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Evaluation of dissolved Fe and Mn fluxes at the water/bottom border for various soil types

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Evaluation of dissolved Fe and Mn fluxes at the water/bottom border for various soil types

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Abstract. On the basis of field experiments the Fe and Mn fluxes for various types of soils were evaluated. It was found that dissolved Fe and Mn fluxes in hydrogen sulphide black silts are significantly lower in the presence of gas bubbles than in their absence.

1. Introduction

Resistance of aquatic ecosystems to human impact on water quality is carried mainly through self-purification processes. Among the elements affecting these processes by sorption followed by sedimentation of suspended compounds Fe and Mn play an important role [1]. Their compounds in the "water-bottom sediments" system involve nutrients, oxygen, heavy metals, etc. into the cycle. Much of these compounds stay in the bottom sediments (BS), the other – get back into the water, being involved in the cycle again. To quantify the self-purification capacity of a reservoir it is necessary to know the density of substance fluxes at the "water-bottom" border.

The purpose of the work - evaluation the dissolved Fe and Mn fluxes from the bottom to the water for various types of soils on the based on field and experimental studies.

2. Materials and methods

Studies of the Fe and Mn fluxes were carried out at the Mozhaisky and Ozerninsky reservoirs, at the lakes in the "Valdaisky" National Park and the floodplain lakes at the Kerzhenets river in the "Kerzhensky" reserve.

The bottom sediments of the Mozhaysky reservoir are gray and gray-olive sandy silt, silty sand and sand. Types of soils are confined to different morphological elements of the flooded river valley.

The silts of the deepest central part of the Ozerninsky reservoir (section I, II) represents black lake silts, very loose, with the presence of gas bubbles, finely dispersed with a large number of burrowing macrozoobenthos. While soil sampling at these stations the odor of hydrogen sulfide was noted. The silts of the section III (confluence of the Hlynya river) are lighter, gray-olive, homogeneous, without the presence of black anoxide layers and burrows. The silts of the upstream part of the section I are yellow-brown of sandy structure, homogeneous, with traces of macrozoobenthos.

Lakes Borovno, Perestovo, Beloye and Ostrovenok are located in the territory of "Valdaisky" National Park . Bottom sediments of the southern pool of the lake Borovno represents dense gray clay silts, rich in organic matter, uniform in thickness. In the lake Perestovo BS are sandy, olive-yellow.

Completely different silts in the lakes Beloye, Razliv and Ostrovenko are loose, dark brown with a semi-liquid, almost black upper layer about 0.5 cm thick.

Sediments of lakes in Kerzhenets floodplain - Chernozerye and Verkhnerustayskoe - are represents black silts, very loose finely dispersed (almost colloid), with gas bubbles. While sampling the odor of hydrogen sulfide was noted. In the black-brown loose silts at lake Krugloe gas bubbles were not detected. The lake Kalachik silts are light yellow-brown, more sandy, contain a lot of fallen leaves.

The dissolved Fe and Mn fluxes at the “water-bottom” border were estimated by the Romanenko-Kuznetsov pipes method [2]. The dissolved manganese and iron content in the water samples was identified by an atomic absorption spectrometry method (thermal atomization) after membrane filtration (d = 0.45 μm) and the addition of nitric acid (special purity grade) [3]. In the experiments the rate of oxygen consumption by bottom sediments (aerobic destruction) and the output of HCO_3 according to which the total destruction of organic matter in BS was estimated was also evaluated. By difference between total and aerobic destruction anaerobic destruction of organic matter in BS was calculated. In the selected BS samples the content of organic matter (OM) by incinerate method was evaluated.

3. Results and discussion

While the results of experiments were analized the data obtained were divided into groups according to the type of bottom sediments (silted sand, sandy silt, silt). Further the silt deposits samples were ranked according to the color.

By the silt color it's possible to determine the conditions that are formed inside the bottom sediments [4]. Yellow and brown color of sediments caused by ferric hydroxides is characteristic of deposits in which oxidizing conditions are created. Gray, greenish (olive) color of silt indicates the presence of conditions when Fe and Mn are reduced without the participation of hydrogen sulfide. The black color means that in the silts due to OM decomposition by saprophytic bacteria [5] H_2S is produced and iron sulfides are formed. BS samples with gas bubbles were diferentiated as a separate group (table 1).

