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«ҚАЗАҚСТАН РЕСПУБЛИКАСЫ ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫ» РҚБ

ХАБАРЛАРЫ

ИЗВЕСТИЯ

РОО «НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК РЕСПУБЛИКИ КАЗАХСТАН»

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NAS RK is pleased to announce that News of NAS RK. Series of geology and technical sciences scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of geology and technical sciences in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of geology and engineering sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы «ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы» ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы Етегдіпд Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді геология және техникалық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия геологии и технических наук» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК. Серия геологии и технических наук в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по геологии и техническим наукам для нашего сообщества.

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HYDROCHEMISTRY AND ION FLOW DYNAMICS OF SYR DARYA TRANSBOUNDARY RIVER WITHIN KAZAKHSTAN

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Abstract. The current study examines the hydrochemistry and ion flow dynamics of the transboundary Syr Darya River within Kazakhstan, focusing on long-term changes in chemical composition under increasing anthropogenic pressure. These transformations pose challenges for water resource management and aquatic ecosystem stability in arid regions.

The research covers the period from 1910 to 2020, analyzing shifts in the river's hydrochemical characteristics. The findings indicate a transition from a bicarbonate-calcium type, typical of natural waters, to a sodium-sulfate type, reflecting significant anthropogenic influence. This shift is driven by intensive irrigation, industrial discharge, and climatic variability. A persistent trend of declining water quality and rising mineralization levels is observed, underscoring the cumulative impact of human activities.

The study employs hydrochemical data analysis, ion composition assessment, and statistical modeling to identify key transformation processes in transboundary water chemistry. These methods enable the quantification of anthropogenic effects and the prediction of future changes.

The results contribute to a deeper understanding of hydrochemical dynamics in transboundary waters, with direct applications in environmental monitoring, water resource management, and ecosystem conservation. The methodology is applicable for forecasting hydrochemical trends in other transboundary basins affected by similar climatic and anthropogenic pressures, supporting the development of sustainable water management strategies.

Keywords: Transboundary waters, Syrdarya, hydrochemistry, water runoff, ionic runoff, chemical composition.

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ҚАЗАҚСТАН ШЕГІНДЕГІ СЫРДАРИЯ ӨЗЕНІНІҢ ТРАНСШЕКАРАЛЫҚ СУЛАРЫНЫҢ ГИДРОХИМИЯСЫ ЖӘНЕ ИОНДЫҚ АҒЫНЫНЫҢ ДИНАМИКАСЫ

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Аннотация. Бұл мақалада Қазақстандағы трансшекаралық Сырдария өзенінің гидрохимиясы мен ион ағынының динамикасы зерттеліп, гидрохимиялық өзгерістердің ұзақ мерзімді тенденциялары анықталған. Мақалада су ресурстарын басқару және құрғақ аймақтардағы су экожүйелерінің тұрақтылығы үшін елеулі проблемалар тудыратын антропогендік әсердің күшеюі кезінде өзеннің химиялық құрамының үдемелі өзгеруіне баса назар аударылады.

Зерттеу 1910-2020 жылдар аралығын қамтиды, Сырдарияның гидрохимиялық сипаттамасының метаморфозаларын талдайды. Алынған нәтижелер айқын антропогендік өзгерістерді көрсететін табиғи суларға тән гидрокарбонатты-кальцийлі типтегі иондық құрамның натрий-сульфатты түріне ауысуын көрсетеді. Бұл түрлендіру гидрологиялық режимге әсер ететін интенсивті суарумен, өндірістік ағындармен және климаттық ауытқулармен түсіндіріледі. Трансшекаралық өзен телімдерінде су сапасының нашарлауының және минералдану деңгейінің жоғарылауының тұрақты үрдісі байқалады, бұл адам әрекетінің гидрохимиялық процестерге ықпалының күшеюін көрсетеді.

