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Trends in the Variability of the Chemical Composition and Quality of Water in the Lower Volga Tributaries under Anthropogenic Impact and Climate Change

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Abstract—The regional features of transformation in the chemical composition of water in the Lower Volga tributaries and its main trends under anthropogenic impact and climatic variations are presented. Most trends for the principle ions (sulfates, carbonates, calcium and magnesium ions) are increasing, which may be a consequence of ongoing climate change. Moderate decreasing trends prevail in the concentrations of nutrients and organic substances in water. It was found that the trends in metal concentrations are multidirectional. All revealed statistically significant trends for iron and copper compounds are decreasing, and those for manganese are increasing. Based on the analysis of the identified trends in the chemical composition, the river ecosystems of the Lower Volga tributaries are classified into two categories: stable ("healthy") and transformed ("transitioning").

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INTRODUCTION

Under modern conditions of intense anthropogenic impact, the qualitative and quantitative depletion of water resources, the degradation of small rivers, and the increasing environmental stress on water bodies take place, especially in industrially developed and water-stressed regions of Russia. High anthropogenic impact and the Volga River control led to environmental changes all along the river, especially in the lower reaches. The intense water use, irrevocable water withdrawal, and chemical pollution disturb the unique ecosystem of the Lower Volga. Environmental changes are manifested in the disturbance of natural biological cycles of aquatic ecosystems, in the reduction of biodiversity and bioproductivity [15].

The main danger of long-term anthropogenic impact on river ecosystems is the occurrence of environmental emergencies. Every year the Volga River and some of its tributaries (the Moskva, Klyazma, Chapaevka rivers, et al.) are among the objects with high and extremely high contamination of water on the territory of Russia [13].

The major ecological problems in the Lower Volga region are the high concentration of a number of pollutants in water, the deterioration of its quality, and the intensification of the ecological regress causing the transformation of the structural organization of plankton and benthos communities against a background of changing natural, climatic, and hydrological conditions [1, 16, 17].

According to the level of development of intra-system processes, the status of the Lower Volga aquatic ecosystems in different periods of their functioning is characterized as "anthropogenic stress with elements of ecological regress" and "the state with elements of ecological regress," when a low and medium level of environmental risk, respectively, is formed. In dynamics, there is an increase in the processes of "ecological regress," which indirectly indicates an increasing anthropogenic impact on aquatic ecosystems in the recent years and a decreasing self-purification capacity of the river [16]. In such context, the investigation of regional features of transforming the chemical composition of water in the Lower Volga tributaries and the revelation of its trends under anthropogenic impact and climatic variations is especially relevant. This will allow making projections of changes in water chemistry and quality under various climatic variations, as well as under ongoing anthropogenic impact in river catchments.

The sources of river water pollution in the Lower Volga basin. As shown before [12, 17], the Lower Volga aquatic ecosystem is affected by the pollution sources of various scales and degrees of danger. Anthropogenic impact on environmental conditions of rivers in the Lower Volga basin is caused by such regional factors as the transport of contaminated wastewater down the stream, the discharge of contaminated and insufficiently treated wastewater from industrial and agricultural enterprises, the influence of small vessels, river control, the diffusive pollution from the catchment, etc.

The highest water rotation coefficient in the Volga River basin is observed for the Lower Volga (92.7%), which is explained by the development of fuel, metallurgic, and chemical industries widely using the recycling water supply. Due to climatic and soil conditions, the irrigated farming is most developed in this arid part of the basin, whose contribution to irrigated lands makes up 60% [4].

In the recent years, federal water-protecting measures [3, 6] led to a decrease in water consumption in the housing and utilities sector and agriculture and in the discharge of industrial wastewater, mine and collector-drainage effluents [4]. Despite this, there is no significant improvement in the dynamics of water quality in the Volga basin and in the lower reaches. On the contrary, there is an increasing role of diffusive pollution, that is comparable (and is sometimes higher) with the contamination from point sources [3].

Climate change in the Lower Volga basin is manifested in an increase in annual precipitation due to an increase in spring and winter precipitation (by 15–30%). The revealed increase in average annual temperature is contributed both by the cold and warm half-years. The absolute value of the temperature rise in the cold half-year is more than twice higher than in the warm half-year [9].

