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Current trends in chemical hydrology of the Pavlovsky Reservoir on the Ufa River

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ABSTRACT

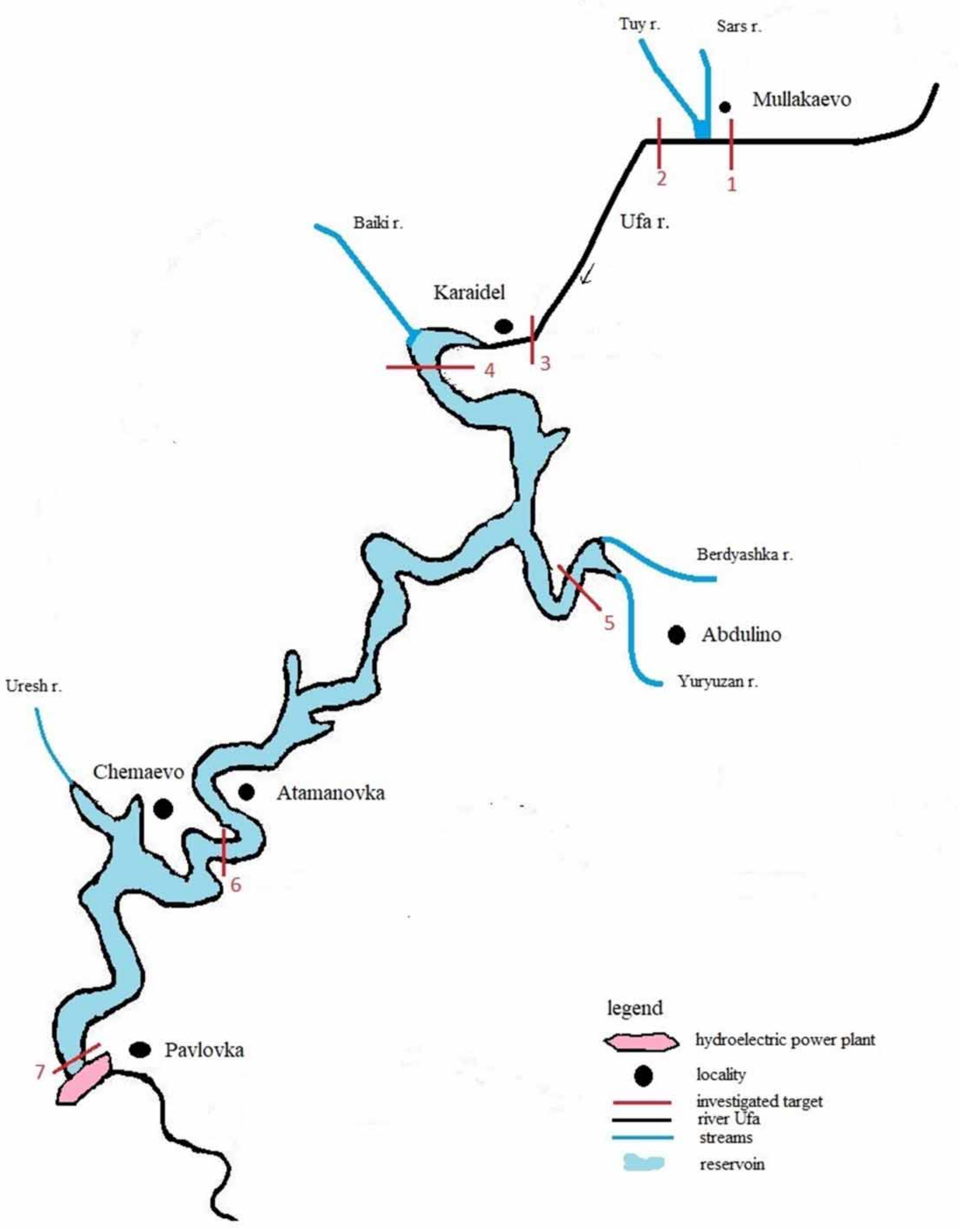
The paper presents an analysis of long-term dynamics and current trends in the hydrochemistry of the Pavlovsky Reservoir by 10 chemical indicators at seven water intake points. The choice of 10 chemical elements was justified in previous studies mentioned in the paper. This approach allows using the observation data of the Bashkir FSBI (Federal State Budgetary Institution Bashkir Hydrometeorology and Environmental Monitoring Department), previous studies conducted in 1986–88 and in 2000 and the results of the present research (2018–2019) making it possible to track the dynamics of changes in the hydrochemical composition of water over 30 years (from 1986 to 2018). It was revealed that throughout the reservoir, from its beginning to the upper reaches, the content of Sr^{2+}, Mn^{2+} and petroleum products in the water decreases; Zn^{2+}, Hg^{2+}, phenols and organic substances increase; Fe total ($Fe^{2+} + Fe^{3+}$), P total are evenly distributed (according to PO_4^{3-}), Cu^{2+}. The study of the features of the long-term dynamics of the hydrochemical indicators of the Pavlovsky Reservoir allows for determining trends in the state of the ecosystem of the water body and proposes measures to preserve the operational properties of the reservoir.

Key words: chemical elements, contamination sources, integrated approach, maximum permissible concentrations, reservoir, water area

HIGHLIGHTS

- Studying the modern processes of chemical hydrology of the Pavlovsky Reservoir.
- The long-term dynamics of the hydrochemical indicators of the Pavlovsky Reservoir.
- Maximum, minimum and average values of the concentrations of Fe, Mn, Cu, Sr, Zn, etc.
- Priority ways to improve the reservoir water quality.

GRAPHICAL ABSTRACT



INTRODUCTION

The negative impact on water resources is increasing, leading to pollution, depletion and degradation of reservoirs and creating a threat to the ecological safety of regions. The problem of water reservoir pollution has recently become the most urgent. In most cases, the use of water reservoirs as fisheries and drinking water supply sources is becoming impossible. The issue of studying the hydrochemistry of reservoirs has become acute. Thus, the study of the chemical composition of natural waters and the patterns of their change under the influence of physical, chemical and biological factors is very important.

Because of the absence of a unified scientific and technical policy in the protection of reservoirs as a single integral ecological system, the scientific and practical study of issues related to effective methods of modern monitoring of the state of reservoirs, elimination of chemical and biological pollution and the improvement of water quality seems extremely insufficient. Scientific institutions conduct studies separately. Scientific developments are sometimes tested locally in certain regions or within a certain water basin.

The creation of medium and large reservoirs entails the transformation of the landscapes of river basins and natural lakes and has many negative consequences, among which the most dangerous one is the pollution of artificial reservoirs. In this regard, there is a need to monitor the state of water quality, predict natural hazards, and develop and implement effective methods of preventing or mitigating their consequences.

A unified concept for determining the water quality of reservoirs in Russia has not been developed yet. There is no clear method for collecting, processing and storing information. Moreover, there are no recommendations for operational, medium-, long-term forecasting of pollution intake and determining pollution sources in reservoirs. There are no recommendations or measures to improve the water quality of reservoirs.

In this regard, there is a need to study the long-term dynamics and current trends in the chemical composition of water (concentration of chemicals) in certain reservoir basins to establish dependencies applicable to some reservoirs. The Pavlovsky Reservoir, which has a series of research results in various years and makes it possible to compare them with each other and modern research, is an ideal water body for the further development of scientifically based recommendations and measures to improve the water quality of reservoirs.

