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## Seasonal variation of methane flux from Mozhaisk reservoir

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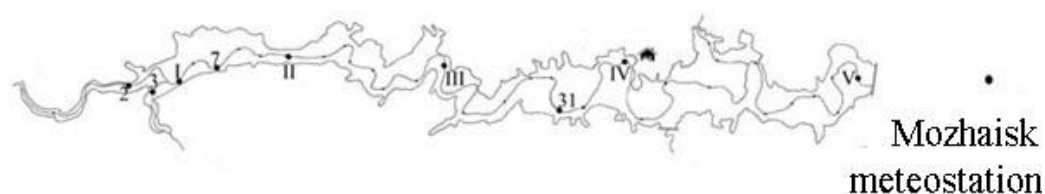
**Abstract.** The paper presents the results of methane flux measuring from the surface of valley type reservoir with a long water residence time. The factors of its spatio-time variations are revealed. The results of calculation and measurements of diffusive flux are compared.

### 1. Introduction

An urgent task is to assess the receipt of greenhouse gases from anthropogenic sources. These include reservoirs, the total area of which is estimated at 205,000-250,000 km<sup>2</sup>, excluding regulated lakes. According to the available data of observations in various natural zones [9] (a total of about 165 reservoirs), the intensity of greenhouse gas emissions depends on the morphometric parameters of reservoirs, geo-ecological conditions of their location (geographical position, landscape conditions in the catchment area, hydrological regime, their age, etc. [4]). The increase in water temperature intensifies the activity of microorganisms and the flow of methane from the surface [11]. The variation of the specific methane flux from reservoirs within different climatic zones [14] is due to the fact that the climate is not the dominant factor. There is a lack of field data flux measurements [12], methane emissions from reservoirs of Russia is poorly studied [10]. The aim of the work is to assess the spatial and temporal variability of the specific methane flux of the low-flow valley reservoir.

### 2. Objects and methods

Object of research - morphometric simple low-flow valley Mozhaisk reservoir (figure 1), located in the upper reaches of the Moscow River with a water exchange coefficient of 1.15 year<sup>-1</sup>, stratified in summer and winter [6].



**Figure 1.** The scheme of the Mozhaisk reservoir.



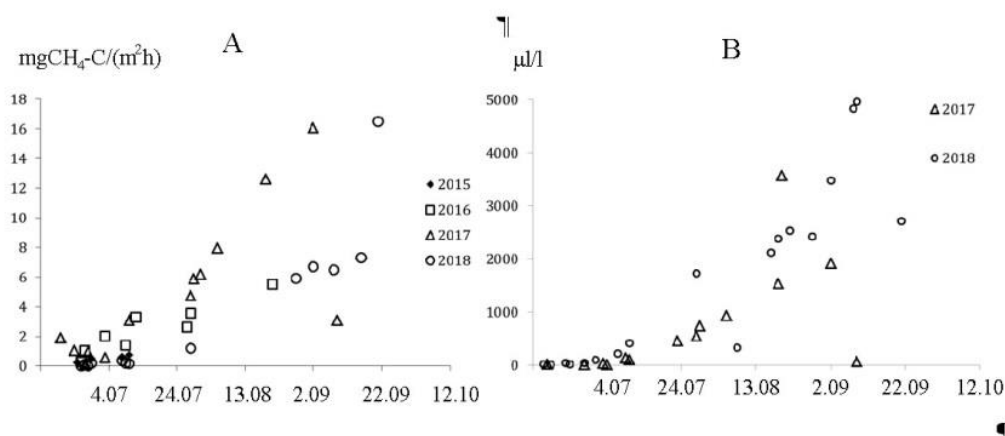
Methane flux density measurements by floating chamber method [7] were carried out in 2015-2018 in the central part of the reservoir (station IV) during the open water period from 4 to 13 times per season with water sampling from the surface and bottom horizons (10-20 times per season) [13]. In 2018, measurements of total and diffusive methane flux were performed by two cameras simultaneously. One chamber (diffusion) had a shield at 70 cm from its bottom to deflect pop-up bubbles. The second camera caught the total (bubble and diffusive) flux of methane. Periodic hydrological and hydrochemical surveys were also carried out along the longitudinal axis of the reservoir (3-5 times a season) [3] at stations located above the flooded riverbed (Roman numerals, figure 1), which differ in the nature of the bottom sediments and the rate of oxygen consumption [2].

