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Changes in the concentration of chloride ions in the Volga water (section of the Zhigulevsky hydroelectric complex)

Abstract

For a quantitative assessment of changes in the concentration of chlorides, an analysis of the data of hydrological and hydrochemical observations obtained on the Volga River in the alignment of the Zhigulevsky hydroelectric complex was carried out. For the period 2001-2018 the average annual concentration of chlorides was 27mg/dm^3, the highest –31mg/dm^3, and the lowest - 24mg/dm^3. The chloride content was characterized by seasonal variability. During the winter season, the concentration of chlorides increased. The maximum was observed in April, before the beginning of the spring flood. During the spring flood, the chloride concentration decreased, reaching the lowest values in May at the peak of the spring flood. In the summer, the concentration of chlorides gradually increased, and in the autumn, it decreased. The intra-annual amplitude of the average monthly concentrations of chlorides was 14-42mg/dm^3. Such significant intra-annual changes in chlorides in the outlet section of the Kuibyshev reservoir are due to the interaction of the surface and underground components of the water flow of the Cheboksary and Nizhnekamsk reservoirs. In low-water years, the concentration of chlorides increased, and in high-water years, it decreased.

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Introduction

Chloride ions are among the main ions in the chemical composition of natural waters. In surface waters, chlorides are ubiquitous, and their content varies within a wide range from 1 to 1000mg/dm^3, depending on natural and climatic conditions.[1] The primary sources of chlorides in surface waters are igneous rocks, which include chlorine-containing minerals (sodalite, chlorapatite, etc.), saline deposits, mainly halite. Significant amounts of chlorides enter water bodies: from the oceans through the atmosphere; as a result of the interaction of atmospheric precipitation with soils, especially saline soils; with volcanic emissions. Part of the chlorides is discharged into water bodies with wastewater from point and diffuses sources of pollution. The introduction of chlorides in wastewater is becoming increasingly important. Chlorides have a high migration capacity, which is explained by their good solubility. They have a weakly expressed ability to sorption on suspended solids, and are not consumed by aquatic organisms.[2–4]

The content of chlorides in water affects the state of aquatic ecosystems, organoleptic properties of water and the human body. The increased content of chlorides impairs the taste of water and makes it unsuitable for drinking water supply, restricts its use for many technical and economic purposes, as well as for irrigation of agricultural land. The maximum permissible concentration (MPC) for water bodies for fishery purposes is 300mg/dm^3, for domestic and drinking water supply –350mg/dm^3. For irrigation of plants, the concentration of chlorides should be at the level of 50-300mg/dm^3, depending on the type of plant.

In the Volga water, the main attention in the study of chloride content was paid to the assessment of the spatial heterogeneity along the length of the river.[5–10] The patterns of seasonal variability of chlorides were estimated fragmentarily.[11] Therefore, the purpose of the study is to provide a quantitative assessment of the seasonal variability of chlorides based on the data of systematic long-term observations obtained on the river Volga in the alignment of the Zhigulevsky hydroelectric complex. Under conditions of high anthropogenic load[12,13] and global warming,[14,15] the relevance of such studies increases.

Materials and methods

Hydrochemical observations were carried out monthly in the period 2001–2018 on the river Volga in the area of the Zhigulevsky hydroelectric complex.[16–18] Almost the entire water flow of the Volga River passes through this section. Zhigulevsky hydroelectric complex is the outlet section of the Kuibyshev reservoir. The entrance sections for it along the Volga branch are the Cheboksary hydroelectric complex, and along the Kama branch – the Nizhnekamsk hydroelectric complex (Figure 1). The Saratov and Volgograd reservoirs are located downstream of the Zhigulevsky hydroelectric complex.

At the Kuibyshev reservoir, seasonal regulation of water flow is carried out by the operating organization – the branch of JSC «RusHydro»–«Zhigulevskaya HPP» in accordance with the "Basic Rules for the Use of Water Resources of the Kuibyshev Reservoir on the Volga", approved by the order of the Ministry of Land Reclamation and Water Management of the RSFSR dated November 11, 1983 No. 596.