Nowadays, reservoirs are the primary sources of water for consumers and users (urban water supply, technological processes of hydroelectric power plants, recreational, fisheries and other activities). Today, reservoirs are the main water sources for urban supply, technological processes at hydroelectric power plants, recreational areas, fisheries and other water users. They form the main industrial, agricultural and household effluents (Yu *et al.* 2018; Liro *et al.* 2020).

There are many studies on the water quality problem of reservoirs and the influence of hydrological and chemical parameters of rivers on their transformation. In the work of Abdrakhmanov *et al.* (2021) it is noted that the chemical hydrology of a reservoir depends on the state and composition of the rivers flowing into it.

The work of Avakian *et al.* (1987) considers the changes in the ecosystem occurring with the creation of reservoirs. The research studies reservoir hydrochemical and hydrobiological states. It notes that immersed soils, peatlands and vegetation replenish reservoirs' water with nitrogen, phosphorus, iron, organic and other substances. Changes in the reservoir water's chemical composition affect the river section's hydrochemical and hydrobiological states located below the waterworks facilities (Grishin *et al.* 2021).

The work of Bogomolov *et al.* (2021) presents the results of studies of the chemical composition of the water of the Argazinsky reservoir of the Cheliabinsk region. The authors performed hydrodynamic modelling and determined the migration routes of pollutants in the water area of the Argazinsky Reservoir. They also proved that the distribution of water quality indicators over the water area of the reservoir is determined by a complex of internal and external factors mainly influenced by the waters of the main inflow of the Miass River.

Some scientists (Zhivetina *et al.* 2021) prove that the chemical composition and quality of water in a run-of-river reservoir depend on the season and its hydrological features. There is also spatial water variability from the upper to the near-dam part of the reservoir.

The paper of Savkin *et al.* (2020) discusses various reasons for changes in the hydrological and hydrochemical characteristics of the reservoir, manifested in the accumulation of pollutants due to the slowing of the river flows, changes in the basic morphometric characteristics of rivers and a decrease in water exchange.

As noted in the works of Calijuri *et al.* (2015) and Setegn (2015), the load on aquatic ecosystems has recently increased significantly due to the increased anthropogenic impact. Under such conditions, the self-purification capacity of reservoirs is not equal to the intake of anthropogenic pollutants, which negatively affects the water quality.

A team of scientists from Australia (van der Linden *et al.* 2012) prove in their work that the quality of water in reservoirs is determined by the interaction of biological, chemical and physical processes occurring in the catchment area and inside the reservoir. Using the example of the Milonga Reservoir in South Australia, they describe the relationship between the water quality in the reservoir and the quality of water coming from tributaries and catchment areas.

In their works, Jiang *et al.* (2016) justify the influence of reservoir operation on water quality. Their research results prove that the water quality in the reservoir directly depends on the tributaries. Thus, NH_3-N and COD (chemical oxygen demand) concentrations in the studied reservoir increase during high-water and decrease during low-water.

In their research, Chow *et al.* (2016) evaluated and interpreted the spatio-temporal model of surface water quality. The research showed that the discharge of water from the dam would lead to a further increase in the concentration of pollutants in the lower river course.

Nikoo *et al.* (2014) developed a method to optimize the water distribution in 'reservoir-river' systems, considering the existing uncertainties in the reservoir tributaries and water needs. But, as the authors note, this model is not suitable for all types of reservoirs.

The problem of water quality in reservoirs is quite extensively studied in detail. However, as many authors note, the water quality of each individual reservoir depends on a combination of various factors. Therefore, any study of the water quality of reservoirs is urgent and should consider a combination of different factors. Besides, there are a lot of works that do not study the relationship between the hydrochemical state of reservoirs and anthropogenic factors (point and diffuse) that cause the transformation of the content of chemical elements along the channels and the length of the reservoir (Dovganyuk *et al.* 2021). Therefore, the hypothesis of this paper is to establish the presence and nature of the relationship (dependencies) between the quality of the reservoir surface waters and the sources of anthropogenic impact along the channels and the length of the reservoir.

Monitoring hydrochemical studies helps assess the quality of surface waters of reservoirs. Such studies aim to observe, assess and forecast the state of the aquatic environment under anthropogenic impact and prevent emerging critical situations that are harmful or dangerous to human health, the well–being of other living beings or communities.

There are many methods in the world for assessing the state of aquatic ecosystems using hydrochemical indicators.

There are a lot of different methods and ways of assessing the quality of surface waters and the degree of their contamination. This is determined by the assessment tasks, the quantity and quality of the initial information, the methods of generalization of analytical material and other factors.

Modern hydrochemical works involve assessment of water quality using two main types of indicators – natural and relatively calculated, which complement each other.

Natural indicators are understood to be ingredients and indicators of the water's chemical composition, which is determined analytically. The present research involves using natural indicators.

The assessment of the current quality of surface waters of the studied region based on the analysis of all natural indicators allows revealing a long-term trend of water quality changes in the selected reservoirs and the basin and the relationship between this trend, changes in water content and pollutants' intake.

Based on the above analysis, the paper studies factors transforming the hydrochemistry of the Pavlovsky Reservoir. The obtained dependencies allow identifying the main ways of improving the hydrochemistry of the Pavlovsky Reservoir and using them for other reservoirs with similar characteristics. Generalization of the results obtained with similar results of other reservoirs allows identifying common factors affecting the hydrochemical state of reservoirs in the future.

The survey of the Pavlovsky Reservoir has important theoretical and practical significance. The reservoir is located on the Ufa River within the Ufa plateau of the Southern Urals. Administratively, the Pavlovsky Reservoir is located near the Pavlovka Village municipal area of Nurimanovsky District of the Republic of Bashkortostan, in the valley of the Ufa River. The reservoir was built in 1959. The length of the reservoir from the dam to the mouth of the Ufa River is 177 km. The Pavlovsky Reservoir is experiencing a significant technogenic impact of industrial, agricultural enterprises and the forestry complex. It provides a year-round uninterrupted centralized water supply to Ufa City. As for the Pavlovskaya hydroelectric power station, it generates electricity for the Republic of Bashkortostan, for the Sverdlovsk, Chelyabinsk regions and Perm Krai (Hafizov *et al.* 2019, 2020). Besides, the Pavlovsky Reservoir has become a major recreational area. There are tourist villages, recreation and sports camps on its banks (Hafizov *et al.* 2018b). All these factors have increased the anthropogenic load on the reservoir and led to changes in the basin and water area of the Pavlovsky Reservoir that affected the chemical composition of the water. At the same time, no large-scale studies of the reservoir water quality have been conducted over the last period of time, thus making the analysis of the trend in the hydrochemistry of the Pavlovsky Reservoir relevant.

The length of the Pavlovsky Reservoir at a full level is 150 km, the greatest width is 1.8 km (the average is 0.8 km), the deepest water is 35 m (the average is 11.7 m), the impounded water level at a full reservoir level is 115.9 km^2, the total storage capacity of the reservoir is 1.41 km^3, its life storage capacity is 0.95 km^3, the dead storage capacity is 0.46 km^3, and the top of conservation storage is 140.00. The estimated average annual water flow in the lower waters of the reservoir hydroscheme is 349 m^3/s.

The Pavlovsky Reservoir is characterized by seasonal stratification. Vertical circulation occurs two times a year. The reservoir is a sewage water body providing seasonal regulation of runoff with water exchange from 0.1 to 0.5 per year. The reservoir belongs to the third category according to water exchange.

