. 21, 2018 in the years with the longest observation series. The preceding periods (Aug. 17–23, 2017 and Aug. 31–Sept. 8, 2018) showed phytoplankton blooms associated with input of autochthonous mineral phosphorus accumulated in the near-bottom horizons during the summer oxygen-free period, after the preceding deep mixing in cyclonic weather conditions. It is likely that input of portions of fresh detritus to the bottom caused an increase in its content in the near-bottom layer to 3570 μL/L on Aug. 20, 2017 and to 4960 μL/L on Sept. 9, 2018 (see Fig. 2, *d*), which increased the methane flux during the subsequent cooling and deepening of the mixing.

The values of the diffusive methane flux as determined by the TBL method above the channel stations from 2015–2018 survey data are presented in Fig. 3. Spatio-temporal variability in the diffusive methane flux has the following regularities. In the case of a direct thermal stratification, the values of the methane flux are 0.03–0.07 and 0.02–0.04 mgC-CH_4/(m^2/hr) in the upper reaches of the water body and at the dam, respectively. The year 2015 and, especially, 2017 shows an increase in the diffusive flux during the summer period, with the largest methane content in the boundary layer (Tables 1 and 2) because of a regular wind mixing with a weak stratification. In July,

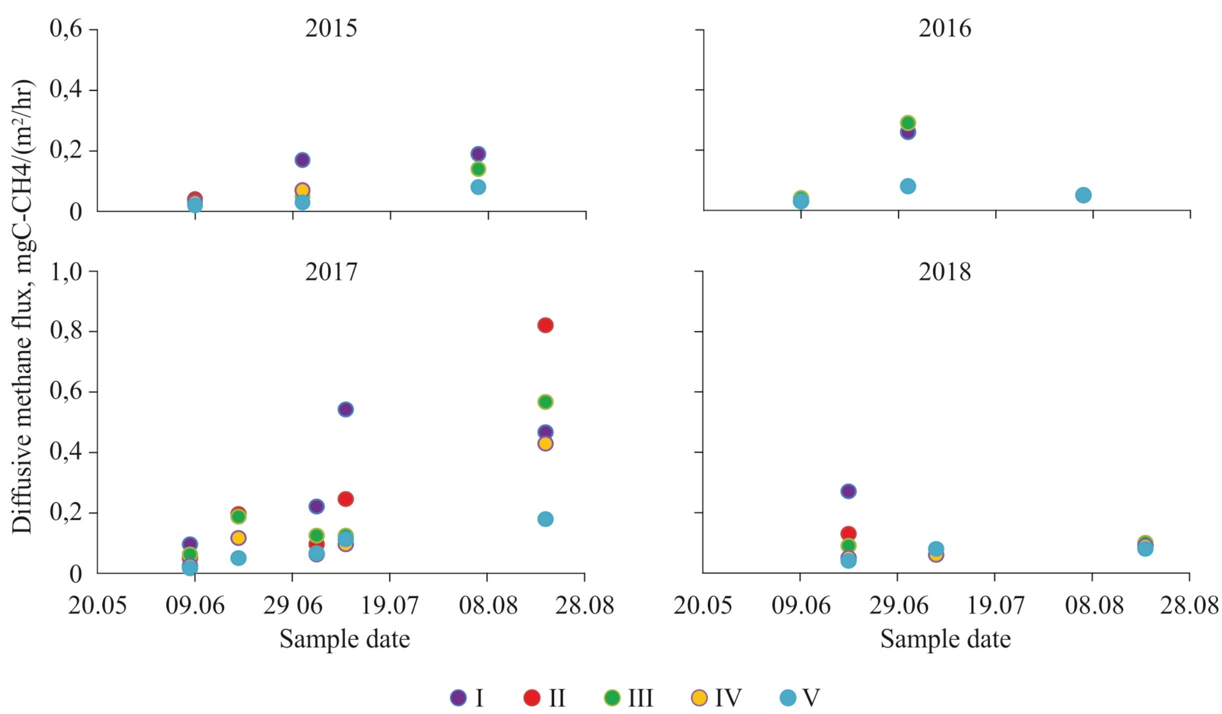

Fig. 3. Diffusive methane flux (mgC-CH_4/(m^2/hr)), calculated by the TBL method from data of hydrological surveys at base stations. I–V – base stations.