The total volume of the Kuibyshev reservoir is 57.3km^3, and the useful volume is 30.7km^3. The average long-term water runoff is 244km^3, the maximum is 366km^3, and the minimum is 148km^3.[19,20] The useful volume allows for seasonal, weekly and daily regulation of water flow in the interests of various water users.

The hydrochemical observation point is located on the left bank of the Saratov reservoir, 2.5km downstream of the Zhigulevsky hydroelectric complex. The structure of the hydroelectric complex includes: a hydroelectric power station, combined with bottom spillways; concrete spillway dam; two-stage gateway. The width of the reservoir at the observation point is 1.0 km, and the depth is 6m.

Water samples were taken with a Molchanov GR-18 bathometer in accordance with the regulatory requirements (GOST R 51592-2000). Water samples were filtered through a 0.45 µm membrane filter. The determination of the mass concentration of chloride ions (Cl^-) was carried out in accordance with the guidelines of Roshydromet (Table 1).

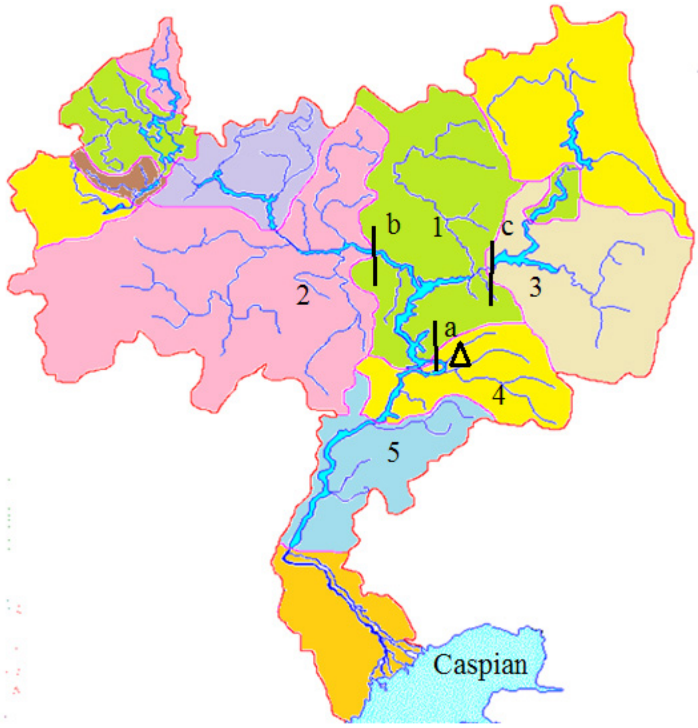

Figure 1 Location of the observation point (Δ) in the catchment area of the Volga River.

Reservoir basins: Kuibyshevsky (1), Cheboksary (2), Nizhnekamsky (3), Saratov (4), Volgogradsky (5).

Gates of hydrosystems: a – Zhigulevsky, b – Cheboksary, c – Nizhnekamsky.

Table 1 Range and accuracy of measurement of the mass concentration of chloride ions (CL^-)

Analysis method	Range measurements of the mass concentration of chlorides (X), mg/dm³	Accuracy index (error limits at probability P = 0.95) ±Δ, mg/dm³
RD 52.24.407-95	from 10 to 250	1.4 + 0.030 X
RD 52.24.407-2006	from 10 to 250	1.4 + 0.030 X
RD 52.24.407- 2017	from 10 to 1000	1.4 + 0.030 X

Results and discussion

The peculiarity of the hydrochemical regime of the Volga River is that it is a large river that flows from north to south at a distance of more than 3.5 thousand km and crosses several geographic zones. Therefore, the chemical composition of the waters of the Volga River does not correspond to the chemical composition of the waters of the side tributaries. At present, the Volga River is a complex natural and technical water system, where the regulation of water flow influences the formation of the hydrochemical regime of reservoirs. At the same time, the main regulator of the Volga river water flow is the Kuibyshev reservoir.