According to the temperature fluctuations during the year, the Pavlovsky Reservoir refers to reservoirs with moderate and variable water temperatures (fluctuations from 0 to 21 °C).

Thanks to the intensive filling with warm spring flood waters in April, the reservoir heats up quickly and the water mass is actively mixed. At the end of the first decade of May, the water temperature is about 10–11 °C. The summer heating period lasts from the beginning of May to the end of August. The greatest warming of the reservoir occurs in August. The water surface temperature reaches its maximum values (20–21 °C) in the third decade of August. The bottom waters are warmed up to 17–18 °C.

The formation of the autumn temperature begins in September. The uniform temperature depth distribution is observed from the third decade of September to the end of November. At this time, the water temperature decreases from 15 to 4 °C. The period of pre-ice cooling of water begins from the third decade of November with a uniform depth temperature distribution (on average 4 °C). Under the influence of negative air temperature values, an inverse temperature stratification is formed. At the beginning of December, the water temperature at the surface decreases to 0 °C and an ice sheet up to 0.9 m thick is formed in the dam part of the reservoir by the end of winter. In shallow-water areas of the reservoir, ice formation begins at the end of October and in the main water area, it occurs at the end of November. The maximum ice thickness is about 0.6 m in the second half of March. The destruction of the ice cover begins with flooding. In winter, the water temperature decreases from 2.4 to 0.3 °C.

The Pavlovsky Reservoir is located near the village of Pavlovka in the Nurimanovsky municipal district of the Republic of Bashkortostan, in the valley of the Ufa River. The reservoir was built in 1959 – the length of the reservoir from the dam to the mouth of the river Ufa is 177 km. The reservoir provides a year-round, uninterrupted centralized water supply to Ufa. The Pavlovsky hydroelectric power station generates electricity for the Republic of Bashkortostan, the Sverdlovsk, Chelyabinsk regions and Perm Krai (Hafizov *et al.* 2019). The capacity of the power plant is 166.4 MW; the average annual electricity generation is 590 million kWh. Moreover, the reservoir is also used for recreational purposes. There are campsites, recreation centres, health and sports camps on its banks (Hafizov *et al.* 2018a).

The reservoir directly impacts the lower course of the Ufa River, determining its hydrological, hydrochemical and hydrobiological conditions (Hafizov *et al.* 2019). The Pavlovsky Reservoir forms the quality, flow and water level in the Ufa River (Hafizov *et al.* 2018b). The water quality in the reservoir depends on the composition and concentration of chemical elements that are directly related to the chemical composition of the water of the Ufa River and its main tributary rivers flowing into the reservoir: the Iuryuzan, the Ai, the Tiui, the Sars and the Baiki Rivers (Abdrakhmanov *et al.* 2021; Abdrakhmanov *et al.* 2018).

The first comprehensive study of the water quality of the Pavlovsky Reservoir was conducted by the Bashkir Branch of the Ural Scientific Research Institute of Water Resources Complex Use and Protection together with the Bashkir Agricultural Institute in 1986–1988. The study involved an assessment of anthropogenic pollution of the reservoir, the content of chemical elements in the water and the determination of the shore protection work scope (Federal State Budgetary Institution, Russian Scientific Research Institute of Water Resources Complex Use & Protection 2017). In 2000, the Federal State Unitary Enterprise of the Russian Scientific Research Institute of Water Resources Complex Use and Protection conducted comprehensive studies of the water quality and phytoplankton of the Pavlovsky Reservoir.

Currently, the monitoring of the water condition of the reservoir is being carried out by the Bashkir Federal State Budgetary Institution (FSBI), 'Bashkir Bureau of Hydrometeorology and Environment Monitoring'. This institution keeps records of the content of some chemical elements in two sections (the village of Karaidel and the village of Pavlovka).

Based on the above, it can be said that large-scale complex studies of the chemical hydrology of the Pavlovsky Reservoir have not been conducted for more than 20 years. With the increase in the anthropogenic load in recent years, the change in the economical use of the reservoir could significantly change its hydrological conditions. Therefore, to develop priority ways for improving the chemical hydrology of the Pavlovsky Reservoir, its current trend needs study (Nikanorov 1989, 2001).

The present research uses an integrated approach and the method of analogy. Therefore, the results of the research can be used by objects with similar natural and climatic conditions. Comprehensive research into the chemical hydrology of a reservoir means the study of the chemical properties of reservoir water with the complex analysis of all the components and processes occurring at the object of research.

The following tasks were performed to achieve the goal: the archive materials of previous studies on the chemical hydrology of the Pavlovsky Reservoir were studied. Water samples were taken to determine their chemical composition in the spring, autumn and summer low-water periods (2018–2019). The volumes of tributaries and water discharges from the reservoir were determined over a long period. Possible ways of entering chemical elements into the waters of the Pavlovsky Reservoir were determined. Dependencies of the content of chemical elements in water on the tributary were established. Priority ways to improve the water quality of the Pavlovsky Reservoir were determined.

MATERIALS AND METHODS OF RESEARCH

Field studies were conducted in the spring pre-high-water season, autumn and the summer low-water periods (2018–2019).

The following factors justify the choice of monitoring points (water sampling stations):

- the need for considering the main morphometric features of the Pavlovsky Reservoir, namely its river, lake and dam parts, tributaries flowing into the reservoir, settlements with their anthropogenic impacts (Nikanorov 1989, 2001; Federal State Budgetary Institution Russian Scientific Research Institute of Water Resources Complex Use and Protection 2017; Abdrakhmanov *et al.* 2018) (Figure 1);
- the possibility of using hydrochemical data on the sites of the current observation network of the Weather Control and Environmental Monitoring Service of the Republic of Bashkortostan;
- the possibility of using the results of previously conducted hydrochemical studies. The monitoring points (water sampling points) are selected so that they coincide with the points (sites) of previously conducted water sampling (1986–1988 and 2000) where the results of hydrochemical studies are available.

The main morphometric features of the Pavlovsky Reservoir, i.e., its river, lake and dam parts, tributary rivers flowing into the reservoir, populated areas with anthropogenic impact, were taken into account when choosing the sections for sampling (Nikanorov 1989; Federal State Budgetary Institution Russian Scientific Research Institute of Water Resources Complex Use and Protection 2017; Abdrakhmanov *et al.* 2018) (Figure 1). The climatic indicators in the water area of the Pavlovsky Reservoir have changed slightly and do not affect the reliability of the results obtained. The sections of the current observation network of the Bashkir FSBI 'Bashkir Bureau of Hydrometeorology and Environment Monitoring' and previous scientific studies were also taken into account.

This approach allows for using the observation data of the Weather Control and Environmental Monitoring Service of the Republic of Bashkortostan together with previous studies conducted in 1986–88 and 2000 and the results of the present studies (2018–2019), making it possible to track the dynamics of changes in the hydrochemical composition of water for over 30 years (from 1986 to 2018).

Thus, there were 10 monitoring points in 2018 and 7 in 2019 (Table 1) (the Maginsk, Aviator Sports and Recreation Camp sections and the low-water sections of the hydroelectric unit were not taken into account).

The number of investigated chemical elements in 2018 was taken to be equal to 30, which is similar to the number of chemical elements investigated during previous studies. Research results of 2018 were compared with their MPCs (maximum permissible concentrations) and excluded from further research if they did not exceed the corresponding MPC. In 2019, the number of studied elements amounted to 10.

