Spatial and Temporal Dynamics Analysis of the Anionic Composition (Sulfates, Fluorides, Chlorides) of the Proletarskoye Reservoir

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Abstract. This research's goal is to study the features and find the patterns of changes in the concentration of chlorides, sulfates and fluorides over the past nine years and also along the longest part of the reservoir. Material and methods. During the research information on the history of the construction of the reservoir, its configuration and the sources used for desalination was used. Regular sampling data at three sampling points during 9 years was used for the research (in 2010-2018) these three sampling points are: one in the salty part of the reservoir and two in the desalinated part. Ion concentrations both annual and monthly average were used. Results. Chlorides, sulfates and fluorides dynamics was analyzed. It was discovered that the eastern part of the reservoir, which is river-fed and which is passing through salt marshes, is the main source of sulfates and chlorides while fluorides come from other sources. Conclusion. The conclusion about the spatial and temporal distribution of the anions also contains recommendations for a more detailed research of the salt composition of the Proletarskoye reservoir. It is also concluded that there is a particular influence of the anthropogenic factor on the development of sustainable ecosystems in such disturbed biogeocenosis as in an artificial reservoir.

1. Introduction

A reservoir is a body of water created by man in the bed of a river and performing household functions. During the formation of the reservoir, one can observe a violation of biogeocenosis and occurrence of a secondary succession. Changes in ecosystem can take decades, while regular human intervention does not provide a chance for a consistent process. As an example of a disturbed biogeocenosis, a reservoir serves not only as an interesting scientific object, but also a water body with a range of problems.

The Proletarskoye reservoir is of particular interest because of its connection with the desalination processes, which happened because of the release of water from the Kuban river through the Nevinomyssky Canal. The Proletarskoye reservoir was created in the 30s in order to satisfy the needs of the national economy of the Krasnodar Krai, Stavropol Krai, Rostov Region and Kalmykia. When the Proletarskaya dam was being built, the Novo-Manycheskaya dam was organized, which contributed to the transition of the entire flow of the Bolshoi Yegorlyk River into Lake Manych-
Gudilo. Thus, the Proletarskoye reservoir was divided into two sections: western and eastern. Unlike the eastern part, the western part and the subsequent Veselovskoye reservoir is more desalinated.

The Proletarskoye reservoir is of the channel type and its total area is more than 100 km² [1]. The reservoir is filled at the expense of other natural reservoirs but it does not cover the loss of water in the result of evaporation, therefore, in order to maintain the water balance, water is supplied from the Kuban River (more than 700 million cubic meters per year) [2]. The reservoir itself was formed by means of flooding the valley of the Zapadnyi Manych River and a number of lakes in the Manycheskaya Basin. Lakes Manych, Podmanok, Aral-Emke and some others turned into gulfs. The original mission of the reservoir was to perform transport functions, but now it is used for fishing purposes. The main tributary streams, except the Nevinomyssk Canal, are the rivers Kirasta, Chikalda, Volochaika, Kozinka, Dunda, Dzhalga, Khagin-Sala, Yegorlyk and Sredny Yegorlyk. However, the supply from these streams is relatively small, not only because of the predominance of water from the Kuban River, but also due to the organization of dams and small water reservoirs situated along most of the rivers listed above.

The length of the western part of the reservoir is approximately 20 kilometers, its width is from 1 to 3 kilometers. The bottom is flat, the maximum depth is 4.5 meters. Most of the water comes from the Yegorlyk River, and in full-flowing periods it also comes through the sluice from the eastern part of the reservoir. The main part of the reservoir in terms of area is the eastern part which is 159 kilometers long.