The concentration of chlorides in the water of the Kuibyshev reservoir is formed mainly under the influence of reservoirs located upstream. The influence of lateral tributaries (Sviyaga, Vyatka, Cheremshan), located in the local drainage area of the Kuibyshev reservoir, on the chloride content in the water is insignificant, since the volumes of water supplied from them are insignificant.

For the period 2001-2018 the average annual concentration of chlorides in the section of the Zhigulevsky hydroelectric complex was 27±2.2mg/dm³, the highest – 31±2.3mg/dm³, and the lowest – 24±2.1mg/dm³. Interannual changes in chloride concentration and water discharge are interrelated. For the same period, the average annual water consumption was 7.7thousand m³/s, the highest –9.0thousand m³/s, and the lowest – 6.2thousand m³/s. 2004, 2005, 2007 and 2013 should be attributed to high-water years, and 2006, 2010, 2011 and 2015 to low-water years. In low-water years, the concentration of chlorides increased, and in high-water years, it decreased (Figure 2).

Seasonal changes in water discharge were much larger than interannual fluctuations. Average monthly water discharge (Q) varied quite significantly from 5.3 to 18.3thousand m³/s (Table 2). The highest average monthly water discharge (Q_{max}) ranged from 6.5 to 26.1thousand m³/s, and the lowest (Q_{min})– from 4.1 to 11.1thousand m³/s.

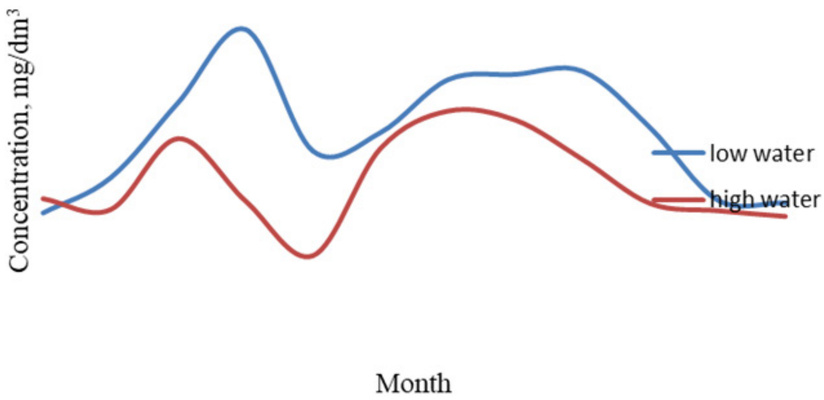

Figure 2 Influence of water content on chloride concentration.

Table 2 Seasonal distribution of water flow rates

Water discharge (thousand m^3/s)	Month											
	1	2	3	4	5	6	7	8	9	10	11	12
Q	5.9	6.2	5.9	11.8	18.3	8.7	6.5	5.8	5.6	5.3	6.2	6.3
Qmax	7.4	9	8.7	18.6	26.1	13.8	14.1	8.1	6.6	6.5	12.4	8.8
Qmin	4.5	4.9	4.2	5.1	11.1	5	4.8	2.1	4.4	4.2	4.1	4.5

It is customary to distinguish three hydrological seasons: winter low water (December-March), spring flood (April-June) and summer–autumn low water (July-November). The shortest is the period of spring flood, when the greatest amplitude of fluctuations in water discharge was observed (8.7-18.3thousand m^3/s). At the beginning of the spring flood in April, an increase in water discharge was observed, in May there was a peak of high water, and in June - a decline in spring flood and a decrease in water discharge to minimum values during the spring flood. Steady water discharge was observed during the winter low-water period and amounted to 5.9-6.3thousand m^3/s. The period of summer-autumn low-water period is the longest when water discharge is stable (5.3-6.5thousand m^3/s).

Seasonally, the average monthly concentration of chlorides (Cl^-) ranged from 22.8±2.1 to 30.6±2.3mg/dm³ (Table 3). The maximum chloride concentrations $(Cl^-)_{max}$ varied from 26.9±2.2 to 41.3±2.6mg/dm³, the minimum $(Cl^-)_{min}$ – from 14.0±1.8 to 24.0±2.1mg/dm³ (Figure 3).