In 2018, 64 selected water samples were analysed for 30 chemical elements. Water samples were taken twice – in the summer and autumn drought periods. In 2019, they were taken three times – in the spring flooding period, in the summer and autumn drought periods. Water samples were taken and examined in laboratories according to the standard procedure (RD (regulatory document) 52.24.309-2016 2016).

The conducted field studies allowed for the drawing of a summary table showing the correlation indicators and the maximum, minimum and average values of the concentration of chemical elements in water samples of the Pavlovsky Reservoir sections (Figures 2–4).

In 2019, the largest one-time excess of the MAC_{px} (maximum allowable concentrations according to fishery requirements) was recorded for mercury (high-water section) and copper (Baiki section). The maximum allowable concentration MAC_{px} (FSBI Hydrochemical Institute 2011) of the average values of the chemical

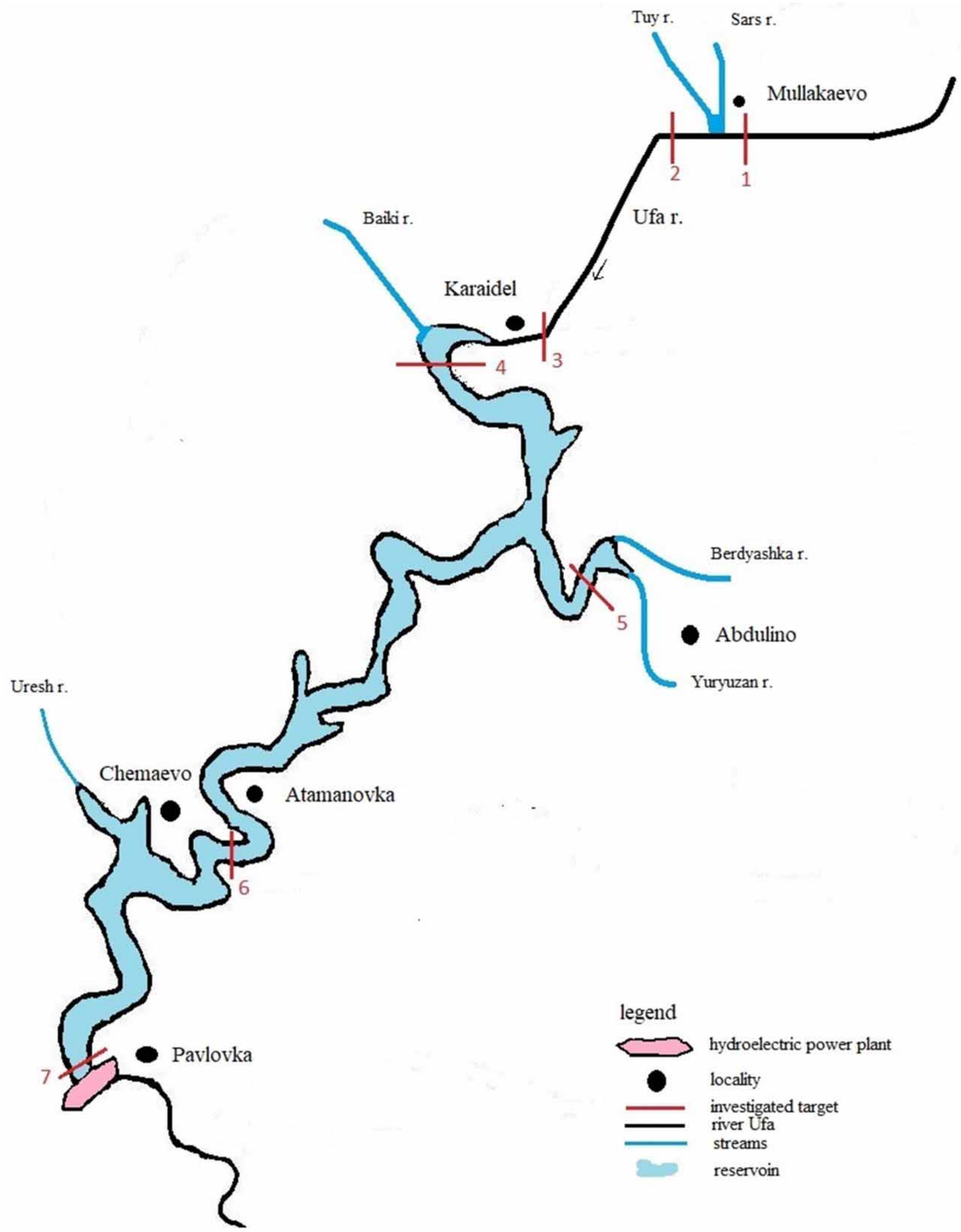


Figure 1 | Water sampling sections of the water area of the Pavlovsky Reservoir: (1) Mullakaevo section; (2) Tiui section; (3) Karaidel section; (4) Bayki section; (5) Iuryuzan section; (6) 'Zvezdnyi' SRC section; and (7) headwater section of the hydroelectric unit.

parameters content was as follows: Fe_{total} ($Fe^{2+} + Fe^{3+}$) by 2.4 times; Zn^{2+} 2.9; Cu^{2+} – 17; Mn^{2+} – 7.1; Sr^{2+} and 6.1; Hg^{2+} – 21; phenol – 1.5; oil – 1.3-fold; P $_{total}$ (according to PO_4^{3-}) and COD-below the MAC_{px}.

Trends in the chemical hydrology of the water area (by length) of the Pavlovsky Reservoir were determined using the average values of water samples taken during the summer low-water season. Chemical elements and sections are given in Table 2. The nature of the chemical hydrology trend along the length of the reservoir was revealed. The sections with peak concentrations of chemical elements and possible ways of entry into the waters of the Pavlovsky Reservoir were determined.

Table 1 | Brief description of monitoring points (water sampling points)

Parameters \ Sections	Section Mullakaevo	Section Karaidel	Section Baiki	Section Maginsk	Section Yuryuzan	The section of the 'Zvezdny' SRC	The headwater of the hydroelectric unit section
Reservoir depth (m)	6	9.5	8.3	10.0	9.0	27.1	30
Distance from dam section (km)	118	95	90	78	70	31	3
Sampling depth (m)	3	3	6	6	3.5	9	10
Type of sampling	Water sampling was carried out in accordance with RD 52.24.309-2016 (2016) 'Organization and conduct of routine observations of the state and pollution of land surface waters'						