Зерттеуде ұзақ мерзімді гидрохимиялық деректерді талдау, иондық құрамды бағалау және гидрохимиялық үрдістердің статистикалық модельдеуін қамтитын кешенді әдістеме қолданылды. Бұл әдістер трансшекаралық сулар химиясындағы негізгі трансформация процестерін анықтауға көмектеседі және уақыт бойынша антропогендік әсерлерді сандық бағалауға мүмкіндік береді.

Алынған нәтижелер Сырдария өзеніндегі заманауи гидрохимиялық процестерді түсінуді терендетеді және қоршаған ортаны бақылауда, трансшекаралық су ресурстарын басқаруда және экожүйені сақтауда қолданыс таба алады. Ұсынылған әдістеме ұқсас климаттық және антропогендік жүктемелерге ұшыраған басқа трансшекаралық өзен алаптарындағы гидрохимиялық өзгерістерді болжау үшін қолайлы. Бұл деректер суды басқарудың тұрақты стратегияларын әзірлеу және трансшекаралық су жүйелеріне антропогендік бұзылулардың ұзақ мерзімді әсерін азайту үшін қажет.

Түйін сөздер: Сырдария өзенінің трансшекаралық сулары, гидрохимия, су ағыны, иондық ағын, химиялық құрамның метаморфизациясы.

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ГИДРОХИМИЯ И ДИНАМИКА ИОННОГО СТОКА ТРАНСГРАНИЧНЫХ ВОД РЕКИ СЫРДАРЬЯ В ПРЕДЕЛАХ КАЗАХСТАНА

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Аннотация. В данном исследовании рассматриваются гидрохимия и динамика ионного стока трансграничной реки Сырдарьи в Казахстане, уделяя особое внимание долгосрочным изменениям химического состава под влиянием возрастающей антропогенной нагрузки. Эти изменения создают серьезные вызовы для управления водными ресурсами и поддержания устойчивости водных экосистем в засушливых регионах.

Представленное исследование охватывает период с 1910 по 2020 год и подробно описывает изменения гидрохимических характеристик реки, учитывая влияние различных факторов, как природного, так и антропогенного характера. Исследование описывает выявление изменений ионного состава от бикарбонатно-кальциевого, характерного для природных вод, к натриево-сульфатному типу, что отражает значительное антропогенное влияние. Этот переход обусловлен интенсивным развитием орошения и его последствий, промышленными сбросами, а также тенденциями в изменениях гидрологического режима, усугубленными климатическими колебаниями. В работе выявлена устойчивая тенденция деградации качества воды и увеличения минерализации, что свидетельствует о кумулятивном воздействии антропогенных факторов на гидрохимический состав водоёма.

Методология включает гидрохимический анализ, оценку ионного состава и статистическое моделирование для выявления ключевых процессов трансформации химического состава трансграничных вод. Эти методы позволяют количественно оценить влияние антропогенной деятельности и прогнозировать дальнейшие изменения.

Полученные результаты способствуют более глубокому пониманию гидрохимической динамики трансграничных вод и находят применение в экологическом мониторинге, управлении водными ресурсами и сохранении экосистем. Методология может использоваться для прогнозирования гидрохимических тенденций в других трансграничных бассейнах, что способствует разработке эффективных стратегий устойчивого водопользования.

Ключевые слова: трансграничные реки, Сырдарья, водный сток, ионный сток, гидрохимия рек.

Introduction. The certain knowledge of modern processes in rivers hydrochemistry and the qualitative composition of natural waters has great scientific and practical significance for the systematization of knowledge and an objective assessment of the aquatic ecosystem.

The natural water of transboundary rivers are an integral part of the ecosystem

and act as a "stimulating factor for close cooperation" (The Water Convention, 2011) in international river basins.