Table 3 Seasonal changes in chloride concentration

Chlorides (mg/dm³)	Month											
	1	2	3	4	5	6	7	8	9	10	11	12
Cl-	24.1	26.4	28.8	30.6	24.5	28.7	30.2	29.9	28.3	25.8	24.3	22.8
(Cl-)max	27.9	39.1	35.6	41.3	34.1	41	39.3	35	36.7	29.8	29.3	26.9
(Cl-)min	20	21.7	20.4	22	14	19.3	21.8	24	22.9	21.8	20.8	18.6

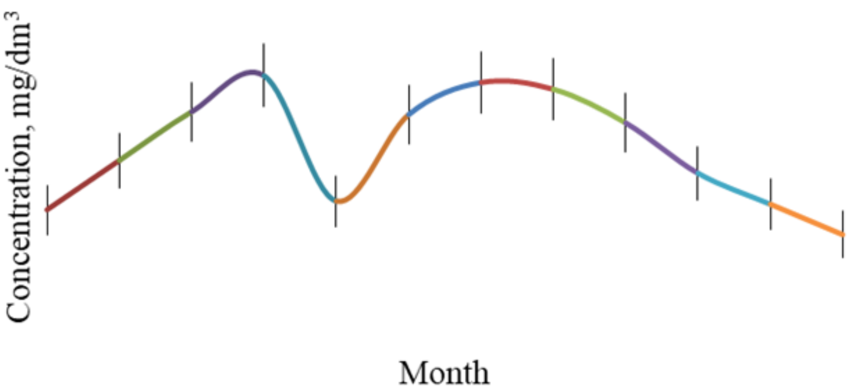

Figure 3 Seasonal changes in chloride concentration (Cl-) (┬, ┴ - vertical error bars).

The chloride content in the outlet section of the Kuibyshev reservoir (section of the Zhigulevsky hydroelectric complex) is significantly influenced by the mixing of the Volga and Kama waters, which differ in chloride content. The concentration of chlorides in the water of the Kama River is 3-4 times higher than that of the Volga River. The waters of the Kama River and the Volga River mix with each other to varying degrees, depending on the water flow rate in the section of the Cheboksary and Nizhnekamsk hydroelectric complexes. The greatest influence of mixing of the Volga and Kama waters on the chloride content in the section of the Zhigulevsky hydroelectric complex is observed during the spring flood.

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Seasonal variability of chloride concentration is due to the change of different water masses, as a result of the interaction of surface and underground components of water flow. During the spring flood, the role of melt waters with a low chloride content in the formation of water runoff increases, and the concentration of chlorides in the Volga water decreases. During the low-water period, the role of underground runoff gradually increases, and the concentration of chlorides increases until the beginning of the spring flood. Within a specific year, the amplitude of fluctuations depended on the volume of spring floods. The greater the flood volume, the greater the amplitude of seasonal fluctuations in the concentration of chlorides in water.

Conclusion

For the period 2001-2018 the average annual concentration of chlorides in the Volga River in the alignment of the Zhigulevsky hydroelectric complex was 27±2.2mg/dm^3, the highest–31±2.3mg/dm^3, and the lowest –24±2.1mg/dm^3. The content of chlorides in the outlet section of the Kuibyshev reservoir is due to the interaction of the Volga and Kama waters. Small interannual fluctuations in chlorides are caused by changes in the water content of the Volga River. The concentration of chlorides increases in dry years, and decreases in wet years.

In the seasonal context, the average monthly concentration of chlorides (Cl^-) ranged from 22.8±2.1 to 30.6±2.3mg/dm^3. The maximum chloride concentrations (Cl^-) max varied from 26.9±2.2 to 41.3±2.6mg/dm^3, the minimum (Cl^-) min – from 14.0±1.8 to 24.0±2.1mg/dm^3. Intra-annual changes in chloride concentration are due to the interaction of surface and ground waters throughout the year. With the dominant role of groundwater in low-water periods, the concentration of chlorides in the Kuibyshev reservoir increases, and with the dominance of surface water (melt and rain), it decreases.

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Conflicts of interest

The authors declare that there is no conflict of interest.

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