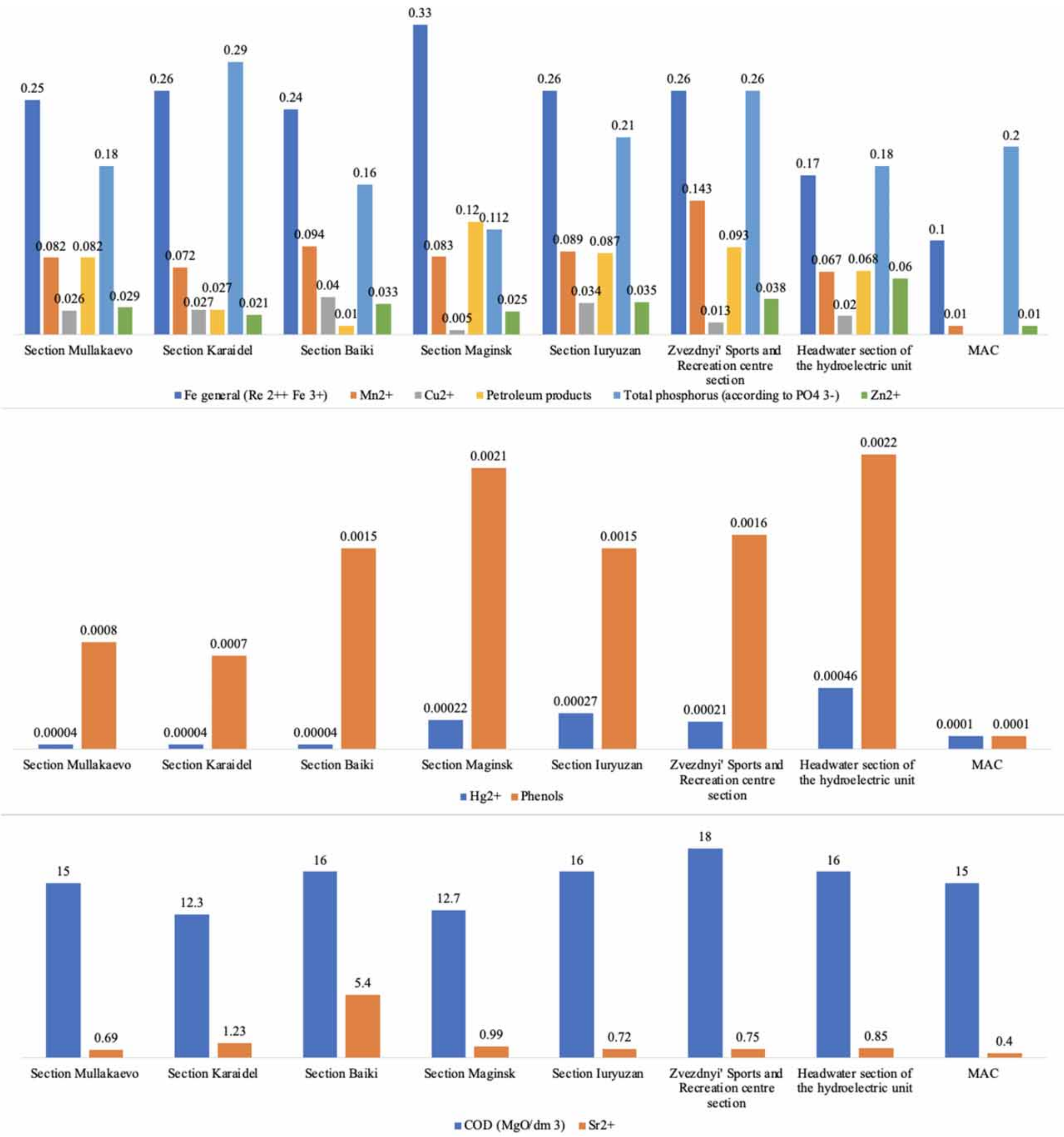


Figure 2 | Concentration of chemical elements in water samples of the Pavlovsky Reservoir sections, their MAC_{px} (FSBI Hydrochemical Institute 2011) mg/dm^3 (max).

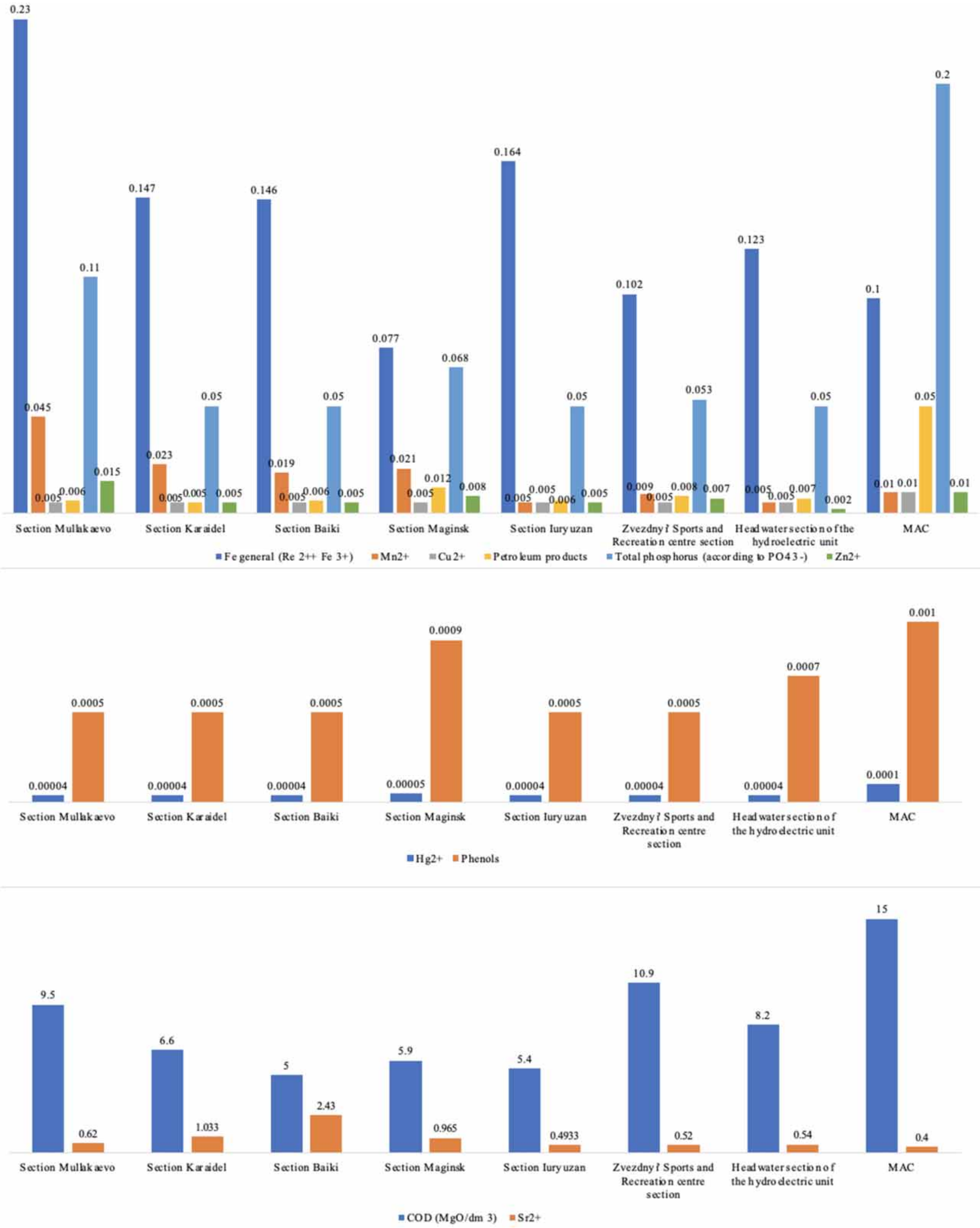


Figure 3 | Concentration of chemical elements in water samples of the Pavlovsky Reservoir sections, their MAC_{px} (FSBI Hydrochemical Institute 2011) mg/dm^3.

