Methods for instrumental assessment of methane emission in reservoirs

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Abstract. Reservoirs are a significant source of methane in the atmosphere. Different estimations of the total methane emission from reservoirs vary greatly. In order to more accurately estimation of the methane emission from reservoirs, it is necessary to investigate the spatiotemporal variability of CH₄ fluxes. To study this variability, detailed instrumental measurements of methane fluxes over a long period are required. Such measurements have been carried out for 6 years at the Mozhaisk Reservoir. These measurements showed that the determining factor of the spatiotemporal methane fluxes variability is the meteorological situation and the water level regime. These factors form the stratification of the water column. The highest values of methane flux into the atmosphere are observed in the middle part of the reservoir. The temporal variation of the methane flux is characterized by a general pattern for all years when the measurements were carried out. The methane flux increases during the summer period and reaches the highest values before the beginning of the autumn mixing stage. Also, high flux values observed during periods of storm events that cause mixing of the water column.

1. Introduction

Water bodies are a significant source of methane in the atmosphere. Particular attention is focused on artificial reservoirs, because of discussion about the carbon footprint, as a result of various anthropogenic activities. The water and energy resources of reservoirs considered as an ecologically clean, but according to various estimates, reservoirs account for 0.5 to 10% of the total methane emissions into the atmosphere [1 – 6].

The main source of methane in the reservoir is the decomposition of organic matter in bottom sediments with anaerobic conditions. The two main pathways of organic matter decomposition are acetate and hydrogenotrophic [7]. Methane generated in sediments rises to the water-atmosphere boundary in the form of two flux components - ebullition and diffusion [8].

The diffusion flux depends primarily on the difference in methane content in neighbour layers. Due to the molecular structure of the diffusion flux, it has a very low speed, its values are usually very small due to the fact that methane molecules dissolved in water are subject to oxidation by microorganisms - methanotrophs. Even at low oxygen concentrations, methane is actively oxidized: about 90% of the methane coming from the hypolimnion can be oxidized by microorganisms [9].
The bubble flux reaches the water surface much faster than the diffusion one and is much less susceptible to oxidation. Gas bubbles occur only when water is oversaturated with dissolved methane. When entering layers less saturated with methane, bubbles can dissolve [10]. Therefore, in general for water bodies there is a pattern means that the shallower the average depth, the greater the value of the bubble flux of methane can be [11, 12].

There are a lot of artificial reservoirs in the world covered by in situ measurements of methane emissions [2 – 4, 6]. Most of such measurements is individual assessment of methane flux in a single time. In order to investigate the spatiotemporal variability of methane fluxes in a reservoir, multiple measurements are required on a well-studied water body. The Mozhaisk reservoir was chosen as such an object. Methane emissions have been monitored here since 2015. The greatest attention in the studies was paid to the summer period, when the greatest spatiotemporal variability of methane fluxes takes place.

2. Materials and methods

The Mozhaisk Reservoir is a typical morphologically simple reservoir of the valley type. Its main characteristics are given in Table 1.

Table 1. Morphological characteristics of the Mozhaisk Reservoir (all characteristics are given for the FSL) [13].

| Length, km | Max Width, km | Average Width, km | Max Depth, m | Average Depth, m | Water Surface Area, km² | Volume, km³ | Level Amplitude, m | Water exchange coefficient |
|-----------|---------------|-------------------|--------------|------------------|------------------------|-------------|-------------------|--------------------------|
| 28        | 2.6           | 1.1               | 22.6         | 7                | 30.7                   | 0.24        | 6                 | 1.78                     |

To study the spatial heterogeneity of methane fluxes in the reservoir, five observation stations over the flooded river bed (I–V) were selected from the reference network of hydrological monitoring stations, which represent representatively the hydroecological regime of the reservoir regions (figure 1).

Figure 1. Scheme of the Mozhaisk Reservoir with reference measurement stations (I–V).

The highest depths of stations from I to V are: 5m, 7m, 9m, 14m and 20.5m, respectively (at FSL). Such placement of measurement stations, at a uniform distance from each other along the length of the reservoir, makes it possible to study the distribution of the characteristics along the length profile from the upper part, influenced by the Moskva and Lusyanka rivers, to the transformation zone in the middle part of the reservoir and to the lower part with a quieter, low-flow regime.

The main method for determining the flux of methane into the atmosphere is the “floating chambers” method [3, 8]. A sealed chamber is placed on the water surface, and the concentration of methane is measured inside the chamber at the beginning and at the end of the experiment (the exposure time is usually about an hour). The change in concentration used to determine the flux of methane from the surface of the reservoir. Chamber allowed to determine the total flux both ebullition
and diffusion. In order to separately determine these components of the flux, two methods of estimation the diffusion flux used. The first is the Thin Boundary Layer calculation method [3]. Based on the parametrization of the methane flux depending on the difference between its concentrations in water and in air. The second method is instrumental, the diffusion flow is measured using a "diffusive chamber" [8]. This is a floating chamber with a protective shield installed at a shallow depth (about 70 cm), which deflects the methane bubbles. Velocity of the diffusive flux is much less than the ebullition, so it doesn’t have time to cover the path from shield to the camera. Bubble flux of methane into the atmosphere is calculated as a difference between the total flux and diffusion.