Based on the analysis of the aridity index variations for the Lower Volga basin, an increase in the moistening of the territory was revealed along with the temperature rise in the cold half-year and in winter. Despite this, according to [9], a considerable lack of moistening is expected in the growing season for terrestrial and aquatic ecosystems of the basin. An increase in the temperature of water accompanied by its deficiency in the warm season is also possible. This may cause increased water blooming and reduce oxygen content in it due to evaporation growth. Thus, climatic variations may cause significant negative transformations in the Lower Volga aquatic ecosystems.

DATA AND METHODS

The objective of the present study is to reveal main long-term trends in the water chemistry and quality in the Lower Volga tributaries against a background of ongoing climatic variations and anthropogenic impact.

The Lower Volga tributaries flowing in the forest-steppe and steppe zones were chosen as research objects. The description of the river reaches under study is presented in Table 1. The chemical composition of water of the analyzed rivers is formed in forest-steppe and steppe zones, but the differences are possible, which are associated with the influence of lithologic and geomorphologic landscape features of physiographic provinces where the river reaches are located.

Initial data included long-term (1985–2017) hydrological information of the Roshydromet observation network about surface inland water conditions. The study was based on such hydrochemical parameters as the concentration of chlorides, sulfates, bicarbonates, magnesium, calcium, ammonium and nitrate nitrogen, BOD_5, COD, oil products, iron, copper, zinc, and manganese compounds.

Observations at the Roshydromet network are carried out in accordance with the unified water sampling and analysis methods, whose standardization is metrologically provided. The periodicity of hydrochemical observations (and, hence, the temporal resolution of resulting annual data) is determined by the category of observation stations. For most selected rivers, the water sampling was performed during the main phases of the river water regime, i.e., at least seven times per year.

The evaluation of transformation patterns for the chemical composition of water and the revelation of trends in pollutant concentrations that change river water quality, are essential for studying time series of hydrological data. The occurrence of the main trend in the dataset can be caused both by the anthropogenic impact and climatic variations, which are inhomogeneous both in the intensity and direction.

The main trends in concentrations of chemicals are revealed by the correlation analysis. The Kendall rank correlation coefficient and the level of confidence probability at which these coefficients can be con-

Table 1. The geographic and hydrological characteristics of the Lower Volga tributaries [2, 8]

River	Observation station	River reach characteristics		River characteristics		
		R, km	*S*, km^2	*L*, km	*S*, km^2	*Q*, m^3/s
Forest-steppe zone Kinel-Kama province						
Samara	Alekseevka	13	45500	594	46500	47.2
Sok	Krasnyi Yar	21	11100	363	11700	33.3
Bol'shoi Cheremshan	Novocheremshansk	64	6050	336	11500	36.1
Padovaya	Samara	–	–	52	266	–
Bugul'ma-Belebei province						
Bol'shoi Kinel'	Timashevo	74	12000	442	14900	34.0
Sok	Sergievsk	–	–	363	11700	33.3
Stepnoi Zai	Al'met'evsk	–	–	291	5020	–
Surgut	Sernovodsk	8.2	1370	97	1450	–
Steppe zone Obshchii Syrt province						
Samara	Buzuluk	242	22000	594	46500	47.2
Tok	Erokhovka	38	5440	306	5930	–
Samara-Irgiz province						
Bol'shoi Irgiz	Pugachev	303	18200	675	24000	23.0
Chapaevka	Chapaevsk	–	4040	298	4310	2.53
Chagra	Novotulka	42	2550	251	3440	3.5
Khoper-Medveditsa province						
Buzuluk	Perevoznikovo	19	4280	248	4460	7.7

The dash means the absence of data. *R* is the distance from the mouth; *S* is the catchment area; *Q* is the water flow in the mouth.

sidered statistically significant are calculated using the Statistica 13.3 software package. The use of the nonparametric rank correlation coefficient is due to application of hydrological data not following the Gaussian distribution. If initial data have a symmetric distribution, the rank correlation coefficients are close to the respective values of the Pearson coefficients.

