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Manganese in Bottom Water and in Bottom Sediments of Mozhajskoye Reservoir:
I. Season Variations in Water

M. V. Martynova

Institute for Water Problems of the Russian Academy of Sciences, Moscow, 119333 Russia

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Abstract—Paper analyses the data on seasonal variations of Mn form content in bottom water (in 6 layers from the bottom) of drinkable reservoir. There is the information about oxidation–reduction conditions layer by layer of bottom water. The connections between Mn and N, P, Fe in the different layers of the bottom water are discussed.

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INTRODUCTION

Mn compounds belong to the third class of hazardous pollutants [1]. Excessive accumulation of Mn in a human body is accompanied by memory impairment, fatigue, narrowing of interest range, and other symptoms. However, at low concentrations Mn protects cells from free radicals, supports normal blood glucose levels, regulates the nervous and endocrine systems, etc. [2].

Maximum contamination level of Mn in water is 0.1 mg l^{-1}. The role of Mn compounds in aquatic ecosystems depends on its concentration in water: at concentrations < 0.1 mg l^{-1} Mn stimulates photosynthesis and protects cells from free radicals, while at higher concentrations it inhibits the growth of algae. The Mn compounds accumulate in the sediments and in higher aquatic flora of water streams and reservoirs. The Moscow suburban water storages for drinking purposes, Uchinskoe, in particular, showed high concentrations of Mn in water (1–3 mg l^{-1} in August-September). It is suggested to pass into water from the sediments [3]. The bottom water and other water reservoirs near Moscow are likely to have high concentrations of Mn.

The above mentioned ideas formed the basis for the studies on the processes of transformation and redistribution of Mn compounds in the bottom layers of Mozhajskoye reservoir constructed for Moscow water supply in 1960.

METHODS

Samples of bottom water and sediment represented by the gray mud were collected monthly during 1974–1975 at the riverbed station of Krasnovidovsky Flatwater located in the middle of Mozhajskoye reservoir. The depth of sampling stations at normal headwater elevation (NHE) was 3.17 m. General characteristics of the reservoir are given in [4].

For stratified sampling the bottom water (0–20 cm, 20–30 cm, 30–40 cm, 40–50 cm and 60–70 cm from the bottom) a stratobatometer and a sampler-tube designed by the author were used [5]. The content of total and dissolved Mn in filtered (through the filter 0.45 μm) and unfiltered water was determined photometrically with a solution of Hg/Ag. The method sensitivity was 1 mg l^{-1}, precision depending on the content of destructive substances was > 0.05 mg sample^{-1} [6]. Eh and pH of water samples were determined within 2 h after sampling. pH value was measured using a glass electrode with a silver chloride reference electrode. Throughout the experiment, pH-meter readings were systematically tested by standard buffer solutions with pH in the range of 4.00–9.22. When measuring the Eh of water two different electrodes were used: a smooth platinum electrode as an inert electrode, a silver chloride electrode as a reference electrode. Cleaning of platinum electrodes and measurement of Eh productivity are described in [7]. To make instal-

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Muza Vladimirovna Martynova, Dr. Sci. (Geogr.), Leading Researcher, Institute for Water Problems of the Russian Academy of Sciences, Moscow, Russia. Scientific areas of focus: hydrogeochemistry, eutrophication and chemical contamination of nature water systems.

Table 1. Content of Mn dissolved in the water reservoir, according to the publications [11] and [12]

Location	Mn, μg l^{-1}	Location	Mn, μg l^{-1}
Mozhajskoye [a]	0.0–17700	Kiev	0.0–441.6
Mozhajskoye	0.0–1200	Kremenchug	17.0–267.0
Uchinskoe	0.0–200	Dneprodzerzhinskoe	5.0–540.0
Volgograd	9.2–145	Zaporozhye	2.0–275.0
Tsimlyansk	0.5–190	Kakhovka	0.0–317.0
Veselovsk	0.2–29.3	Gokchalkovitskoe	100–200

[a] Author's data.

lation capacity quick the platinum electrodes were saturated with hydrogen [8] before measurements of mud Eh. Reproducibility of the Eh was 10–25 mV. The concentration of dissolved oxygen in water was determined due to Winkler data [9]. Other characteristics were determined by standard methods.