The following linear trends of changes in the content of chemical elements in water are observed throughout the water area of the reservoir: zinc, mercury, phenols and COD are increasing. Strontium, manganese and petroleum products are decreasing. Iron, phosphorus and copper are dispersed throughout the entire water area with minor decreases or increases. There is a trend of a decrease in the content of some chemical substances throughout the reservoir's water area, which indicates their fall into the upper reaches of the reservoir along the main river or tributaries. The entry of some chemical substances increases with their intake from the private catchment of the reservoir, especially in the sections of Karaidel and Maginsk Villages, the 'Zvezdny' SRC (Sports and Recreation Centre) section and the headwater of the hydroelectric unit section.

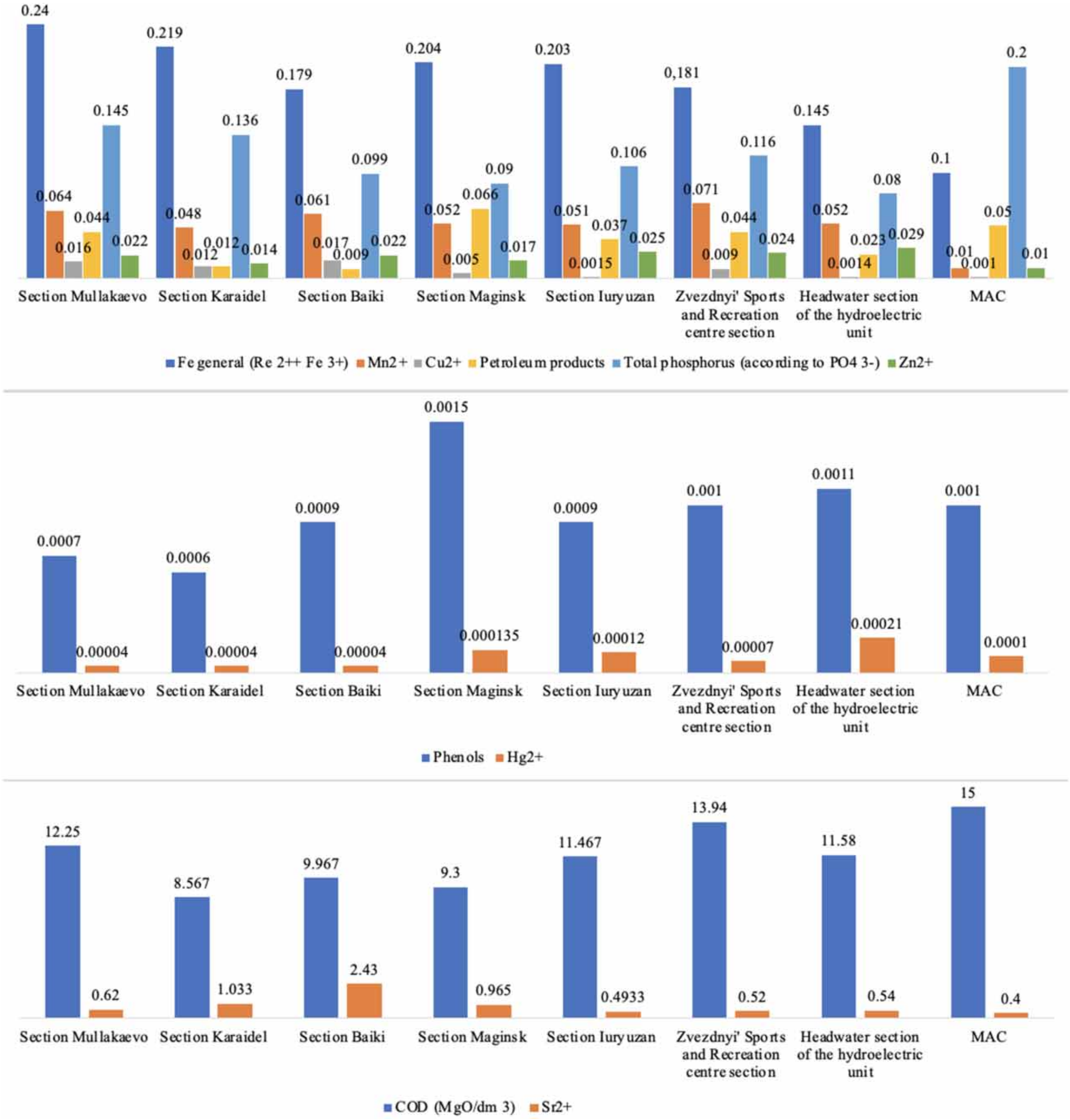


Figure 4 | Concentration of chemical elements in water samples of the Pavlovsky Reservoir sections, their MAC$_{px}$ (FSBI Hydrochemical Institute 2011) mg/dm^3 (average).

The dispersed content of chemical elements in the water area of the reservoir implies the equilibrium state between their intake and self-purification. Having analysed the peak concentration of the chemical elements in water (graphs in Figure 5), it can be assumed that iron, phosphorus, manganese and organic substances enter the reservoir along the Iuryuzan River; strontium, manganese, mercury, zinc and organic substances along the Baiki River; and iron, manganese, zinc, mercury and organic substances along the Ufa and the Tui River.

Possible sources of strontium pollution are the village of Karaidel and 'Zvezdny' SRC; zinc and mercury – the 'Zvezdny' SRC and the headwater of the hydroelectric unit; petroleum products – the villages of Karaidel and Maginsk; phenols – the villages of Karaidel and Maginsk, 'Zvezdny' SRC and the headwater of the hydroelectric unit; organic substances – all rivers and 'Zvezdny' SRC.

The basis for the study of the long-term dynamics of the chemical hydrology of the Pavlovsky Reservoir is the research of 2018–2019 and previous studies on this topic conducted by the Ural Scientific Research Institute of Water Resources Complex Use and Protection and the Bashkir State Institute of Agriculture in 1986–1987, the Ural Scientific Research Institute of Water Resources Complex Use and Protection in 1989 and the Russian Scientific Research Institute of Water Resources Complex Use and Protection in 2000. Besides, the state

Table 2 | Trends in the chemical hydrology of the Pavlovsky Reservoir

Chemical elements	Changes occurring in the water areas of the reservoir	Sections with peak concentrations	Possible ways of entry
$Fe_{total.}$	Dispersed with a small decrease	Mullakaevo section, Iuryuzan section	R. Ufa, R. Tiui, R. Iuryuzan, the water area of the reservoir
Sr	Decrease	Baiki section	R. Baiki, Karaidel village, 'Zvezdny' sports and recreational centre
$P_{total.}$	Dispersed with a small increase	Iuryuzan section	Iuryuzan River, the entire catchment area
Mn	Decrease	Mullakaevo section, Baiki section, Iuryuzan section	R. Ufa, R. Tiui, R. Baiki, R. Iuryuzan,
Cu	Dispersed with a small decrease	Baiki section, Headwater section of the hydroelectric unit	R. Baiki, Headwater
Petroleum products	Decrease	Karaidel section, Maginsk section	Karaidel village, Maginsk village
Zn	a small increase	Mullakaevo section, Baiki section, 'Zvezdny' sports and recreational centre section, Headwater section of the hydroelectric unit	R. Ufa, R. Tiui, R. Baiki, 'Zvezdny' sports and recreational centre, Headwater of the hydroelectric unit
Hg	Increase	Mullakaevo section, Baiki section, 'Zvezdny' sports and recreational centre section, Headwater section of the hydroelectric unit	R. Ufa, R. Tiui, R. Baiki, 'Zvezdny' sports and recreational centre Headwater
Phenols	Increase	Karaidel section, Maginsk section 'Zvezdny' sports and recreational centre section, Headwater section of the hydroelectric unit	the bottom of the reservoir in the villages of Karaidel and Maginsk, 'Zvezdny' sports and recreational centre, Headwater of the hydroelectric unit
COD	Increase	Mullakaevo section, Baiki section, Iuryuzan section 'Zvezdnyi' SRC section	R. Ufa, R. Tiui, R. Baiki, R. Iuryuzan, 'Zvezdny' sports and recreational centre

statistical reporting data of the Bashkir FSBI 'Bashkir Bureau of Hydrometeorology and Environment Monitoring (1996–2004, 2008) were used.