Table 1. The intensity of the OM anaerobic destruction and the Fe and Mn fluxes from the BS into the water column for different types of soils (the numerator is the average, the denominator is the maximum)

Types of soils	OM, %	Anaerobic destruction mg C/m^2 day	Fe issue, mg Fe /m^2 day	Mn issue, mg Mn /m^2 day
Silty sand	3.0 / 3.2	330 / 616	18 / 18.3	15 / 15,5
Sandy silt	16 / 25	105 / 219	64 / 112	17 / 48
Gray olive silt	16.4 / 20	308 / 1550	92 / 264	44 / 85
Black silt (with gas bubbles)	19,1 / 33	240 / 1200	241 / 607	30 / 59
Black brown silt	37 / 72	105 / 193	270 / 3084	220 / 550

The decomposition of organic matter with the participation of Fe and Mn oxides is one of the most important biogeochemical reactions in anaerobic environments. Redox processes with variable valence compounds most often take place with the participation of microorganisms [6,7] for the development of which a substrate is necessary (availability of organic matter). However, as can be seen from the table 1, the OM content is not an indicator of the intensity of anaerobic destruction of OM in BS.

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The intensity of Fe emission from BS into water on average increases with increasing of OM content in the soil. It is a noticeable fact for Mn that in soil samples with gas bubbles the emission of Mn is lower than in gray-olive silts, despite the higher content of OM in them. Correlation analysis did not identify the dependence of emission intensity of dissolved Fe and Mn on OM content in sediments for none of the groups.

An important condition for the Fe and Mn soluble forms reduction is the anoxide environment in sediments. As shown in figure 1 the high - intensity release of these elements from BS is noted when the content of O_2 in the near-bottom water get less than 1 mg/l. Although anaerobic conditions can be formed in bottom sediments also in the presence of O_2 in the near-bottom water the dissolved Fe and Mn realized from the BS then oxidize under aerobic conditions and transform into insoluble forms. As illustrated in fig. 1 in some cases under aerobic conditions a negative Fe and Mn emission was observed, due to the predominance of the oxidation process in the near-bottom water over the reduction process in BS. Therefore further analysis was carried out for the results of soils experiments, for which the O_2 content in water contacting with the soil was less than 1.5 mg/l.

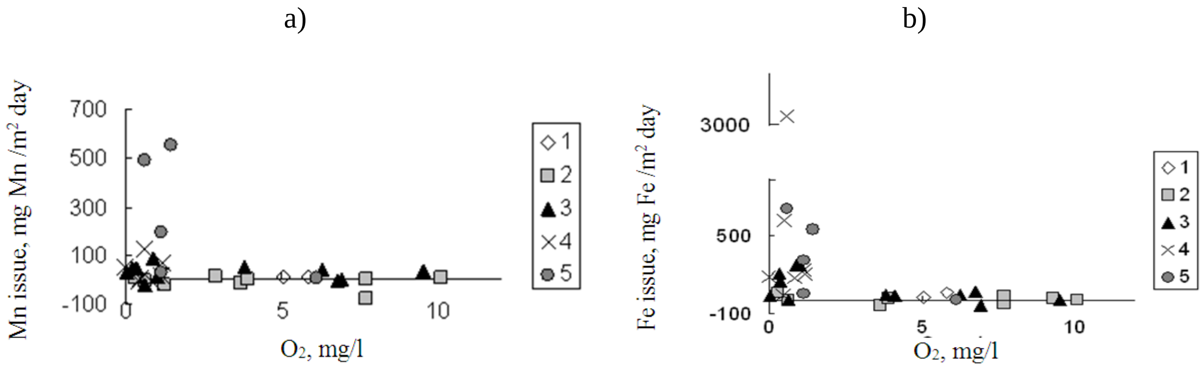

Figure 1. Connection between the value of dissolved Mn (a) and Fe (b) emission and O_2 content in the near-bottom water for silted sand (1), sandy silt (2), gray (olive) silt (3), black with gas bubbles (4) and black brown (5) silt.

Since the Fe and Mn dissolved forms reduction is a result of anaerobic decomposition of OM by microorganisms it can be expected that the intensity of the OM anaerobic destruction in BS should affect the fluxes value of these elements. It can be seen in figure 2-b that there is a tendency to increase the intensity of Fe emission from the BS with the growth of anaerobic destruction of OM in sediments.