RESULTS AND DISCUSSION

Mozhajskoye reservoir was filled to normal headwater elevation in 1961, the maximal depth is 22.6 m (at NHE) at the dam. The water body belongs to the valley type reservoirs, being low flowing (the average water exchange of 1.8 y^{-1}), with intra-annual level fluctuations up to 7 m. The duration of ice cover is at the average 5 months (from November to April) [4].

Total content of Mn (Mn_{tot}) in the bottom water at riverbed station Krasnovidovsky Flatwater of the Mozhajskoye reservoir compared to the maximum allowable concentration (MAC) is very high. During the year it ranges between 0–17 mg l^{-1}, averaging for the different water layers 4–8 mg l^{-1}. According to the estimations by atomic-absorption spectrophotometric method in August 1972, the concentration of Mn in the bottom water of Krasnovidovsky Flatwater was equal to 9.3 mg l^{-1} [10]. The similarity of the results obtained by different methods indicates their validity.

Excessive concentration of Mn in water reservoirs, especially near the bottom is not a rarity, though the marked maximum concentrations are significantly lower than in Mozhajskoye reservoir (Table 1). There are some reservoirs, where concentration of Mn in water is close to or higher than that of Mozhajskoye reservoir. Thus, in zone of maximum depth of Lake Red (Punnus-Jarvi) it reaches 8.2 mg l^{-1} near the bottom [13], in Lake Vetasyarvi (Sweden), the concentration of dissolved Mn (Mn_{dis}) in May at a distance of 60 cm from the bottom it was equal to 1.12 mg l^{-1} [14], in the water of Lake Nordbiternet (Southern Norway) it was 67 mg l^{-1} (period of stagnation) [15]. In all cases, the main source of Mn in water is a watershed. In Mozhajskoye reservoir, in addition to watershed, a coastal moraine is another important source of Mn, the destruction of which affects the formation of silt deposits. Compounds of Mn being dissolved in the course of their transformation in silt, Mn in pore solution diffuses into the water [16].

The average annual content of total manganese in the layers 40–70 cm from the bottom in the unfiltered and filtered water is the same and is equal to 4.0 mg l^{-1}. Virtually, Mn found here is in the dissolved form (Tables 2 and 3). This corresponds to the information that in the river waters with pH range 4.2–7.0 the average content of Mn_{dis} is equal to 85% in the range of 46–99% [17].

Vertical distribution of Mn_{dis} as well as Mn_{tot} in the bottom layers of water is characterized by a gradual increase in their contents to the bottom. The increase in Mn concentration at its approach to the bottom indicates that its main source for bottom water is sediment.

Contents of suspended Mn (Mn_{sus}) in water layers at 30–70 cm from the bottom does not exceed tenths of MAC mg l^{-1} almost the whole year and is outside the accuracy of the analysis. Only in December, after the whole November mixing of water in the reservoir, the local increase of Mn_{sus} up to > 1 mg l^{-1} is marked. For the water layers of 30–40 and 50–60 cm from the bottom the relative concentration of Mn_{sus} reaches 42% and 53% of Mn_{tot} respectively. These fluctuations occur at a time when high concentrations of O_2 amounting to 5.9–6.9 Mg l^{-1} (44–51% saturation), which changes have been different compare with changes in the content Mn_{sus} content. In the water layer of 0–20 cm from the

Table 2. The average annual variations of some properties of bottom water in the reservoir

Parameters measured	Dates of observation											The average variation
	04.09. 1974	03.10 1974	01.11. 1974	26.12. 1974	12.02. 1975	12.03. 1975	12.04. 1975	22.05. 1975	19.06. 1975	16.07. 1975	15.08 1975	
Hydrological parameters												
T bottom,°C	16.5	14.0	6.9	1.8	2.3	2.0	6.6	8.2	13.2	14.4	17.2	9.4
Water level, m abs level	181.50	180.90	180.57	180.37	179.78	179.36	182.67	182.22	181.88	181.26	180.54	181.0
Hydrochemical properies (layer 0–20 cm up the bottom)												
O_2, mg l^{-1}	0.6	6.9	9.7	2.6	2.4	0.7	10.6	3.6	4.3	0.3	6.4	4.4
Eh, мВ	322	270.0	432.0	345.0	485.0	340.0	480.0	315.0	330	315	300.0	378
pH	7.75	8.24	8.00	7.55	7.30	7.15	7.80	7.50	7.27	7.35	8.70	7.7
Mn_{tot}, mg l^{-1}	17.7	< 1.0	« 1.0	11.7	9.4	16.9	« 1.0	4.7	9.0	16.6	4.5	8.2
Mn_{sol}, mg l^{-1}	10.9	< 1.0	« 1.0	6.3	8.7	15.4	« 1.0	3.0	7.4	16.0	2.2	6.4
Mn_{sol}, % от Mn_{tot}	62.0	–	–	54.0	92.0	91.0	–	64.0	82.0	96.0	49.0	78.0
Fe_{susp}, % Fe_{tot}	91.0	89.0	86.0	90.0	80.0	83.0	100.0	40.0	81.0	64.0	84.0	81.0
NH_4^+, mg l^{-1}	0.31	0.34	0.09	0.68	0.66	0.67	0.25	0.21	0.84	2.15	0.15	0.58