The methane flux from bottom sediments was calculated by the tube method [14, 15]. Using the Ecman-Berdge bottom grab, upper layer of bottom sediments was sampled and placed in glass tubes, which were filled above with bottom water. In parallel with the soil tubes, empty water tubes (without bottom sediments) were filled. The tubes were exposed in laboratory conditions at a temperature close to in situ for two days. After that, according to the difference in the concentration of methane in the soil and empty water tubes, the methane flux from bottom sediments was estimated. This measurement method has a fairly large number of disadvantages; the main one is the loss of a significant part of bubbles flux. At the end of the experiment, only the concentration of methane dissolved in the tube can be determined; therefore, it is impossible to fully determine the bubble component of the methane flux.

In 2020, a new method started to use for assessment of the flux from bottom sediments - the “bottom chamber”. The principle of calculations is quite similar to the "floating chamber" - the flux from the soil is determined by the difference in methane concentrations at the beginning and at the end of the experiment. At the moment, this method is developing, so the results of methane flux from bottom sediments estimation with this method are not presented in this paper.

An important part of research was the estimation of the accuracy for the tube method, “floating chamber” method and determining the methane concentration in water. In the summer of 2020, a series of equally accurate measurements of these characteristics were carried out in a reservoir under quasi-stationary conditions. Such series of measurements included several representations of determining these characteristics at different mean values in different times. In order to compare the measurement errors between the obtained series, the relative error was calculated. The results showed that there is no relationship between the number of values in the series or the mean value with a relative error. The largest values of the relative error for each of the characteristics were taken as a measurement error for these methods. For determination of the methane concentration in water, the relative error is 16%, and for “floating chamber” method the relative error is 27% and for the tube method the relative error is 56%.

3. Results and discussion
The most detailed study of the spatiotemporal variability of fluxes was carried out in the summer period of 2018 (figure 2) and 2019 (figure 3).

The water level in 2018 was close to the FSL (about a 1 m below the normal level). An increase in methane fluxes from June to August was determined due to its accumulation in the bottom layers. This is explained by the water stratification in the reservoir. The water body was strongly stratified during all summer period (0.14 g/m² on average in depth for the entire summer period). Also, there were no significant storm events that could destroy the stratification and lead to aeration of the bottom layers and the methane oxidation.

The anoxic zone rises in hypolimnion during the summer when the stable stratification has place. So, the methane flux from bottom sediments increases during the summer period at all stations as well, because methane can be accumulated in the water column with anaerobic conditions. The best combination of factors for the high methane generation rate in the bottom sediments is the depth of the station sufficient to establish stratification, but not too large depth for a stable supply of organic matter to the bottom and a low pressure of the water column, that allows to the ebullition reach the atmosphere easier. Station III corresponds to the described optimal conditions, where the highest
values of the flux from bottom sediments observed in August (195.9 mgC·CH₄·m⁻²·d⁻¹). Lower values of the flux from bottom sediments at stations IV and V are also associated with low water temperatures, that can inhibit the generation of methane due to a decrease of methanogens activity.

Figure 2. Spatiotemporal variability of methane fluxes at the measurement stations for the summer period of 2018.

Figure 3. Spatiotemporal variability of methane fluxes at the measurement stations for the summer period of 2019.

The most significant flux into the atmosphere is also observed at station III in August (149.1 mgC·CH₄·m⁻²·d⁻¹). On the shallow stations the flux is lower due to the fact that the water column is completely mixed and saturated with oxygen. At deep stations, small values of the flux are connected with methane intense oxidation in the water column; bubbles are also more likely to dissolve.

Summer conditions in 2019 were very different from 2018. At the beginning of the summer period, there were several powerful storm events (26.06 and 6.07). These events destroyed the temperature stratification, end the density gradient was very low during the rest of summer period (before 6.07, the average stability was 0.17 g/m⁴, after 6.07 - 0.06 g/m⁴). Also, the reservoir level was significantly lower than in 2018 (about 4-5 m below the FSL).

The measurement results show that in 2019 there is an excess of the methane flux into the atmosphere over the flux from the bottom. The reason is associated with errors, that occurs with the tube method measuring. This method underestimates the values of the ebullition flux component (see the materials and methods part of this article). This is especially noticeable in August, with a significant flux of methane and, consequently, a high proportion of the bubble component (according to the results of measurements by the diffusive chamber, the bubble component can reach 99% of the total methane flux into the atmosphere).