Phase equilibrium degassing technique [1, 5, 7] was applied to determine the methane concentration in water and air samples. The second chamber caught the total (bubble and diffuse) methane flux. Diffuse methane flux for 2017 was calculated by thin boundary layer method [13] with exchange coefficients parameterized according to [8].

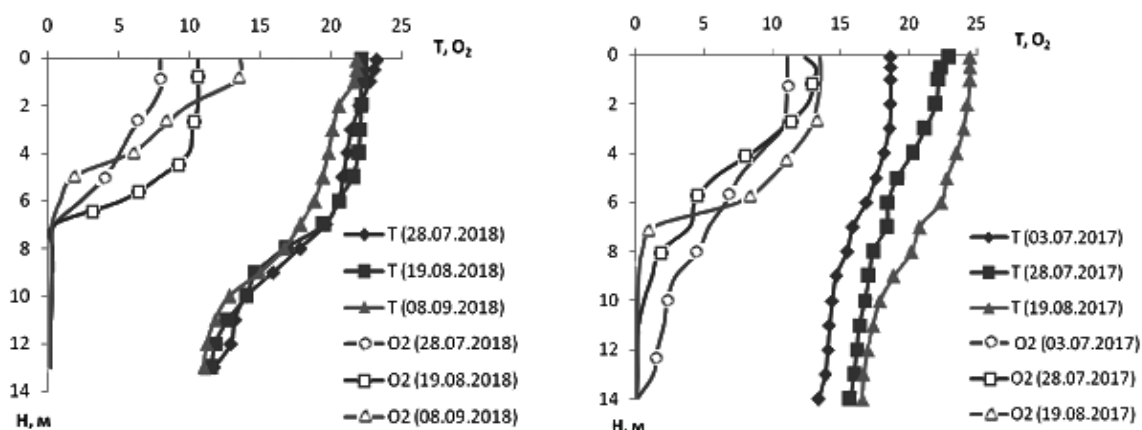
### 3. Results and discussion

Due to the current synoptic situation in 2015 and 2017, wind mixing led to the formation of less stable stratification than in 2016 and especially in 2018, when the difference in water temperature on the surface and at the bottom reached significantly higher values. In 2015 and 2017, anoxic conditions in the central area of the reservoir were formed in the 2nd week of June and the 1st week of July respectively, and aeration in the destruction of stratification was observed in the 3 week of August and 1st week of September, respectively. In 2016 and 2018 oxygen-free conditions were observed longer: from 2 decade of June to 2 decade of September and from the first decade of June to 1 decade of October. These features of the hydrological regime affected the regime of changes in methane content and emission in the years covered by the observations.

According to floating chambers measurements in the central part of the reservoir, a significant increase in the total methane flux values by the end of the summer stratification period was revealed (figure 2A). In 2018, the values of the methane flux density for the stratification period are lower compared to the same periods in 2017, and reached maximum value in the third decade of September (figure 2A). Processes of methanogenesis at a lower temperature of bottom water (figure 3) occur less actively, but due to longer oxygen-free conditions in 2018 in September, the methane content in the bottom horizon is higher than in 2017 (figure 2B). The maximum values of methane content in the bottom horizon are observed after outbreaks of "flowering" phytoplankton (source of autochthonous organic matter). According to complex measurements, a significant seasonal increase in methane flow occurs when the water temperature gradient in the water column decreases and the upper boundary of the oxygen-free zone reaches the lower boundary of the epilimnion (figure 3).



