Dynamics of various forms of manganese in the pond waters

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Abstract. The forms of migration of manganese in pond waters are suspended matter and truly dissolved forms, including free manganese cations, as well as complex compounds formed by manganese with organic substances. The aim of the work was to study the dynamics of the content of various forms of manganese in the water of fish ponds. The content of individual forms of manganese was established according to the method developed by Linnik and Nabivanets. According to the methodology of Alekin, Semenov and Skopintsev determined hydrochemical parameters. It has been established that the dynamics of the content of manganese forms in different seasons depends mainly on the concentration of dissolved oxygen, pH value, inflow from sludge waters and the content of dissolved organic complexing substances in the water. In winter, free uncomplexed ions are the dominant form of migration. In other seasons, the content of complex forms exceeds the concentration of uncomplexed manganese. The dominant form of manganese migration in spring, summer, and autumn is Mn suspended, while in some periods of the same seasons, Mn dissolved predominates, which is explained by the influence of the intensity of water exchange, where suspended particles settle under conditions of slow runoff.

1. Introduction
The main forms of manganese migration in pond waters are suspensions and truly dissolved forms, including free manganese cations (Mn²⁺) and its complex compounds with dissolved organic substances (molecular weight 0.5-1.5 thousand and 1.5-5 thousand). The manganese content in the water of fish ponds, especially in phytoplankton, depends on the pH of the water, soil and the nature of fertilizers [1, 2]. Only with fertilization with ammonium sulfate is it possible to increase the manganese content in water, soil and in organisms of hydrobionts, i.e. the amount of manganese received by hydrobionts is determined by its content in individual ingredients of the trophic chain of water bodies. Literary sources indicate that the lack of manganese in the habitat of ingredients and hydrobionts causes disturbances in growth and development, changes in the skeleton, the coefficient of mobility and fish death [3, 4, 5].

The aim of this work was to find out the dynamics of the content of various forms of manganese in the water of fish-breeding ponds and compare the results with previously obtained similar data, which are influenced by the biological resource potential of water bodies.
2. Materials and methods
The studies were conducted in 2016 and again in 2017 in the pond farms of LLC "Khamovykh" (V ecological and phenological zone) of the Tersk district of the Kabardino-Balkar Republic [3]. Water samples to determine morphometric parameters were taken in the morning and evening every week.

The content of individual forms of manganese was established according to the method developed by Linnik and Nabivanets [4]. Water samples taken at the surface and bottom were mixed and, in addition to the content of certain forms of manganese, some hydrochemical parameters (the amount of dissolved oxygen, pH, dichromate oxidizability) were determined in them according to the method of Alekin, Semenov and Skopintsev [1].

3. Results and discussion
The content of $\text{Mn}_{\text{total}}$ and its individual forms in the water of fish-breeding ponds (V fish-breeding zone, Figure 1, 2) varies over a fairly wide range throughout the year. The maximum concentrations of $\text{Mn}_{\text{total}}$ and $\text{Mn}_{\text{dissolved}}$ fall mainly in the winter and early spring (pre-flood) periods, 1.7 and 1.65 mg/l, respectively. In winter $\text{Mn}_{\text{dissolved}}$ dominates, and the $\text{Mn}_{\text{suspended}}$ content is minimal (39-79 μg/L). The smallest amount of $\text{Mn}_{\text{dissolved}}$ (33-42 μg/l) was recorded in the spring-summer period (end of April-August). In addition to the well-defined peak of $\text{Mn}_{\text{dissolved}}$, in the winter-spring time the two largest maxima of the concentration of this form were noted at the end of August and at the end of October.

![Figure 1. Dynamics of total, dissolved and suspended manganese in the water of fish ponds (2016).](image)

In spring, summer and autumn the predominant form of manganese migration is a fine mechanical suspension. This is consistent with the conclusions that the main amount of manganese is transported by river waters in a suspended state [6, 7, 8]. The largest amount of $\text{Mn}_{\text{suspended}}$ (about 415 μg/l) was found in August.
Figure 2. Dynamics of dissolved forms of manganese: 1 - uncomplexed ions (Mn$^{2+}$); 2 - sum of complex compounds; 3, 4 - complex compounds with a molecular weight of, respectively, 0.6-1.6 thousand and 1.6-5.1 thousand.

The manganese content in natural waters is subjected to significant fluctuations depending on the values of the redox potential and the pH conditions [9].

High concentrations of Mn$_{\text{dissolved}}$ in winter can be explained by the occurrence of reducing conditions in the water supply, which contribute to an increase in mobility, and, consequently, in the content of manganese. At the same time the concentration of dissolved oxygen in February decreased to a minimum (about 0.51 mg/l), and the pH was equal to 7.46 (Figure 3). During the ice period the content of Mn$_{\text{suspended}}$ decreases due to the recovery of its oxidized forms, and the amount of suspended particles, on which it depends, is minimal. In winter uncomplexed ions predominate among the dissolved forms of manganese (Fig. 2); their concentration in February is maximum (1.3 mg/l, or 80% of the total amount of Mn$_{\text{dissolved}}$). Complexed forms are represented mainly by compounds with a molecular weight of about 0.5-1.5 thousand and 1.5-5.0 thousand: concentrations are equal to 180 and 80 μg/l, or 11.6 and 5.0% of Mn$_{\text{dissolved}}$. In addition to them complexes with a molecular weight of about 70 thousand and more than 120-150 thousand were found, but their share in the total amount of dissolved forms of manganese does not exceed 3-5% (only 50-70 μg/l). Since in other seasons of the year the concentrations of these complexes were even lower or were not detected at all, their dynamics is not considered.
Figure 3. Dynamics of dissolved oxygen (1), PH (2), and bichromatic oxidability (3).