Table 3. The average annual characteristics of properties of various layers in bottom water

Water layers, cm from bottom	O_2, mg l^{-1}	pH	Eh, mV	Mn forms, mg l^{-1}		Mn_{dis}, % from Mn_{tot}
				Mn_{tot}	Mn_{dis}	
60–70	6.17	7.78	378	3.9	**3.7** [a]	**95**
50–60	5.86	7.79	376	4.1	**4.0**	**98**
40–50	5.60	7.78	375	3.9	**3.8**	**97**
30–40	5.38	7.78	374	4.1	**3.9**	**95**
20–30	5.32	7.74	371	6.2	**6.0**	**97**
0–20	3.02	7.69	360	7.7	**6.3**	**82**

[a] Values of correlation coefficients ≥ 95% are marked bold.

bottom of the increased concentrations of Mn_{sus} are marked 4 times y^{-1} and almost all of them correspond to the highest relative concentrations of Fe_{sus} (Table 2) [18]. Considerable proportion of Mn_{sus} may exist in the form of sorbed Fe (III).

Intra-annual fluctuations in the Mn content in bottom water (layer of 0–70 cm from the bottom) of Mozhajskoye water reservoir is characterized by two minima (October-November and April-May) and two peaks (February-March and July) (Fig. 1). The main regulator of these variations is the O_2 content in water. During the year the concentration of O_2 in the bottom water of the reservoir varies from 0.3 to 11.2 mg l^{-1} (from 3.3 to 94% saturation) averaging to 5.6 mg l^{-1} for 20–70 cm layer and to 4.4 mg l^{-1} for 20–70 cm layer. The highest concentrations of O_2 (up to 9.7–11.0 mg l^{-1}) are observed during the autumn and spring water circulation when the concentration of

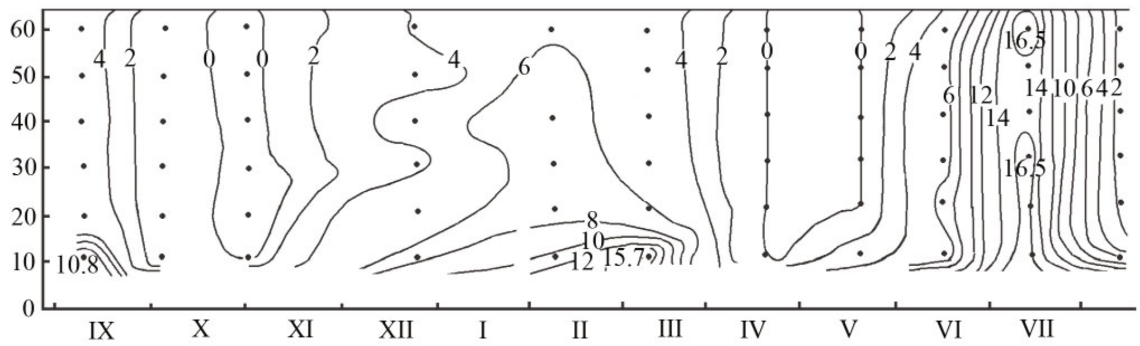

Fig. 1. Intra-annual variations in the concentration of total manganese in the bottom water layers (0-70 cm from the bottom) in Mozhaiskyi reservoir. Isolines drawn at intervals 2 mg^{-1}.