From a hydrological and biocenotic point of view, one can distinguish three stages of construction of the Proletarskoye reservoir. Before the construction of the dam in 1948, the territory, which is now occupied by the Proletarskoye reservoir, was a chain of rain-fed lakes. The water salination used to reach the mark of 300 g/l in the summer months, and some lakes used to dry up completely. At the second stage, in 1948-1989, when the water supply from the Kuban and Don rivers was organized, the salination dropped to 12 g/l, the Proletarskoye reservoir got the status of a fishing reservoir, and the species diversity of flora and fauna increased. At the third stage, from 1990 up to the present, there was a reduction of the water supply through the Nevinomyssk Canal. Fishing importance of the Proletarskoye reservoir has been almost completely gone.

This research aims at tracing the dynamics of the salt composition of the Proletarskoye reservoir and identify trends and its current state. In order to do this there was an analysis of the salt composition; cations and anions with the highest concentrations were isolated and their dynamics was studied both during the year and by average annual values over the past 15 years. In order to analyze the nature of high salination, there was noted a connection between changes in the concentration of various ions.

During the research the author used the monitoring data obtained by the hydrochemical laboratory of the Federal State Institution "Management of water resources of the Tsimlyansk reservoir". The research was conducted in 2005-2018 by Department of Water Quality Research and Analytical Activities of Federal State Institution "Donvodinform Center". Observation is carried out at 5 points in the territory of Rostov region. In order to analyze the dynamics of the salt composition, we have chosen three sections of the reservoir: the area of the gauging station, not far from the Novo-Manychevskaya dam, near the confluence of the Sredniy Yegorlyk River and near the headwater (Figure 1).

Thus, the entire length of the Proletarskoye reservoir was covered. It allows us not only to study the salt composition of the reservoir, but also to assess the influence of the feeding rivers on its chemical composition.
During the research of natural and anthropogenic factors which affect the chemical composition of the Proletarskoye reservoir, one pays attention mainly to the river Manych which feeds this reservoir. The Manych begins flowing in Kalmykia and passes through the lands referring to salt licks and salt marshes. It is known that this type of soil is rich with soluble salts, particularly, sulfates and chlorides [3]. The Manych river is a primarily rain- and snow-fed river, so the transfer of soluble salts from the soil cover to the reservoir is a natural process.

The tables below show the average annual concentrations of the considered anions grouped by sampling points. As can be seen from Tables 1, 2, and 3, regular observation of the chemical composition in these points started to be carried out in different years (in 2005-2010), therefore, in order to conduct a comparative analysis, we considered the interval from 2010 to 2018. These data served as the basis for evaluating the dynamics of the salt composition, which will be presented below.

Sulfate composition analysis of the Proletarskoye reservoir.

The increased content of sulfate anions in the water of the Proletarskoye reservoir is explained by its feeding in the eastern part at the expanse of the water of the Manych River, which is highly salinated.
During this long-term analysis based on the average annual concentrations of sulfate anions, one can observe its high values in the area of the gauging station. In some years (2013-2014), the concentration reaches 17000 mg/dm³ and even exceeds this value. Moreover, the sulfate dynamics at this point does not correlate with changes in the sulfate contents in the area of the Novo-Manycheskaya dam and near the headwater. So, in 2017, the concentration of sulfates in the area of the gauging station slightly decreased compared to the previous four years, while its concentration at the headwater was steadily increasing, moreover there was a sharp increase in its concentration and the area of the Novo-Manycheskaya dam (Fig. 2A and Fig. 2B). Figure 2B is shown to scale the data at two sampling points where the concentration of sulfates is approximately the same. Thus, it can be seen that the discussed sharp increase in $\text{SO}_4^{2-}$ concentration occurs only near the Novo-Manycheskaya dam and is not observed further. During a detailed research of this phenomenon, we discovered that a sharp increase in concentration occurred in June 2017 (up to 4635 mg/dm³) and had an impact on the average annual value. The dry period which leads to shallowing of the reservoir and an increase in salt concentration may be one of the reasons of this process [4]. However, referring to the weather diary of the meteorological service Gismeteo.ru [5], this situation was not observed. Another reason for this phenomenon can be the testing on the dam, which led to a short-term sharp increase in the value discussed in this research. If at the same time a small volume of saline water was discharged from the eastern part of the Proletarskoye reservoir, then there occurred a sufficient dilution up to the next sampling point (near the headwater). In general, there is no connection in the concentration of sulfates in samples from the first and two other subsequent sampling points. This can be explained considering the regulation of the runoff both by supply of highly saline water from the eastern part of the reservoir, and at expanse of fresh water from the Nevinomysskoye canal.