Graphs of changes in the average annual content of chemical elements in the waters of the Pavlovsky Reservoir over the years are shown in Figure 2. The graphs show the MAC_{px} according to the FSBI Hydrochemical Institute (2011) and in case of their absence, according to Sanitary Regulations and Norms 2.1.4.1116-02 (as amended on June 28, 2010) 2010.

A comparison of the long-term dynamics of the average annual content of chemical elements in the water of the Pavlovsky Reservoir with the values of average annual inflows (Figure 5) showed that there is a direct (with an increase in inflow the concentration of chemical elements in the water increases) or an inverse (with a decrease in inflow the concentration of chemical elements decreases) relationship between them. For example, iron and magnesium have a direct relationship, while phosphorus, copper, zinc, phenols and COD have an inverse relationship. The deviation of the limit values of the graphs in both directions is 2–4 years (Table 3). Note that information on the specific characteristics of monitoring points (water depth, distance to inflow, sampling depth, and sampling type) is given in Table 1.

RESEARCH RESULTS

The long-term dynamics of the hydrochemical indicators of the Pavlovsky Reservoir were analysed by linear trends of chemical elements (Table 2) and their relationship with the average annual inflows was analysed by linear trends of the average annual inflow (Table 3) shown in Table 4.

Table 4 shows a decrease in the long-term dynamics of iron and manganese concentrations, petroleum products, phenols and COD in the entrance tributary. There was a minimum average annual decrease in organic pollutants (2.1%) in the exit tributary (headwater section). The decrease in manganese was maximal (3.5%).

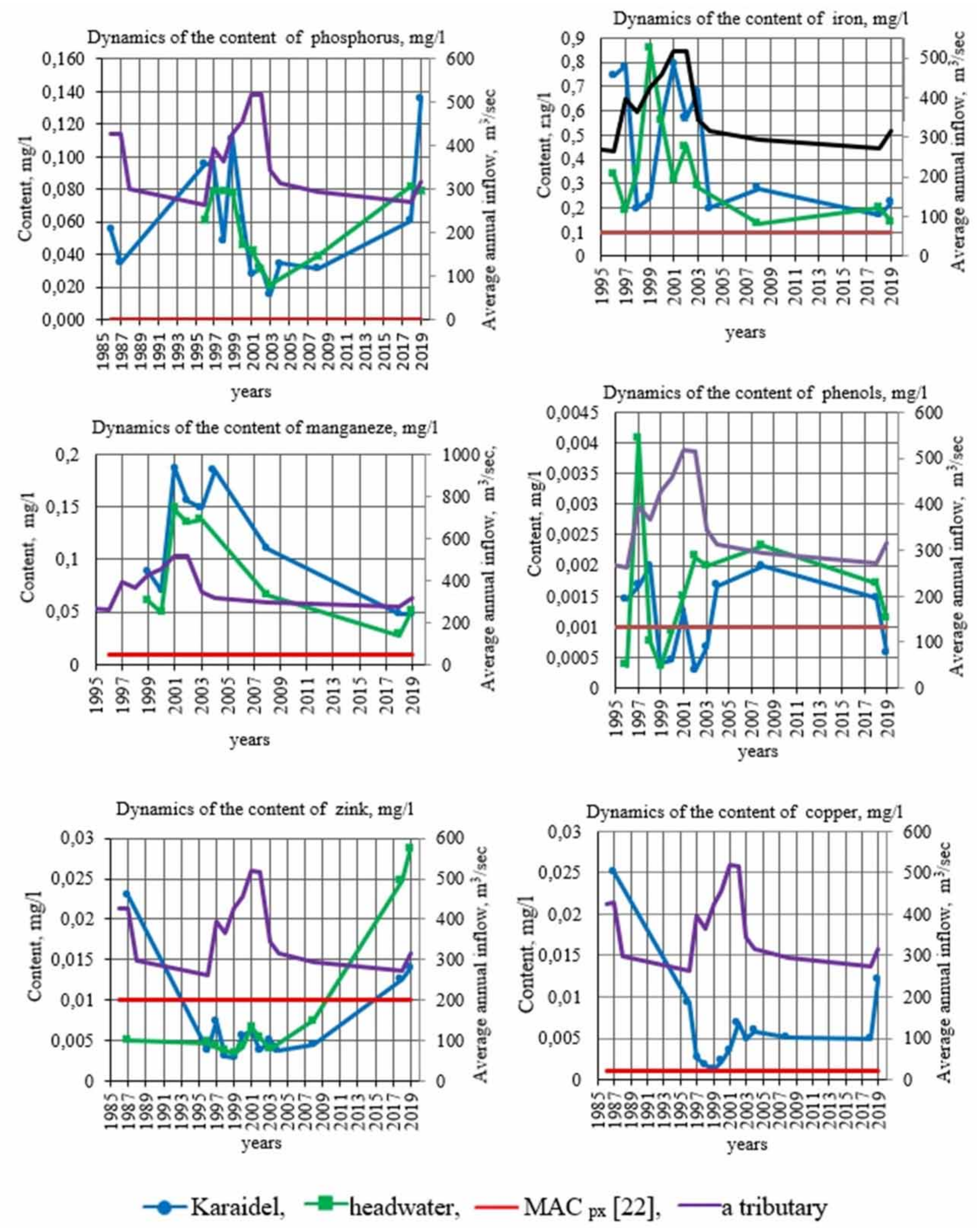


Figure 5 | Graphs of changes in the concentration of chemical elements in water over the years and according to average annual tributaries.

The content of phosphorus, copper, zinc, and phenols tended to increase (in the output range). The average annual increase in copper in the exit tributary was maximum (3.1%) and the increase in phenols was minimum (0.5%). Trends have been determined based on the assumption of the constancy of measurement errors of chemical elements. The average annual trend values (%) in different years have also been determined.