Table 1. Characteristic values of the characteristics of hydrological regime of the water column of the Mozhaisk reservoir according to data of surveys

Date	Station	Water temperature, °C			Dissolved oxygen, mg/L		
		surface	bottom	max deg	surface	bottom	upper boundary of oxygen-free zone, m
1	2	3	4	5	6	7	8
June 9,2015	I	18.8	14.5	2.4	8.9	2.7	Absent
	II	18.6	14.6	3.5	8.9	2.3	Absent
	III	18.8	11.7	2.4	10.6	1.3	Absent
	IV	19	11.1	2.3	11.4	1.0	Absent
	V	20.6	9.9	3.3	10.3	4.7	Absent
Jan. 1, 2015	I	22.4	15.8	1.8	8.8	0	4
	II	22.6	16.2	1.1	8.8	0.3	4
	III	22.4	14.9	1.2	9.7	0.3	6
	IV	21.3	12.8	2	12.1	0.4	8
	V	23.1	9.9	1.9	12.2	0	10
June 8, 2015	I	21.5	19	1.3	9.1	4	Absent
	II	21.7	19.4	0.7	12.9	1.2	Absent
	III	23	18	2.2	19.1	0	7
	IV	23	16.5	1.3	14.9	0.3	9
	V	23.6	11.2	1.9	15.5	0.2	11
Sept. 6, 2016	I	–	–	–	–	–	–
	III	14.7	10	3.1	8.9	3.6	Absent
	V	–	–	–	–	–	–
Apr. 7, 2016	I	26.9	16.3	4.5	11.4	0.4	5
	III	26.1	13.5	2.7	11.2	0.3	5
	V	24.9	7.3	3.9	11.8	0.3	6
Aug. 22, 2016	I	19.8	16.3	1.2	9.7	5.7	Absent
	III	20.5	18	0.3	9.3	0	9
	V	21	8.8	1.7	9.8	0.3	10
June 18,2017	I	19.6	13.2	4.6	9.6	4.6	Absent
	II	17.9	13.5	1.4	9.1	4	Absent
	III	18.5	11.7	3.3	11.4	1.4	Absent
	IV	16.5	11.5	0.9	9.3	1.8	Absent
	V	17.6	8	1.1	10.3	1	Absent
July 10, 2017	I	16.6	13.6	0.9	7.7	3.3	Absent
	II	16.5	15.6	0.2	7	6	Absent
	III	17.1	14.4	1	8.5	0	9
	IV	17.3	13.8	0.9	9.3	0	12
	V	18.6	9.1	3.3	10.7	0	15
Aug. 20, 2017	I	24.6	19.3	1.6	16.3	2	Absent
	II	24.3	19.5	1.4	14.8	0.3	6
	III	24.3	19.1	1.8	13.4	0.2	6
	IV	24.5	16.2	1.7	13.1	0.1	7
	V	24.1	9.8	1.7	11.3	0	8
June 6, 2018	I	23.6	15.9	3.2	11.7	1.5	Absent
	II	22.9	14.8	2.7	12.9	0.2	6
	III	22.6	12.6	4.3	14.2	0.2	8
	IV	22.6	9.2	2.5	14	0.1	10
	V	22.7	6.2	3.2	12.2	2.8	–

Table 1 continued

1	2	3	4	5	6	7	8
July 7, 2018	I	21.1	17.7	1.3	10.5	1.5	Absent
	II	20.8	18	0.8	10	0.2	6
	III	–	–	–	–	–	–
	IV	20.1	10.1	1.9	10.1	0.1	9
	V	20.3	6.7	2.8	9.8	0.5	18
Aug. 19, 2018	I	–	–	–	–	–	–
	II	21.3	19.6	0.9	11.3	2.8	–
	III	22.3	15.9	1.1	12.5	0.3	6
	IV	22.5	12	3	10.7	0.2	8
	V	22.6	7.8	1.9	8.4	0.1	7

Note. Here and in Table 2: dash – no data.

Table 2. Methane content in the water of the Mozhaisk reservoir according to data of hydrological surveys for 2015–2018

Date	Station	Methane content, μL/L	
		surface	bottom
1	2	3	4
June 9, 2015	I	2.57	7.75
	II	2.27	5.13
	III	–	–
	IV	1.48	6.41
	V	0.98	2.06
Jan. 7, 2015	I	10.91	505.03
	II	4.63	86.94
	III	2.98	683.16
	IV	3.47	948.26
	V	2.25	702.51
Aug. 6, 2015	I	14.59	202.57
	II	–	–
	III	8.45	1452.55
	IV	–	–
	V	4.59	2329.98
June 9, 2016	I	–	–
	III	2.8	49
	V	–	–
July 4, 2016	I	12.36	453.05
	III	8.89	948.43
	V	3.8	63.32
Aug. 22, 2016	I	4.79	7.03
	III	5.41	2475
	V	4.42	–
June 18, 2017	I	9.30	10.30
	II	6.35	18.56
	III	4.61	9.08
	IV	3.90	10.00
	V	2.27	8.88
July 1, 2017	I	22.61	14.14
	II	11.06	284.94
	III	4.21	23.67
	IV	4.32	95.08
	V	4.86	274