2. Chloride composition analysis of the Proletarskoye reservoir

During analysis of the chlorides concentration at the sampling points, in general, one can observe the dynamics similar to the dynamics of the sulfate composition (Figure 3).
The proximity of the concentrations at the sampling points near the Novo-Manycheskaya dam and the headwater is complemented by a sharp increase in concentrations in 2017 (up to 4653 mg/dm3), and also correlates with a sharp increase in sulfates in the same period. However, during observation of other parts of the graphs and comparing them with the dynamics of sulfates in the same period of time, some significant differences can be seen. For instance, a sharp decrease in the concentration of chlorides in 2017 at the reservoir inlet is not accompanied by the same changes in the concentration of sulfates, and the ratio of the concentrations of sulfates and chlorides at the reservoir outlet (headwater) and near the Novo-Manycheskaya dam also differ. Thus, the concentration of sulfates at these two points until 2015 are almost identical, while with the situation with chlorides is quite different. Until 2014 the concentration of chlorides near the headwater was on average 20% higher, but then the situation changes, and it is chlorides that prevail at the sampling point near the Novo-Manycheskaya dam.

3. Fluoride composition analysis of the Proletarskoye reservoir
Fluorides in the water of the Proletarskoye reservoir have increased indicators only at the inlet - in the area of the gauging station (Figure 4). Here, the average annual concentration of fluoride ions rarely
drops below 0.75 mg/dm³, which does not exceed the MPC standards for chemicals in the water of water bodies for domestic, drinking and cultural use [6].

A simultaneous analysis of the dynamics of the average annual concentration of fluorides shows that there is no clear connection between the indicators at all three sampling points. For instance, with a sharp increase in concentration (1.6 times) in the area of the gauging station in 2017, there are no significant changes in the water taken near the Novo-Manycheskaya dam and near the headwater. Moreover, there is also no general trend for these two sampling points until 2014. Starting from this period, the character of increases and decreases in fluoride concentration at the reservoir outlet and in its central part is the same.

It is also necessary to pay attention to the fact that the decrease in fluoride concentration in the western part is not as significant as it was observed for sulfates and chlorides. Thus, it is clear that the waters that were used for desalination (Nevinomyssky canal) are also enriched with fluoride anions.

4. Conclusion
As a result of observation of the dynamics of fluorides, chlorides and sulfates in the water of the Proletarskoye reservoir, one can come to the following conclusions:
- Despite the fact that the basis of the water balance in the western part of the reservoir is the Nevinomyssky Canal and the eastern part of the reservoir, which is separated by a dam and fed by the Manych River, there is no connection at three sampling points for any of the considered values.
- Sulfates and chlorides come mainly from the Manych River. Fluorides come from all sources of water that confluence the Proletarskoye reservoir. The predominant contribution is made by those rivers that are fed by underground sources.
- Genesis of a stable ecosystem and ensuring a stable water-salt balance in artificial reservoir implies the absence of sudden impacts. The regulation of the water balance should be carried out in such a way as not to lead to the exit of the biocinotic community from the optimal and tolerable zone. In the observed reservoir, salinity changes during several years can lead to suppression and death of many species of flora and fauna [9, 10].
- In order to conduct a detailed research on the water balance and salt composition of the Proletarskoye reservoir, it is necessary to observe both the water of the reservoir itself and the reservoir which are feeding it regularly. During regulation of the water balance (water discharge from the dam, water inflow from the Nevinomyssky canal), it is necessary to consider the parameters of dilution and account for the volumes of incoming waters.
5. References

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