Table 4. Correlation coefficients for connections of Mn forms with other bottom water properties

Connections	Layers of bottom water, cm from bottom					
	0–20	20–30	30–40	40–50	50–60	60–70
$Mn_{tot} - O_2$	**−0.93** [a]	**−0.85**	**−0.86**	**−0.81**	**−0.72**	**−0.75**
$Mn_{sol} - O_2$	**−0.88**	**−0.81**	**−0.80**	**−0.77**	**−0.76**	**−0.65**
$Mn_{tot} - Fe(II)_{dis}$	0.49	**0.70**	**0.68**	**0.88**	**0.90**	**0.79**
$Mn_{sol} - Fe(II)_{dis}$	0.48	**0.65**	**0.76**	**0.76**	**0.67**	**0.67**
Mn_{sol} – pH	**−0.64**	−0.62	−0.59	−0.58	−0.49	−0.51
$Mn_{sol} - P_{min\ dis}$	0.29	0.60	**0.69**	0.59	**0.70**	0.59
$Mn_{sol} - P_{org\ dis}$	−0.02	0.56	0.52	**0.68**	0.12	0.72
$Mn_{tot} - P_{min\ dis}$	0.38	**0.63**	**0.65**	0.59	**0.70**	0.58
$Mn_{tot} - P_{org\ dis}$	−0.06	0.51	0.58	**0.67**	**0.65**	**0.68**

[a] Values of correlation coefficients ≥ 95% are marked bold.

Mn_{tot} in water < 1 mg l^{-1} or equal to 0. It should be noted that in May in the water layer 0–20 cm from the bottom at a concentration of O_2 of 3.6 mg l^{-1} the concentrations Mn_{tot} and Mn_{sus} reach 4.7 and 3.0 mg l^{-1}, respectively. In December the corresponding values are 2.6 mg l^{-1} for O_2 and 11.7 and 6.3 mg l^{-1} for Mn_{tot} and Mn_{sus}. In December in the water layer of 20–70 cm from the bottom at an average concentration of O_2 equal to 6.2 mg l^{-1} (42% saturation) the concentrations of Mn_{tot} and Mn_{sus} are 5.9 and 4.2 mg l^{-1}, respectively. Thus, at relatively high concentrations of O_2 in the bottom water the high concentrations of Mn are marked.

On the other hand, the highest concentrations of Mn are observed at the lowest concentrations of O_2. At the end of the freezing-up (March) the maximum concentration Mn_{dis} reaches 4.15 mg l^{-1}, due to the content 91% of Mn_{tot}. During the summer stratification (July), it slightly higher and is 16.0 mg l^{-1} and 96%, respectively. In both cases, the concentration of O_2 in water (the layer 0–20 cm from the bottom) does not exceed a few tenths mg l^{-1} (3–5% of saturation) (Tables 2 and 3).

High concentrations of Mn in the bottom water with high content of O_2 are caused not only by the slow oxidation of Mn (II) [17] but, apparently, by its greatest influx from sediment. Due to this, there is the hysteresis of its oxidation depending on the changes in O_2 concentration. In water of the Dnieper reservoirs (Table 1) and in hypolimnial waters of Swedish lakes the highest concentrations of Mn are observed during the freezing-up. The bottom sediments are their main sources also [11, 14].