Herewith for black and black brown silts the Fe release is much larger (ratio of Fe emission to anaerobic destruction is > 1) than for gray olive and sandy silts at close values of intensity of anaerobic OM destruction (ratio of yield of Fe to anaerobic destruction <1). For the Mn release (figure 2a) its rapid growth is noted with an increase of anaerobic destruction in case of black brown silts (the ratio of Mn emission to anaerobic destruction is > 1.5), but for black silts with gas bubbles such a rapid growth of release while increasing of anaerobic destruction is not observed (the ratio of of Mn emission to anaerobic destruction <1,5). In gray olive silts the ratio of Mn emission to anaerobic destruction was less than 0.5.

In general terms, the reduction process of Fe and Mn dissolved forms can be described as follows [8-12]:

In reducing silts (without hydrogen sulfide) the reduction of soluble Mn and Fe forms is a result of OM decomposition by anaerobic microorganisms. Also the reducing of manganese is possible while the oxidation of dissolved iron with manganese oxides is occur.

In addition to the above, in hydrogensulfide silt (black brown due to the presence of iron sulfide) manganese reduction taking place under the reaction of manganese oxides with hydrogen sulfide and with iron sulfide.

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With the gas bubbles presence, the concentration of H_2S dissolved in the pore solution is likely decreasing, and perhaps the manganese reduction through the reaction of its oxide with hydrogen sulfide is limited. That is, apparently, there are only three ways out of four for manganese reduction (compared to hydrogen sulfide silt without bubbles) what leads to the fact that the emission of dissolved manganese from BS is less than in black brown silts without gas bubbles.

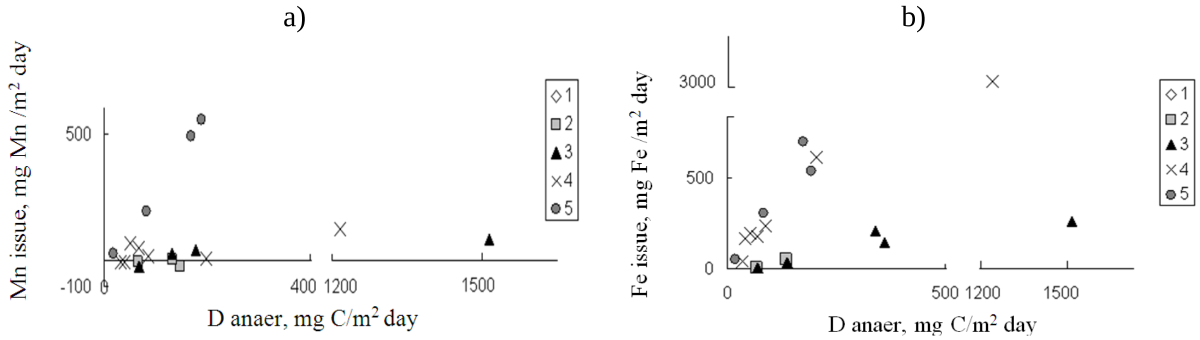

Figure 2. Connection between Mn emission (a) / Fe emission (b) and the anaerobic OM destruction in BS for different types of soils when O_2 content in near-bottom water is less than 1.5 mg/l (the designations are the same as in figure 1.

The appearance of bubbles in the black silts does not affect the dissolved iron emission, since in interaction of hydrogen sulfide with iron oxide reduction of its soluble forms does not occur, and slightly soluble iron sulfide is produced. The formation of soluble iron forms occurs during the reaction of manganese oxides with iron sulfide. That is, in black brown silts and in black silts with gas bubbles the iron reduction mechanisms are the same, therefore, the correlation between the dissolved Fe emission and the anaerobic destruction of OM in BS for these types of silt is the same.

4. Conclusion

Dissolved Fe and Mn fluxes from various soil types were evaluated.

Under conditions close to anoxic, there was noted a trend of increasing the emission of dissolved Fe from BS with increasing the anaerobic OM destruction for grey olive silt, black-brown silts and black silt with gas bubbles and besides the ratios of Fe emission to anaerobic destruction for hydrogen sulfide silts are close to each other and significantly higher than for grey olive silt.

For hydrogen sulfide silt it is noted that the presence of gas bubbles in the soil significantly reduces the release of Mn from BS.

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