Influence of hydrological structure on exchange processes between water and bottom sediments in Mozhaysk Reservoir

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Abstract. The results of studies of exchange processes at the “water – bottom sediments” border for the summer period 2017–18 at the Mozhaisk reservoir are presented. The factors that determine the intensity values of methane and mineral phosphorus fluxes from bottom sediments as well as their spatial non-uniformity, associated with the soils distribution characteristics in the valley-type reservoir, are analysed.

1. Introduction

Between the bottom sediments (BS) and the near-bottom layers of water column mass and gas exchange processes taking place constantly, both in aerobic and anaerobic conditions depending on hydrological situation in the reservoir. Without taking into account the processes of organic matter (OM) bacterial destruction in the BS and migration of methane, which is an important component of the destruction processes, it is impossible to understand the aquatic ecosystem functional patterns. When OM is mineralized in BS the phosphates are released and enter the pore solution [6]. The phosphorus release from bottom sediments may result in secondary pollution of the water column with nutrients.

The decomposition of organic matter in silts is a result of the activity of various microorganisms (both aerobic and anaerobic) [12]. The necessary conditions for the methanogenic bacteria activity are anaerobic conditions inside the bottom sediments. The destruction processes of organic substances are influenced by various environmental factors: water temperature, the content of dissolved oxygen in it, the presence of easy oxidizable organic matter in soils, etc.

The purpose of this work was to assess the impact of various factors that affect the intensity of the methane and mineral phosphorus (P min) fluxes into the water column.

Object of study. Studies were carried out at the Mozhaysk reservoir - a typical dimictic valley-type reservoir of seasonal and over-year run-off control located on the upper Moscow River. The area of the water surface at the normal headwater level (NHL) is 30.68 km², the length is 28 km, the average width is 1.1 km. The reservoir volume is 235.18 million m³, the average depth is 7.66 m, the average water level fluctuation during the year is 6 m. The annual water exchange coefficient is on average 1.8 [4]. In the period of summer hypolimnion stratification in the Mozhaisk Reservoir in recent decades there were a growth of anoxid zones, which size could reach 30% of the reservoir volume by mid-July [5].
2. Materials and methods
Estimation of the OM gross destruction intensity (Dgr) at the “water-bottom” border was carried out by the method of V.I. Romanenko and S.I. Kuznetsov [2,7] and was measured by the amount of HCO$_3$ released from the silt column into the near-bottom water. The value of aerobic destruction (Daer) was determined by the amount of oxygen consumed in the silt tube, the value of anaerobic destruction (Danaer) - as the difference between Dgr and Daer. For ease of comparison flux values were converted to carbon content. The methane content in water was determined by gas chromatography [8, 10]. Methane fluxes F (CH$_4$) and phosphorus fluxes F (P) values were also calculated by the difference of these elements concentrations in the control tube and the tube with silt column. The value of methane flux was also reaccount for carbon units (mgC / m$^2$day). The experiment was carried out under two conditions - in a refrigerator at a temperature of about 10 °C and at room temperature about 20 °C - in order to use in the calculations the methane flux, which value is closer to in situ conditions.

As characteristics of the hydrological structure the stratification of the water column, the near-bottom water layer resistance to mixing and the thickness of the anoxide water layer were considered.

3. Results and discussion
During the June surveys with a sufficiently high intensity of destruction processes in the BS (emission of HCO$_3$ under laboratory conditions reached 800 mgC / m$^2$day) the release of CH$_4$ from the BS even with low (less than 1 mg/ l) O$_2$ content in the near-bottom water was less than 40 mgS / m$^2$day, the release of Pmin from the river-bed silts varied from 8 to 14 mgP / m$^2$day. The reservoir was strongly stratified - the average vertical temperature gradient was about 1°C/m, and the maximum gradient - 2.5-3°C / m.

By August in both survey years almost in the entire reservoir, except the transient backwater area, anoxide conditions in the hypolimnion formed, the intensity of destruction processes in silts evaluated by the HCO$_3$ release decreased to 50–200 mgC / m$^2$day, and the methane flux increased to 200 mgC / m$^2$day. The Pmin release at this time reached 24 mgP / m$^2$ day. The average vertical temperature gradient varied from 0.3 to 0.9 about 1 °C / m, and the maximum, 1 to 2 °C / m.

An important task was to identify the most significant factors determining the methane flux from bottom sediments. Link with the water temperature was noted only during the reservoir warm-up at the beginning of summer. There is a good correlation (r$^2$ = 0.86) between the methane flux determined by the “cold” experiment and ratio of the temperature at laboratory experiment to the temperature in situ for June 2017 -18. Thus, when studying methane fluxes, it is necessary to take into account the temperature in the near-bottom layer of water in the reservoir at which bacteriocenose developed in BS. The value of methane flux was taken either from the "cold" or from the "warm" experiment, depending on the water temperature in situ.

In general, for all the observations an increase of the CH$_4$ flux from silts from the deep dam area to the transient backwater zone may be noted. The maximum measured values in the near-dam deep for the entire observation period didn’t exceed 56 mgC / m$^2$day (2017), while in the upper areas they reached 196 mgC / m$^2$day (2018). Both maxima are observed in August, since by this time a powerful oxygen-free zone is formed in the hypolimnion in the whole water body. At the beginning of summer, during the warm-up period, the flux from the BS is much less, since the anoxide zone in the reservoir is just beginning to form.