Data on the year ranked in ascending order were used as an independent variable, and the average annual concentration of a specific chemical for this year was used as a dependent variable. The negative value of the rank correlation coefficient points out a gradual decrease in average annual concentrations with time (over 30 years), and the positive value indicates their gradual growth (i.e., the water quality deterioration).

Taking into account inhomogeneity of sampling dates and intraannual variations in hydrochemical data, the relationship was estimated using the linear correlation coefficient and the following criteria: if $r = 1.00$, the correlation is functional; if 0.75 $r < 1.00$, the correlation is very high; if 0.50 $r < 0.75$, the correlation is high; if 0.25 $r < 0.50$, the correlation is moderate; if 0.00 $r < 0.25$, the correlation is low.

RESULTS AND DISCUSSION

River water with complex chemical composition is formed in the Lower Volga basin: it includes bicarbonate fresh water with medium mineralization (in the north of the territory) and brackish mixed-type surface water. Some Lower Volga tributaries are characterized by the high concentration of sulfates and chlorides in water: these are the Sok, Surgut, Chapaevka, Chagra, Bol'shoi Kinel', and Padovaya rivers. In terms of water chemistry, these rivers are from the chloride or sulfate class, with the dominance of calcium or sodium and potassium ions [14].

As noted before [14], the concentration of biogenic and organic substances in the Lower Volga tributaries varies greatly and periodically exceeds the maximum permissible concentration (MPC) by tens of times. The highest concentrations are observed in the Padovaya and Chapaevka river catchments, which may be a reason for the intensification of anthropogenic eutrophication of river ecosystems. River water is also characterized by high concentrations of heavy metals, especially of iron, copper, and manganese, whose concentrations significantly vary and can exceed maximum permissible concentration by dozens of times.

The quality of river water in the Lower Volga basin generally varies between the categories of the 3rd and 4th quality classes: "polluted," "very polluted" or "dirty," "very dirty" due to a high concentration of a number of pollutants (manganese, copper, iron, phenols, biogenic and organic substances) [14].

Such inhomogeneity in the composition of river water in the analyzed tributaries predefines a need to reveal and estimate its major trends (trends in concentrations of chemicals).

In total, 36 (of 70 possible) statistically significant trends in the concentration of principal ions in water were revealed for the investigated Lower Volga river ecosystems: 11 for sulfates, 8 for chlorides, 7 for magnesium ions, 6 for bicarbonates, and 4 for calcium ions. Most trends are increasing. The revealed statistically significant correlation is most often low for the principal ions and increases to the moderate level only in single cases (Table 2).

It should be noted that statistically significant increasing trends were detected in most cases for the concentration of carbonates, sulfates, calcium and magnesium ions, which may be an effect of climate change. For example, some publications [5, 10, 11, 19] consider increase in the concentration of inorganic carbon, carbonates, and bicarbonates in water as one of the climate change consequences for surface water, which is primarily associated with the increase in the concentration of carbon dioxide in the atmosphere and with its additional absorption by the water environment. It is also noted that as precipitation increases, the washout of bicarbonates and principal cations (magnesium and calcium) from rocks is activated.

The distribution of the revealed trends over the natural zones is uniform (18 trends each) (Table 2). Considering the variability of the chemical composition in individual river reaches, it should be noted that the ion composition is most stable in three areas of the study territory: these are the Samara (Alekseevka station), Sok (Krasnyi Yar), and Surgut (Sernovodsk) rivers, where only one trend is available. The water composition is most transformed in the Chapaevka River reach in the area of Chapaevsk, where four increasing trends were revealed. As known, this river is among the most contaminated watercourses in the Volga basin and is ecologically unfavorable.

The river reach in the area of Chapaevsk is characterized by high anthropogenic load. The areas of ecological disaster with a high level of chemical pollution and the zone of ecological crisis were locally detected here [7].

The correlation analysis of variability in the concentration of biogenic and organic substances revealed 45 (of 70 possible) trends in 14 river ecosystems of the Lower Volga basin: 12 for oil products and organic matter (in BOD_5) each, 9 for nitrate nitrogen, 7 for the total amount of organic matter (in COD), and only 5 for ammonium nitrogen (Table 2).