Analysing these results and comparing them with the conclusions drawn from Figures 1–4, it is possible to conclude the main ways of chemical elements entering the Pavlovsky Reservoir. Manganese and iron increase with an increase in the inflow and decrease along the length of the reservoir, since these substances enter the upper reaches of the reservoir through tributaries. The concentrations of phenols and petroleum products decrease with

Table 3 | Annual dynamics of the average annual inflow and chemical elements in the water of the Pavlovsky Reservoir

Chemical elements	Time intervals of changes in the content of chemical elements, year			
		Limit values		
	Increase	Maximal	Minimal	Decrease
Average annual inflow of water to the reservoir	from 2001	2001–2003	–	from 2003
$Fe_{total.}$	before 1999	1999–2003	–	from 2003
$P_{total.}$	from 2005	–	2001–2005	before 2001
Mn	before 2001	2001–2005	–	from 2005
Cu	from 2002	–	1998–2002	before 1998
Petroleum products	before 1988	1988	–	from 1988
Zn	from 2004	–	1997–2004	before 1997
Phenol	2003–2008	2008	1999–2003	before 1999 and from 2008
COD	2003–2007	2007–2009	2001–2003	before 2001 and from 2009

Table 4 | The relationship of the chemical composition of the Pavlovsky Reservoir water with the average annual inflow and its long-term transformation

Chemical indicators/ Margin of error[a]	For the period, year	Long-term dynamics of the chemical composition of water				Connection with the tributary
		Karaidel section (beginning)		Headwater section		
		Trend direction[b]	The average annual trend value[c], %	Direction of the trend[b]	The average annual trend value[c], %	
Fe_{total}/0.07	1996–2004, 2008, 2018–2019	Decrease	3.5	Decrease	3.2	Direct
P_{total}/0.07	1986–1987, 1996–2004, 2008, 2018–2019	Increase	1.3	Increase	0.7	Inverse
Mn/0,015	1999–2004, 2008, 2018–2019	Decrease	3.1	Decrease	3.5	Direct
Cu/0,007	1987, 1996–2004, 2008, 2018–2019	Decrease	1.8	Increase	3.1	Inverse
Petroleum products/0.04	1986–1988, 1996–2004, 2008, 2018–2019	Decrease	2.4	Decrease	2.6	No connection
Zn/0,012	1987, 1996–2004, 2008, 2018–2019	Increase	0.1	Increase	2.4	Inverse
Phenol/0.0011	1996–2004, 2008, 2018–2019	Decrease	0.3	Increase	0.5	Inverse
COD	1996–2004, 2008, 2018–2019	Decrease	3.2	Decrease	2.1	Inverse

[a]Maximum measurement error, mg/l.
[b]Linear trend line.
[c]Trend value, determined in % relative to the highest trend value.

an increase in the flow and increase along the length of the reservoir, where there are point pollution sources, which allows the conclusion that these substances come from the reservoir bed and adjacent catchment areas. The conclusion is also confirmed by the results of surveys of coastal territories. Residents living near the reservoir carry out unauthorized firewood extraction, which leads to the penetration of phenols into the water from bottom sediments. Besides, the refuelling of small vessels leads to the entry of petroleum products into the water. The annual increase in the illegal extraction of firewood results in an increase in the concentration of phenols. Moreover, in recent years, the lack of constant navigation has led to a decrease in the concentration of petroleum products in the water.

The phosphorus concentration decreases with an increase in the inflow and increases along the length of the reservoir, since this chemical element comes from the catchment area. At the same time, the total water consumption in the catchment area is currently decreasing (Hafizov *et al.* 2018a, 2019). In contrast, the specific water consumption increases, which explains the long-term dynamics of the phosphorus concentration increase. Copper and zinc come from outside and from the reservoir bed or adjacent territories with point sources of pollution. Copper decreases with increasing flow and increases along the length of the reservoir, which means the copper entry from the reservoir bed or adjacent territories with point sources of pollution. There are no long-term data on strontium and mercury. A significant strontium entry to the upper reaches can occur through tributaries. Mercury can enter both from outside and from the reservoir bed or adjacent territories. According to Abdrakhmanov *et al.* (2021) and Abdrakhmanov *et al.* (2018), strontium in water is formed due to natural factors.

DISCUSSION

The results of the research confirmed the hypothesis that, because of the dilution effect, there is a relationship (dependence) between the quality of the surface waters of the reservoir and the sources of anthropogenic impact along the channels and the length of the reservoir, which increases due to the presence of point sources of pollution. The following trends (communication patterns) have been also established:

- When chemical elements enter from upstream, their content decreases along the length of the reservoir; when they enter from private catchments of the reservoir, the content of chemical elements increases;
- With an increase in inflow, the concentration of chemical elements in the water increases and reduces when the inflow decreases.

The reliability of the obtained trends in reservoir water quality changes under the influence of anthropogenic factors is confirmed by the results of studies by Amineva & Gareev (2019), Litvinov (2018) and Volosukhin *et al.* (2020) conducted using other techniques.

To verify the convergence of the survey results obtained for the Pavlovsky Reservoir, they were compared with the results of similar surveys of large reservoirs such as the Nugushskoye, Yumaguzinskoye and Slakskoye in the landscape zone of the Southern Urals. The same dependencies have been found there as at the Pavlovsky Reservoir. This confirms that the acquired dependencies of reservoir water quality on anthropogenic factors and the method of determining pollution points proposed during the survey of the Pavlovsky Reservoir are relevant for other reservoirs with similar landscape characteristics, such as catchment area, climate, soil, vegetation, geological structure, relief and including hydrological parameters (water and ice regimes, sediments, shape and volume of the reservoir).

CONCLUSIONS

The research established that an increase in the volume of tributaries increases the concentration of substances coming from them (e.g. manganese, iron) and reduces the concentration of substances coming along the length of the reservoir (e.g. phenol, copper). Chemical elements enter the waters of the Pavlovsky Reservoir both from tributaries and along the length of the reservoir. Iron, phosphorus, manganese and organic substances enter the reservoir along the Yuryuzan River; strontium, manganese, mercury, zinc and organic substances (COD) – along the Bayki River; iron, manganese, zinc, mercury and organic substances (COD) – along the Ufa River and the Tui River. Strontium comes from the gates of Karaidel village and the 'Zvezdny ' SRC; zinc and mercury come from the upstream of the hydroelectric unit; petroleum products and phenols – from villages of Karaidel and Maginsk; organic substances – from the 'Zvezdny ' SRC.

After the conducted studies of the trend of hydrochemistry in the water area of the Pavlovsky Reservoir, it is possible to determine priority ways to improve the water quality of the Pavlovsky Reservoir and recommend them for other reservoirs with similar hydrological characteristics located in similar landscape zones:

- According to the obtained differentiation of the chemical elements entering the reservoir with tributaries and for establishing the sources of pollution and the content of chemicals discharged through the tributaries of the reservoir, monitoring studies and analysis of information submitted to controlled organizations should be made (e.g.: 2TP – (water farm)). It is necessary to identify the enterprises that create the highest concentrations of chemicals in the discharge line and inform the relevant executive and law enforcement agencies in the territory where these enterprises are located. It is also necessary to carry out studies and calculations to establish the dependence of the concentration of chemical elements on the isolated river channels, at the discharge site and at their mouths (at the confluence with the reservoir) in order to establish the maximum volume of discharge of specific enterprises.

- To the administrations of municipalities located in the coastal zones of reservoirs to organize an inventory of enterprises that are sources of chemical substances, taking into account the information received on the differentiation of pollution sources in the water area of the surveyed reservoir.
- Based on the results of the inventory, it is necessary to develop specific measures for each polluting enterprise to reduce the discharge of chemical and organic substances into the water area of the surveyed reservoir.

Future studies of the hydrochemistry of the Pavlovsky Reservoir should aim to forecast its ecological state and control chemical indicators of water quality over the entire area of key sections of the reservoir's water area. Such studies will help identify the main sources of pollutants entering from and distributing through surface waters. Moreover, revealing zones of pollutants' accumulation will allow making recommendations on minimizing the load on the water body.

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All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by A.H., D.K. and L.K. The first draft of the manuscript was written by A.Kh. and A.Ku. All authors read and approved the final manuscript.

DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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