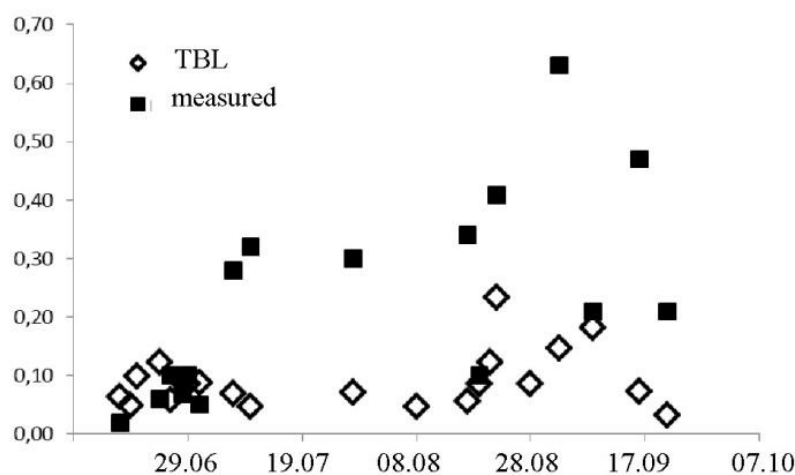
**Figure 2.** Specific density of total methane flux  $\text{mgCH}_4\text{-C}/(\text{m}^2 \text{ h})$  obtained by floating chambers at station IV in 2015-2018 (A), methane content in the bottom horizon,  $\mu\text{l/l}$  (B).



**Figure 3.** Vertical distribution of water temperature ( $^{\circ}\text{C}$ ) and dissolved oxygen  $\text{O}_2$  (mg/l).

According to measurements by two cameras in 2018 until the end of July, the specific flow values measured by both cameras (diffusion and total) are almost identical (on average  $0.2 \text{ mgCH}_4\text{-C}/(\text{m}^2 \text{ h})$ ). After the oxygen-free zone reached the lower boundary of the epilimnion, the measured values of the specific flow of methane in the "diffusion" chamber were less than in the "total" chamber. Moreover, the part of diffusion flux decreased as the total flux increased from 26 to 1.3%, which indicates a significant role of the bubble flux in the total methane emission in the low-flow stratified reservoir.

The values of the methane diffusion flux determined by the TBL method from upstream to the dam decrease due to the increase in the thickness of the aerated water layer and the decrease in the distance to the methane source - bottom sediments (table 1). This pattern manifested itself in 2015 and 2017 with less pronounced stratification. In 2016 and 2018, the values of the diffusion flux during the summer did not increase significantly and spatial changes were expressed only in early summer.



**Figure 4.** Results of diffusion flux calculation and measurement in 2018 ( $\text{mgCH}_4\text{-C}/(\text{m}^2 \text{ h})$ ).

A comparison of the methane diffusion flux determined by the TBL method and measured by the chamber showed good convergence in June. Further, the measured values exceed the calculated values (figure 4), which may be due to the imperfection of the exchange rate in the calculation, or the imperfection of the chamber (insufficient area deflecting bubbles shield or their dissolution under the shield). However, the part of diffusion flux at the end of summer is negligible in comparison with bubble flux.

**Table 1.** Calculated values of the methane diffusion flux in the Mozhaisk reservoir ( $\text{mgCH}_4\text{-C}/(\text{m}^2 \text{ h})$ ) according to measurements in 2015-2018.

Stations	June			July			August		
	mean	min	max	mean	min	max	mean	min	max
I, II	0,1	0,03	0,27	0,16	0,07	0,26	0,3	0,05	0,82
III, IV	0,1	0,04	0,19	0,16	0,05	0,29	0,21	0,05	0,57
V	0,04	0,02	0,11	0,06	0,03	0,08	0,13	0,03	0,43

For 2017 and 2018, with the most frequent observations an estimate of the average methane flux for the period of open water in the central part accounted for 90 and 63  $\text{mgCH}_4\text{-C}/(\text{m}^2 \text{ h})$ , respectively. That is, the difference between synoptic conditions and hydrological regime leads to significant fluctuations in the total flow of methane from the surface of reservoirs.

#### 4. Conclusion

In the low-flow valley reservoir there is a significant spatio-temporal heterogeneity of the specific methane flux due to the difference in the hydrological regime of its areas of medium depth. The methane content in the reservoir is determined by the synoptic situation, features of the density stratification, thermal and oxygen regime of the reservoir.

#### Acknowledgments

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