Table 2 continued

1	2	3	4
Aug. 20, 2017	I	24.24	14.40
	II	23.03	11.86
	III	15.89	1752.71
	IV	11.98	3569.10
	V	9.44	2508.98
July 19, 2018	I	13.4	26.4
	II	6.5	141.1
	III	5.7	106.6
	IV	3.7	3.4
	V	2.6	6.7
July 7, 2018	I	–	–
	II	–	–
	III	–	–
	IV	4.8	215.9
	V	4.2	5.8
Aug. 19, 2018	I	–	–
	II	–	–
	III	9.0	–
	IV	6.8	2384.8
	V		1016.4

according to survey data, the oxygen concentration in the upper water layer was the lowest in 2017; in august of the same year, the upper boundary of the oxygen-free zone was at the highest level (compared to the years 2015 and 2016, at 1–3 m). In 2016 and 2018, the largest values of the flux (as large as 0.3 mgC-$CH_4/(m^2/hr)$ in the upper reaches) were characteristic, on the contrary, for the first half of the summer. In 2018, because of the most stable and long-lasting stratification, the upper boundary of the oxygen-free zone was also located at 7–8 m, as was the case in 2017, but the low water temperature in the near-water layer of the deep-water compartments was responsible for the lower methane content in the near-bottom horizon when compared with 2017 (by a factor of 1.5 and 2.5 at stations IV and V) and, respectively, also at the surface (by a factor of 1.8 and 1.4).

The values of a diffusive methane flux from the upper reaches to the dam decrease due to an increase in the thickness of the aerated water layer, and to a reduction in the distance from the source of methane, i. e. bottom sediments. This regularity is observed for the years 2015 and 2017 with a less clearly pronounced stratification. In 2016 and 2018, the values of the diffusive flux during the summer did not increase substantially, and spatial changes are pronounced at the beginning of the summer only. Thus the value of the diffusive flux (which is determined largely by methane content in the boundary layer) depends heavily on the depth of the station and the mixed layer, the position of the upper boundary of the oxygen-free zone, and on methane content in the near-bottom horizons. The generalized regularities of the values of the diffusive methane flux are listed in Table 3. Data obtained from

Table 3. Characteristic calculated values of the diffusive methane flux in the Mozhaisk reservoir (mgC-$CH_4/(m^2/hr)$ from data for 2015–2018

Area	Month								
	June			July			August		
	av	min	max	av	min	max	av	min	max
Upper reaches	0.1	0.03	0.27	0.16	0.07	0.26	0.3	0.05	0.82
Central	0.1	0.04	0.19	0.16	0.05	0.29	0.21	0.05	0.57
Near-dam	0.04	0.02	0.11	0.06	0.03	0.08	0.13	0.03	0.43

investigating the small boreal lakes of Arkhangelsk oblast [15] did not show any significant spatial changes in the diffusive methane flux as contrasted to the valley-type reservoir. The values of the diffusive methane flux in Lake Temnoe and Lake Svetloe for the spring period were estimated at 0.05–0.1 mgC-CH_4/(m^2/hr).

The findings obtained are in agreement with the database for different components of an integral methane flow from reservoirs of different natural zones as reported in [16].

CONCLUSIONS

A series of investigations that were made for the first time on the Mozhaisk reservoir with a focus on the study into the amounts of methane emissions from the surface of a low-flow artificial water body provided characteristic values of contents of this gas in the water column and its flow into the atmosphere. The investigations were made in accordance with the methods accepted in international practice, which ensures reliability of results obtained. The weather conditions in the years of research that influenced the special features in the formation of the hydrological structure of the reservoir made it possible to reveal the influence of the intra-reservoir processes on the resulting methane flow from the reservoir surface.

The studies revealed a spatio-temporal non-homogeneity of the values of the methane flux caused by the difference of the hydrological regime of its areas distinguished by a moderate depth. Methane content in the reservoir is determined by the synoptic situation, the characteristics of density stratification and of the thermal and oxygen regimes of the reservoir in a particular year. According to observational data, the methane flux reaches the largest values prior to destruction of direct stratification, 16 mgC-CH_4/(m^2/hr). When calculating the annual emission from the reservoir surface, it is always necessary to take into consideration the spatio-temporal inhomogeneity of the distribution of the values of the methane flux which is characteristic for valley-type reservoirs (which include most of artificial water bodies across the globe). It is possible to use mathematical models, such as reported in [17], to make a more thorough assessment of methane emissions from the reservoir surface, especially in the case of unexplored water bodies or when irregular expedition-based data are available.

As some prospects for further research, we want to mention a number of its areas, such as involving the study of methane flows at the “water – bottom deposits” interface, assessments of gas emissions for the periods of spring and autumn mixing as well as input with the inflow and degassing in the case of water discharge from behind the dam. To continue the study into spatio-temporal variability of the methane flow, it would be advantageous to carry out a tie-coincident monitoring of the intensity of production processes which lead to super-saturation of the boundary layers with oxygen and to an enhancement in sedimentation of organic matter. In the presence of a pronounced stratification and in the absence of oxygen at the bottom, the factor for transverse changes in the amount of the methane flow can be represented by upset phenomena causing upwelling of cold, methane-rich, waters of the hypolimnion.

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