Essential condition for the activity of methanogen bacteria is low O$_2$ content in water [9]. Figure 1 shows a graph of the relationship between the oxygen content in the tube in which the sampled soil was and the methane flux. The magnitude of the flux is generally inversely related to the O$_2$ content, however (as can be seen in figure 1) in some cases methane release was observed with the O$_2$ content exceeding 1 mg / l.

Since after getting the density stratification the anoxide conditions in the hypolimnion develop gradually, the available data were divided into 2 groups according to the thickness of the water layer with O$_2$ content of less than 1 mg / l (at the station at the sampling time). The first group includes data
for stations with an oxide layer thickness in the water column not exceeding 1 m, that is an oxide conditions were either absent or only started to develop in the near-bottom level. As second group were classified the stations with an anoxide layer thickness of more than 1 m, where low oxygen conditions had been lasting for some time.

![Figure 1. Correlation CH₄ flux to the O₂ content in the tube set for the exposure.](image)

The depth of O₂ penetration inside the bottom sediments is related to the intensity of its consumption processes in the near-bottom water layer and at the upper border of the BS. To take into account these processes a parameter (NBWC + Daer) was proposed, showing the cumulative intensity of the process of O₂ aerobic consumption by bottom sediments and the intensity of OM destruction in a 10-cm layer of near-bottom water.

For the first group of points (figure 2a) it had been found the relation between the CH₄ release and the total OM aerobic destruction in the BS and in the near-bottom water, which is explained by the fact that the higher the rate of oxygen consumption by the soils and the near-bottom water, the faster the anoxide conditions in the soil are set. In addition, methane coming from BS intensifies O₂ consumption in water. For the second group (figure 2b) it had been obtained the dependence of the CH₄ release on the oxygen content in the water above the silt.

![Figure 2. Relation of CH₄ flux with total OM aerobic destruction in BS and near-bottom water when a layer thickness with O₂ content <1 mg / l at station no more than 1 m (a) and O₂ content in at the experiment when a layer thickness with an O₂ content <1 mg / l at station more than 1 m (b)](image)

The total organic matter content and soil moisture (an indirect indicator of the "freshness" of OM) don’t have a pronounced effect on the methane flux neither for different months, nor for different areas of the reservoir. The Mozhaisk reservoir has a mesotrophic status, therefore, during the whole summer period in the reservoir the neoformed OM exist, which is actively decomposed by methanogens.
For different areas of the reservoir factors affecting the methane flux from bottom are different. So, for deeper middle and lower areas the important indicator is the stability of near-bottom water layer to mixing. The dependence of methane flux on the stability of the near-bottom water layer for these areas is direct ($r^2 = 0.77$). The stability of near-bottom water layer at deep stations prevents the enrichment of the silt’s surface with oxygen, which leads to an increasing intensity of methanogenesis. For the upper zones of the reservoir, where the water column is often mixed to the bottom, the stability of the near-bottom water layer does not affect the value of methane flux. For this part of the reservoir, the near-bottom water temperature determines the intensity of OM destruction stimulating the intensity of bottom microorganisms activity ($r^2 = 0.68$).

The phosphorus flux from the bottom is formed as a result of the following processes [6]: destruction of the phosphorus-containing part of OM on a continuously renewed bottom surface; phosphorus input from deeper layers of BS; phosphorus desorption from silts, occurring mainly under anoxic conditions; convective phosphorus flux with gas bubbles released from BS (in reservoirs with active gas emission). Studies carried out at the Mozhaisk Reservoir [1, 11] showed that the most significant factors affecting the intensity of the P flux from the BS to the water for that reservoir are phosphorus desorption and OM destruction.

In the analysis the available data on the Pmin emission were also divided into 2 groups according to the water layer thickness with the O$_2$ content <1 mg / l (figure 3). For cases with thickness of the layer with O$_2$ content <1 mg / l less than 1 m for the river channel silt, a connection between the Pmin release and the OM content in the soil was detected (except for the near-dam area, where the P$_2$O$_5$ content in the silts is almost two times less than in the rest of the reservoir). For the second group of points (cases with a layer thickness with O$_2$ <1 mg / l more than 1 m) the relation between the value of the Pmin release and the total anaerobic destruction of OM in the BS (emission of HCO$_3$ and CH$_4$) is noted, that is the OM destruction not only on the silt surface, but also includes the organic matter decomposition by methanogenic bacteria in deeper layers of BS [3].

**Figure 3.** Connection of Pmin release with OM for cases with a thickness of a layer with O$_2$<1mg / l less than 1 m (a) and with total OM anaerobic destruction (anaerobic fluxes of HCO$_3$ and methane) for cases with a thickness of a layer with O$_2$<1mg / l more than 1 m (b).

### 4. Conclusion

Gas transfer and mass transfer at the border “water-bottom sediments” is a complex and multifactorial process, which is affected by the hydrological structure of the reservoir (stratification of the water column).

The magnitude of the methane flux from the BS varies depending on the growth of the anoxic zone in the reservoir. The intensity of aerobic processes occurring in the near-bottom layer of water and the upper layer of BS influences the methane flux from the soils.
For different parts of the reservoir areas factors that have a decisive impact on exchange processes are different. Thus, for methane flux, in addition to the oxygen content near the bottom, in deep-water areas the stability of the near-bottom water layer is a determining factor. In areas with depths less than 8m the main factor is the temperature of the near-bottom water layer, as a stimulator of destructive processes.

When the thickness of the anoxide layer is less than 1 m the phosphorus release from BS increases with increasing of OM content in the upper layer of BS. Under conditions of long-term anoxia (the thickness of the anoxide layer is more than 1 m, the phosphorus release depends on the ensity of the destruction processes in the silts.

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