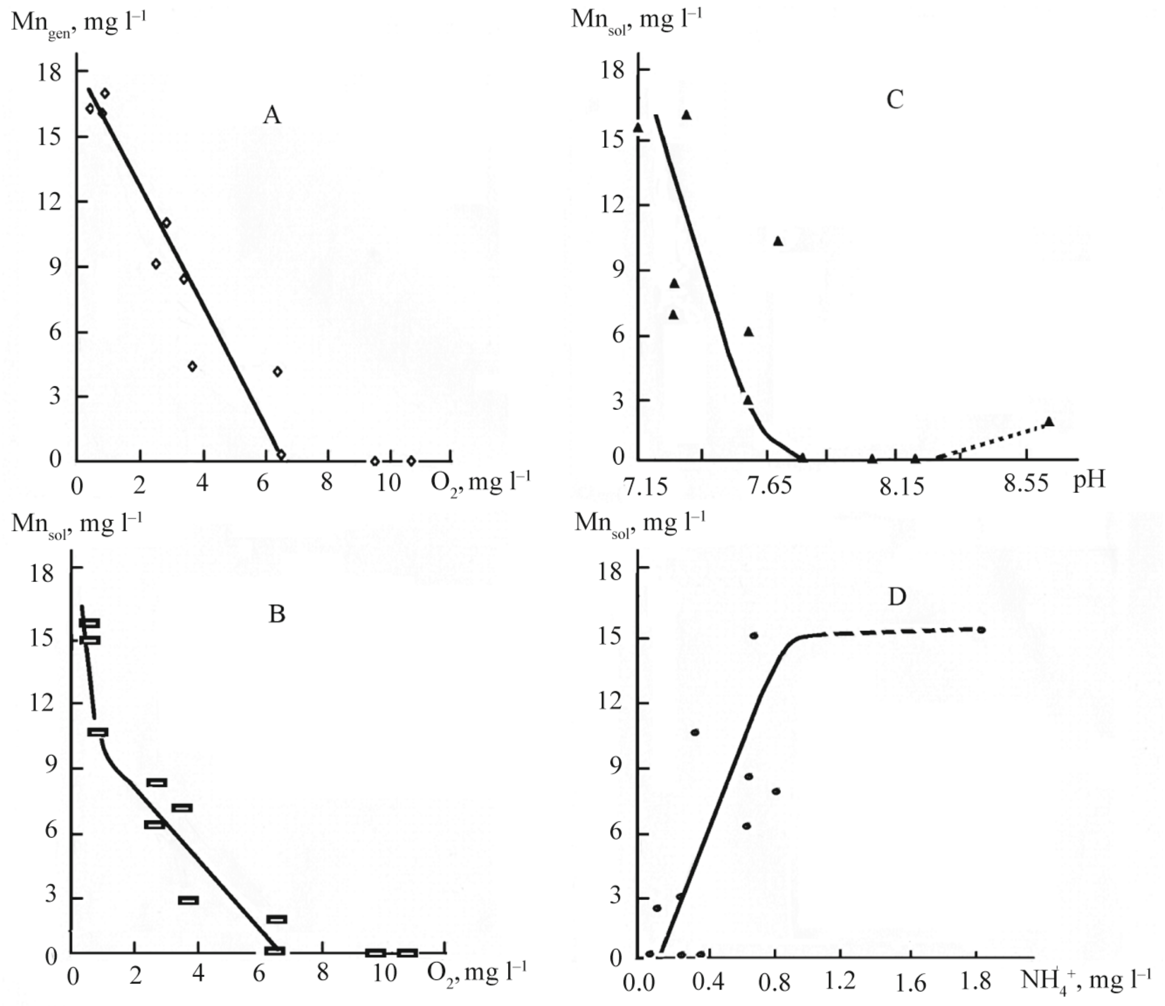

Fig. 2. The links between the Mn forms in the bottom water (layer of 0–20 cm from the bottom) and other characteristics of the medium: Mn_{tot} and Mn_{dis} as functions of O_2 concentrations (A, B); Mn_{dis} as a function of pH and NH_4^+ concentrations (C, D).

All studied layers of the bottom water of Mozhajskoye reservoir are characterised by feed-back concentrations of Mn_{tot} and Mn_{dis} with O_2 (Table 4). In the layer of 0–20 cm from the bottom the link on Mn_{tot} and O_2 is of linear character, whereas the link Mn_{dis} and O_2 is non-linear (Fig. 2, A and B). A link between Mn_{dis} and O_2 is also found in the bottom water of the Weinbach reservoir (Germany), which is represented by a hyperbolic shape of the curve. [19]. Linear relationship of Mn and O_2 in Mozhajskoye reservoir can be explained by the fact that both dissolved and suspended forms of Mn are taken into account, which are formed in this layer of water at oxidation (or sorption) of dissolved form.

Concentration of O_2 at which Mn compounds disappear from the bottom water due to their oxidation and sedimentation is 6.4–6.9 mg l^{-1}. For comparison: the critical content of O_2 for the existence of dissolved Fe_2 at pH 7.0 is 0.5 mg l^{-1} [20]. In the Weinbach reservoir Mn oxide ssaturates out at a concentration 4–5 mg O_2 l^{-1} [19].

Dissolved Mn in contrast to Fe is capable to form a more stable system, where only a small fraction is subjected to reduction-dependent cycle between the water and sediments. In solutions with pH < 8 spontaneous oxidation of Mn^{2+} ions is inhibited [15]. The annual average pH value of different layers in bottom water at observation stations is 7.7–7.8. Apparently, in this case the oxidation of Mn (II) near the bottom occurs more slowly than its diffusion from the sediments.