The increase in the concentration of free uncomplexed manganese in the winter-spring period is explained by its influx from the silt waters. The latter are characterized by relatively low pH values (6.8-7.2) and redox potential (-80 to -140 mV) as a result of which the accumulation of divalent manganese is possible in them. In the course of special experiments, it was found that water-soluble forms of manganese in silt waters contain uncomplexed ions in an amount sometimes more than 12-17 mg/l. Part of the manganese coming from the silt water is bound into complex compounds by dissolved organic substances. However, the water in ponds is characterized by a low content of dissolved organic compounds, especially in winter (the concentration of organic matter was judged by the value of dichromate oxidizability (Figure 3), and, therefore, for complete binding of the incoming manganese, there are apparently lack of complexing compounds ... The proportion of complex forms of manganese in the winter-spring period did not exceed 19% of Mn\textsubscript{dissolved}. The facts of detecting manganese complexes with a molecular weight of about 70 thousand and more than 110-160 thousand in river water indicate the possibility of their supply from silt waters, where concentrations reach 260-320 μg/l.

With the onset of snow melting and the disappearance of the ice cover aeration of the river water occurs which can be seen from the rise in the dissolved oxygen concentration curve (Figure 3). The onset of oxidizing conditions leads to a sharp decrease in the content of dissolved forms and, above all, in the concentration of uncomplexed manganese as a result of its oxidation to tetravalent and precipitation in the form of hydrated MnO\textsubscript{2} oxide (IV).

In summer the dynamics of Mn\textsubscript{dissolved} is characterized by the predominance of not complexed forms over noncomplexed ones (Figure 2). Similar data were obtained in the autumn period. At relatively high pH values (8.7-9.2) noted in these seasons, the accumulation of free uncomplexed manganese ions in river water is practically impossible, since at pH ~ 8.5 it already undergoes hydrolysis and oxidation.

At the end of August, the concentrations of Mn\textsubscript{dissolved} and especially of its complex forms, slightly increase (Figure 2), which, apparently, can be explained by an increase of the role of intra-water body biological processes in the manganese cycle. A similar peak, but more clearly expressed, was noted at about the same time for ponds in 2017, the bioproductivity of which is undoubtedly higher than in
rivers. This phenomenon can be explained by the decomposition of phytoplankton (mainly blue-green algae), which is capable of accumulating manganese during development.

About 60-70% of the Mn\textsubscript{dissolved} released during such decomposition is free uncomplexed manganese, which can later bind into complex compounds by dissolved organic substances contained in natural water [10]. As you can see (Figure 3), the concentration of dissolved organic matter in summer is sufficient to bind Mn$^{2+}$ free ions. This can explain the increase in the concentrations of complex forms of manganese in August and their dominance in the total amount of dissolved forms.

The appearance of a peak in dissolved forms in October is possible either as a result of the decomposition of the remains of aquatic organisms that consumed manganese in the process of development or in connection with an increase in the role of groundwater supply. For a final conclusion many years of research are required. It is characteristic that in this period, too, complex forms prevailed over free manganese, accounting for about 62% of Mn\textsubscript{dissolved}.

Comparison of data on the dynamics of manganese migration forms in ponds in 2016-2017 allows us to note that its content and distribution between different forms in different seasons depends mainly on the concentration of dissolved oxygen, pH value, input from sludge waters and the content of dissolved organic complexing substances in the water. In winter when recovery conditions arise in the waters the dominant form of migration is free uncomplexed ions. Their concentration at this time reaches 80% of Mn\textsubscript{dissolved} in 2016 and 60% in 2017. In other seasons the content of complex forms exceeds the content of uncomplexed manganese.

It is also important that in the dynamics of manganese migration forms characteristic stages are observed that practically coincide in time but more clearly expressed in 2017. In 2017 the diversity of manganese complex compounds in ponds is wider than in 2016. In winter complexes with a molecular weight of ~ 70 thousand and ~ 0.5-1.5 thousand prevail, while in summer during the period of intensive vegetation of aquatic vegetation, the share of the latter is minimal, apparently, due to their consumption by hydrobionts. Throughout the year other complexes with a molecular weight of 120-150 thousand and ~ 1.5-5 thousand were discovered. In 2016 complex manganese compounds with a molecular weight of 120-150 thousand and about 70 thousand were presented in a noticeable quantity only in winter. Apparently, in this case, a different nature of the feeding of both ponds is manifested, and therefore in 2017 there are more high-molecular-weight humic compounds in ponds than in ponds in 2016, and their role in the complexation of heavy metals, including manganese, is well known.

In 2016, the dominant form of manganese migration in spring, summer, and autumn is Mn\textsubscript{suspended}, where as in 2017 in some periods of the same seasons Mn\textsubscript{dissolved} prevails. The latter is explained by the influence of the intensity of water exchange where suspended particles settle under conditions of slow runoff.

**Conclusion**

Analysis of data on the dynamics of various forms of manganese in water in 2016 showed that the content of uncomplexed forms sharply increases and dominates in the under-ice period, while in spring, summer, and autumn, complexed forms predominate.

In all seasons with the exception of the winter-spring (February-March), the relative concentrations of dissolved forms of manganese are lower than Mn\textsubscript{suspended}. Compounds with a molecular weight of ~ 0.5-5 thousand dominate among the complex forms. Complexes with a molecular weight of more than 120-150 thousand and about 70 thousand are present in noticeable quantities only in the winter-spring period.

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