For the analyzed river reaches, decreasing trends prevail for the concentration of ammonium nitrogen, oil products, and organic substances (in total, 34 decreasing trends), and increasing trends dominate for nitrates. At the same time, more than a half of the trends in the concentration of biogenic and organic substances have moderate correlation.

The number of statistically significant trends for individual river reaches varies from 2 to 5. The river reaches in the steppe zone stand out: the Samara (Buzuluk) and Tok (Erokhovka) river reaches each having five differently directed trends. For them an increasing concentration of nitrates is synchronously observed against a background of a decrease in the concentration of the other components (Table 2). Despite the statistically significant decrease in the concentration of organic and biogenic substances, the presence of trends indicates the instability of water chemistry in these tributaries.

For the investigated Lower Volga river ecosystems, 27 (of 50 possible) statistically significant trends were revealed in the concentration of heavy metal compounds: 13 for iron, 6 for copper, 5 for manganese, and 3 for zinc. Most trends are decreasing, the correlation is low for two thirds of the total number. The distribution of the revealed trends over the natural zones is inhomogeneous: most trends were found for the river reaches in the forest-steppe zone (Table 2).

Table 2. The values of the Kendall rank correlation coefficient between the sampling dates and concentrations of principal ions, biogenic and organic substances, as well as heavy metal compounds in the water of the Lower Volga tributaries

River	Principal ions					Biogenic and organic substances					Heavy metal compounds			
	Mg^{2+}	Ca^{2+}	Cl^{-}	SO_4^{2}	HCO_3	Am. ions	N	Organic substances		Oil products	Fe	Cu	Zn	Mn
								in BOD_5	COD					
Forest-steppe zone														
Kinel'-Kama province														
Samara	0.09	0.01	–0.03	*0.18*	0.08	–0.07	*0.31*	**–0.33**	–0.04	**–0.44**	**–0.37**	**–0.13**	0.01	*0.08*
Sok	0.10	0.07	0.10	*0.17*	–0.02	0.06	*0.24*	**–0.36**	**–0.11**	**–0.39**	**–0.39**	**–0.16**	0.04	0.01
Bol'shoi Cheremshan	*0.24*	*0.11*	–0.04	0.03	*0.25*	**–0.24**	0.09	**–0.27**	–0.04	0.07	**–0.16**	–0.09	**–0.13**	f/d
Padovaya	*0.14*	0.04	**–0.21**	*0.15*	*0.27*	–0.07	*0.30*	**–0.17**	0.01	**–0.29**	**–0.21**	**–0.17**	–0.07	*0.14*
Bugul'ma-Belebei province														
Bol'shoi Kinel'	0.06	0.01	**–0.21**	*0.26*	0.04	0.09	*0.35*	**–0.35**	**–0.12**	**–0.39**	**–0.37**	**–0.17**	–0.02	0.01
Sok	*0.14*	*0.15*	0.05	*0.20*	0.04	0.06	*0.32*	**–0.33**	**–0.17**	**–0.35**	**–0.31**	–0.08	0.04	*0.15*
Stepnoi Zai	*0.18*	–0.05	**–0.14**	*0.19*	0.09	0.0001	*0.51*	0.0001	**–0.25**	**–0.23**	**–0.56**	**–0.18**	*0.27*	f/d
Surgut	–0.06	**–0.13**	–0.07	–0.07	–0.09	–0.01	–0.09	0.0001	0.03	0.06	0.07	0.02	0.0001	**–0.10**
Steppe zone														
Obshchii Syrt province														
Samara	0.09	–0.07	**–0.16**	**–0.27**	*0.13*	**–0.18**	*0.25*	**–0.31**	**–0.19**	**–0.28**	**–0.20**	–0.01	0.03	n/a
Tok	*0.18*	0.05	**–0.13**	–0.07	*0.20*	**–0.14**	*0.31*	**–0.31**	**–0.16**	**–0.18**	**–0.39**	0.0001	–0.08	n/a
Samara-Irgiz province														
Bol'shoi Irgiz	*0.16*	–0.03	*0.17*	*0.21*	0.01	–0.08	–0.10	**–0.21**	*0.07*	**–0.08**	**–0.08**	**–0.27**	**–0.13**	f/d
Chapaevka	*0.13*	*0.13*	*0.17*	*0.15*	0.02	–0.08	0.07	**–0.24**	–0.02	**–0.34**	**–0.34**	–0.06	–0.04	*0.20*
Chagra	–0.04	–0.05	**–0.17**	*0.11*	**–0.11**	**–0.11**	0.09	**–0.36**	–0.01	**–0.35**	**–0.32**	–0.06	0.07	0.03
Khoper-Medveditsa province														
Buzuluk	0.05	–0.09	–0.06	**–0.31**	*0.19*	*0.28*	*0.19*	**–0.26**	–0.04	**–0.31**	**–0.19**	0.0001	–0.07	n/a