The chemical composition of natural waters in quantitative and qualitative terms primarily depends on the environment of formation and the conditions of interaction in the river basin. Accordingly, the formation of hydrochemistry of rivers is a very complex process that occurs under the influence of various factors. (Junju, et al., 2022). Numerous works are devoted to these studies, including those on the hydrochemistry of the glaciated watersheds of Central Asia (Yapiyev, et al., 2021) and trends in hydrochemistry. Salt deposits of drinking water in the Syr Darya river basin within Kazakhstan (Sharipova, et al., 2022), locating in the arid zone, waters contain a high concentration of pollutants due to both the region geological component and anthropogenic activities. Considering importance of monitoring and detection of "tipping points" in hydrological phenomena and processes, is important to prevent the level of threshold hydrochemical load as a result, there is a possibility of system disturbance and irreversible processes, especially in the aquatic ecosystem.

Hydrochemistry data of natural waters is important for the conservation and optimal functioning of the ecosystem. Therefore, sustainable water management depends on the availability of resources, and quality of this water, from a certain level of knowledge about hydrochemical processes, as the suitability of water sources for a particular use.

With the impacts of global warming, and the increased demands for food and energy due to rapid population growth throughout Central Asia the water resources (Ilyin et al., 1969) are facing increasing pressure. Water -related issues in Central Asia have recently received increasing attention from international community.

The current study significantly complements the existing deficiencies in the field of hydrochemical research according to the ratio of the main ions in the chemical composition of water, the spatial distribution of salinity in the Syrdarya River and impact of irrigation on river water quality make significant adjustments in the study of the metamorphization of the chemical composition of the transboundary waters of the arid zone and increase the level of knowledge about hydrochemical processes (Leng, et al., 2021). Chemical ions in water are regarded as natural "tracers", and the analysis of the main ion composition in water can be used to identify and control the basic processes affecting the chemical composition of the water. It should be emphasized that 38% of water resources in Kazakhstan fall on the transboundary waters of the Syrdarya River where the rural population is 53.6% (Issanova, et al., 2018) and the water quality of the transboundary basin is deteriorating. (Micklin, 2014).

2. MATERIAL AND METHODS

2.1 Study area

Syr Darya river – unique transboundary watercourse of Central Asia which flows through the territories of four countries: Kazakhstan, Uzbekistan, Kyrgyzstan, and Tajikistan. The river is the main water artery of the arid region and one of the systems–forming links of the infamous drying Aral Sea.

The examined river basin stretches 800 km from north to south and 1600 km from west to east. The length of the river, determined by the large basin area, is formed by the confluence of the Naryn river (Kyrgyzstan) and the Karadariya river (Kyrgyzstan, Uzbekistan) in the intermountain valley of the Tien Shan Mountains Fergana Valley, with a total length of 2212 km, of which about 65% passes through the territory of Kazakhstan (Bernauer and Siegfried, 2012).

The study area covers approximately 240 km², which constitutes 52% of the total area of the transboundary basin within Kazakhstan.

The significant terrain elevation determines of mountainous in the southeast (headwaters) and plain (desert) in the northwest (estuary) with elevation amplitudes exceeding 3000 meters. Elevation differences within Kazakhstan are 204 m (Fig. 1).

The basin water supply regime is extremely diverse, the average annual precipitation is from 100 to 1300-1500 mm. The main sources of water supply to the watercourse are meltwater from snow cover and, to a lesser extent, glacial and rainfall flow. The water regime is characterized by a prolonged spring-summer flood, which was considered suitable for the development of agriculture.

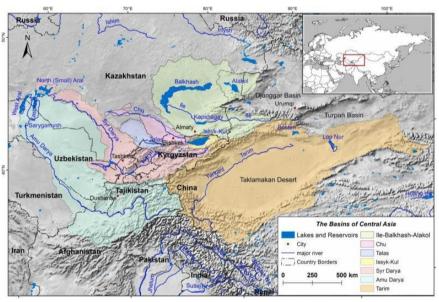


Figure 1 – The Syr Darya river basin within Central Asia (WGS-84-UTM42 projection) (Lehner et al., 2008, Lehner and Grill, 2013)

The research area belongs to the geographical zone with an arid climate, and water is the main limiting factor for sustainable development, hydrochemistry of rivers and the quality of natural waters are the key to the successful functioning of the aquatic ecosystem. In accordance with the peculiarity of natural complexes, the aquatic ecosystem of the region is extremely vulnerable, requiring a special approach and deep study.