The highest values of the flux into the atmosphere in 2019 were observed at station IV in August (400.3 mgC·CH₄·m⁻²·d⁻¹), since this year the water level of the reservoir was very low, and the most
favourable conditions (was mentioned earlier) shifted downstream in the reservoir. Also, the high values of the flux at station II in July (415.2 mgC-CH₄·m⁻²·d⁻¹) connected with huge values of bubble flux. Almost all bubbles can be freely emitted into the atmosphere due to low water level. The other reason of this maximum in methane flux is macrophytes vegetation. The decomposition of water plants leads to increasing of organic matter flux on bottom sediments and activate more intense methane production.

The share of the diffusive component of methane flux can vary from 1 to 80% of the total methane flux into the atmosphere (figure 4).

![Figure 4](image_url)

**Figure 4.** The share of the diffusion flux in the total methane flux into the atmosphere according to the results of measurements in the summer period of 2018 and 2019.

The diffusive component prevails in the methane fluxes into the atmosphere at most stations in summer period of 2018. The high values of density gradient during the summer leads to accumulation of methane in water column near the epilimnion and reduce the distant from methane saturated zone to “water – atmosphere” boundary – so the less amount of methane can be oxidized. Share of diffusive flux is especially high in June at all stations except III (70 - 80%), as well as at deep-water stations IV and V in August (50 - 55%). The high values of the methane diffusive flux at the shallowest water stations are explained by the difference in methane concentrations in water and in air. Since the concentration of methane in the air varies in nonsignificant range with comparison to the dynamics of methane content in water, the magnitude of the diffusive flux is primarily determined by the methane content in the surface water layers. At stations I and II, the distance from bottom sediments to the water surface is very low (depths is 5 and 7 m, respectively), therefore less methane will be oxidized in the water column and the concentration at the surface water layers will be higher. At stations IV and V, the high proportion of the diffusion component is associated with the low intensity of methane generation in the soils due to low water temperatures and less of organic matter sedimentation (on near dam stations most of detritus flux decompose in water layers and cannot reach the sediments).

In 2019, at all stations during the entire summer period, the share of the diffusion flux is much smaller than in 2018 - from 1 to 15%. The conditions of this summer lead to very high values of ebullition flux. The diffusive flux has much lower magnitude in variability, so the high values of total flux into atmosphere associated with bubbles component. The water column was well mixed and aerated, due to the low-density gradient of water column in the July and August of 2019. Therefore, methane didn’t accumulate in the water. An exception is station V in August, when, as a result of two weeks of warm and calm weather, anoxic conditions formed in the bottom layers of the deepest part of the reservoir.

The temporal variability of the methane flux into the atmosphere, based on the results of frequent observations at station IV, has a general trend for 2015 - 2018 (figure 7). The methane flux is insignificant in early summer, as the anoxic zone in the hypolimnion is just beginning to form. Flux values increase gradually by the end of the August with a slow weakening of temperature stratification, as in 2017 (maximum 2.09.2017, 16.1 mgC-CH₄·m⁻²·h⁻¹), or an increase occurs sharply, with a rapid destruction of stratification due to a strong wind-wave impact, as in 2018 (maximum
21.09.2018, 16.5 mgC·CH₄·m⁻²·h⁻¹). In 2019, several significant values of the methane flux were observed (27.06.2019 - the highest flux value is 19.7 mgC·CH₄·m⁻²·h⁻¹). The reason is strong storm events at this time (wind gusts reached 20 m/s), that destroyed the temperature stratification. So, the methane accumulated in the hypolimnion since mid-May began to actively enter the atmosphere. After that, no stable stratification was observed in the reservoir, and the flux of methane in the rest of the summer was constantly on high level.

![Figure 5. Temporal variation of methane flux into the atmosphere during the summer period on station IV.](image)

4. Conclusion

The methane flux values and its variability during the summer period directly depend on the prevailing meteorological conditions on the reservoir, that determine the stability of density stratification and the intensity of wind-wave mixing impact. In addition, the level regime of the reservoir is an important factor.

The greatest values of the methane flux are observed in the middle part of the reservoir due to the most favourable conditions - sufficient depth for the stability of temperature and density stratification, but not as large as in the downstream part of the reservoir, where most of the flux is oxidized in the water column. Moreover, such optimal conditions can be observed at different stations, depending on the level of the reservoir. Also, high values of the flux are observed in the shallowest parts, provided there is an abundant supply of organic material during the decomposition of both phytoplankton and aquatic macrophytes vegetation.

The measured bottom methane flux can be lower, then the flux on “water – atmosphere” boundary. The tubes method provides some systematic errors by losing the part of bubbles flux. So, the bottom chamber method is tested and will be included in the observation program. The ratio of the diffusive and bubble components of the methane flux varies greatly depending on the depth of the station, the rate of methane generation in the sediments, and the methane content in the water. The most significant is ebullition component of the methane flux. The high flux values can content 99% of the bubble component.

The methane flux into the atmosphere increases over the summer and reaches its maximum value before the beginning of the autumn convection stage in years with stable density stratification during the summer period. Also, with intense wind-wave impact, which destroys temperature stratification during the summer, large values of methane flux into the atmosphere can be observed.

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