Statistically significant rank correlation coefficients with $p < 0.05$ and higher are highlighted: the bold script means a decreasing trend, the italicizing means an increasing trend; f/d is "few data available for analysis"; n/a is "no data available." Am. ions is ammonium ions; N is nitrates. The observations stations on the rivers correspond to those in Table 1.

Statistically significant trends toward an iron compound concentration decrease were found for all studied river reaches. The same direction of trends was also registered for copper compounds in more than 40% of cases. Such conjugate spatiotemporal variability of these metals may be caused both by common natural and climatic factors of water chemistry formation and by the metal migration in natural water under changing environmental conditions (water mineralization, acidity, or redox potential).

The revealed multidirectional pattern of the main trends in the chemical composition of river water in the Lower Volga catchment causes the instability of the chemical composition of water in the tributaries. Consequently, the greater the number of hydrochemical parameters varying in time is, the more unstable a river ecosystem is as a whole.

The portion of parameters that have long-term trends can be used to assess the water body status. This methodological approach was described in [18], where the authors classified ecosystems into "healthy" (where trends are available for less than 50% of parameters), "disturbed" (>75%), and "transitioning" (50–75%) ones.

According to the combination of indicators of the chemical composition of water that have long-term trends, it is possible to divide the studied river ecosystems of the Lower Volga tributaries into two categories:

—healthy ecosystems (stable, 43% of river reaches): the Samara (Alekseevka), Sok (Krasnyi Yar), Bol'shoi Cheremshan, Surgut, Chagra, and Buzuluk rivers;

—transitioning ecosystems (transformed, 57%): the Sok (Sergievsk), Padovaya, Bol'shoi Kinel', Stepnoi Zai, Samara, Tok, Bol'shoi Irgiz, and Chapaevka rivers.

The absence of the reaches classified as disturbed ecosystems among the analyzed river ecosystems points out a relative stability of the Lower Volga tributaries.

CONCLUSIONS

The long-term trends in the concentration of chemical substances in river water under conditions of anthropogenic load and climatic variations were revealed for the Lower Volga tributaries.

Increasing trends dominate among statistically significant trends in the concentration of principal ions, but the correlation is low. An increase in the concentration of sulfates, carbonates, and calcium and magnesium ions was found, which may be an effect of climate change.

Decreasing trends prevail for biogenic and organic substances in the water of the Lower Volga tributaries. This is more typical of oil products and organic substances against a background of increasing concentrations of nitrate nitrogen compounds. The revealed trends are mainly moderate.

All statistically significant trends for iron and copper compounds are decreasing, and those for manganese are increasing, most trends are weak.

Such different direction of the main trends in the chemical composition of river water causes different degrees of river ecosystem stability. The stable (healthy) ecosystems made up 43% of the total number of the analyzed river reaches, and the transformed (transitioning) ecosystems made up more than a half (57%).

The results of the present study may help to solve urgent problems of assessing and predicting the quality of water in the ecologically stressed Volga basin, to develop regional criteria for the assessment of water quality and aquatic ecosystem status, as well as to plan ecologically reasonable water-protecting activities aimed at the preservation and restoration of river ecosystems.

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