The oxidation rate of Mn (II) depends on the pH and rises with its increase [11]. For the water layer 0–20 cm (Fig. 2, B) an inverse relationship between changes in concentration of Mn_{dis} and pH of water was obtained, which supported the thesis of the bottom waters of Mozhajskoye reservoir. Despite the significant value of correlation coefficient (Table 4), a linear bond between these components is obtained only during 6 months (Fig. 2, B). At $pH \geq 7.75$ concentration of Mn (II) in water is close to 0. All the values of pH in bottom water exceeding 8 (Table 2) can be explained by the invasion of reservoir surface waters. Increase in the content of Mn_{dis} at increasing pH from 8.24 to 8.70 can be explained by hysteresis of oxidation of Mn (II) in the case of the recent overturn of the water column during destratification of water in August.

In the upper layers of water any significant relationship between Mn_{dis} concentration and pH was not detected (Table 4). Probably, another processes which-control the concentration of Mn compounds in water take place.

In all layers of the bottom water, excluding a layer of 0–20 cm from the bottom, there is a direct link between fluctuations of Mn and Fe (II) forms (Table 4). It is determined by fluctuations of O_2 concentration. Disturbance of this bond in the water layer of 0–20 cm is likely due to the large flows of Mn from the sediments during the year.

In some segments of the bottom water the relationship between Mn forms and dissolved P (Table 4) was revealed. Studies in Lake Oneida (USA) also showed that Mn in the water column was related to the general cycle of P [21]. In our case, such relations were local and characterized the properties of hydrochemical structures of bottom water layers [22]. Apparently, they are mediated by fluxes of these elements in the system of water–water microorganisms.

The direct relationship between concentrations of NH_4 and Mn_{dis} in a layer of 0–20 cm from the bottom (Fig. 2, F) is also mediated, which is determined by the fluxes of these compounds from sediment. When Mn_{dis} concentration in different seasons is ~ 16 mg l^{-1}, the concentration of NH_4 increases sharply to 2 mg l^{-1} only in summer. This indicates that the role of sedimentation and decomposition of organic matter in surface sediments (as a source of nitrogen) is more significant for the nitrogen cycle in bottom water than for the cycle of Mn. The latter is defined by a concentration of O_2 (Table 2).

In publication [17] the complexing of Mn in the water with organic matter, which proceeded most intensively during summer was marked. In Kiev reservoir the content of Mn bound into complexes varied within 35–80%. Any evidence of Mn complexing with organic matter in the bottom water of Mozhajskoye reservoir was not revealed. The author considers the estimation of Mn fluxes from the bottom, based on the rate of Mn_{tot} accumulation in the water layer70 cm in some periods of the year to be false. Though, the annual Mn fluxes from the bottom (from 5.3 mg m^{-2} day^{-1} during the ice period to 32.0 mg m^{-2} day^{-1} in April-May) may reflect their seasonal variation correctly, the absolute magnitude of these flows should be well under-estimated. The thickness of the layer of water with high concentrations of Mn with sediments as their sourse extends for several meters [10] and can be an order greater than studied in this work.

CONCLUSIONS

Mn_{tot} concentration in bottom water of Mozhajskoye reservoir (layer 0–70 cm from the bottom) is very high and reaches 6.16 mg l^{-1}.

Fluctuations of the concentration of Mn forms in bottom water is characterized by rotating periods of maximum highest and maximum lowest possible values regulated by the content of O_2.

Throughout the year, Mn_{dis} dominates. The main part of Mn_{sus} is formed in the bottom layers at Mn_{dis} oxidation.

Maximum concentrations of Mn_{dis} correspond to the minimum content of O_2, however, high concentrations of Mn_{dis} in water containing ≥ 5 mg l^{-1} O_2 are also marked.

In all layers of water, excluding the layer of 0-20 cm from the bottom, the relationship between seasonal fluctuations of Mn_{tot} and Mn_{dis} with Fe (II) are revealed.

For the water layer 0–20 cm an inverse relation between Mn_{dis} and pH of the water is revealed and direct relation between the concentrations in water of Mn_{dis} and NH_4^+.

The main source of Mn in the bottom layers of water is its flow from the sediment.

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