The hydrochemical study zone involves the flow dispersion related to the lower reaches of the transboundary river. Denoting the significant role of this site in the process of moisture transfer and distribution of flow over residual water bodies (delta lakes, the North Aral Sea), which should be considered as sensitive indicators of the state of the ecosystem of the entire river basin.

2.2 Data sources

These studies were focused on the transboundary Syr Darya River within Kazakhstan, spanning from the Shardara Reservoir to the Northern (Small) Aral Sea.

The work uses data obtained on the basis of field studies for over 20 years, using, among other things, modern water quality analyzers Horiba U-53, (Japan), which allows recording and obtaining parameters of the current state of the aquatic environment in real time, DR-3900 spectrophotometer (HACH-LANGE, Germany). During the measurements, was widely used the mobile weather station Davis 6242, (USA).

The first hydrochemistry data about the Syr Darya river has been available since 1910. (Ilyin, 1969).

For the purpose of comparative and statistical data analysis, materials from other researchers of previous years (1910-1970) were also utilized. The present study encompasses the outcomes of hydrochemical investigations conducted in the field, spanning over a duration of more than two decades. These investigations involved the implementation of cutting-edge water quality analyzers, such as those manufactured by Horiba and Hach. These advanced analyzers facilitated the real-time monitoring and acquisition of fast data parameters, thereby enabling the assessment of the contemporary condition of the aquatic environment.

The primary hydrochemical characteristics were obtained from the hydrological station Kazaly, located approximately 13.0 km away from the Kazaly railway station in southwestern Kazakhstan. The local topography surrounding the station comprises a desert plain, which signifies the transition from the Kyzylkum sands on the left bank to the Karakum sands on the right bank. The river channel in the vicinity of the hydrological station exhibits a rectilinear morphology, accompanied by a wide floodplain and areas characterized by the presence of marshes.

Owing to constraints on time allocation for a singular-phase hydrochemical analysis across all eight measurement points located at a distance more than 1400 km, hydrochemical parameter measurements were conducted through route monitoring observation, during short time period of 30 hours.

Overall, hydrochemical investigations made use measured data for the last hundred years, encompassing the period from 1910 to 2020.

2.3 Methods

The research of hydrochemical parameters and their spatiotemporal trends is founded upon employing standard statistical methodologies to analyze the observed data, followed by subsequent analytical processing of the obtained results. To discern specific patterns, the calculated statistical data (series of observations) were

examined within defined timeframes (periods) with two transitional conditions, using a 10-year interval:

- a) the undisturbed (natural) flow regime (1910-1960);
- b) anthropogenically disturbed flow regime from 1960 to the present.

The selection of hydrochemical measurement points took into consideration the characteristics of the watercourse, the presence of hydraulic structures, and potential influences on river water hydrochemistry. Additionally, supplementary control measurement points were strategically positioned downstream. The measurements were conducted using a reconnaissance control method, Considering the local conditions and the designated research areas within Kazakhstan, the hydrochemical measurement points were selected. A background section was established at the border of the transit part (middle reaches of the river), followed by a lower reaches zone or dispersion zone where the river flow accumulates into deltaic lakes and, indeed, the Northern (Small) Aral Sea. This approach allowed for the identification of diverse hydrochemical effects and determination of the primary influencing factor.

To establish quantitative relationships between the ionic composition of individual components and their cumulative sum, the data were subjected to a common statistical processing method employing correlation and factor analysis.

In these investigations, field monitoring observations were widely employed, as they were deemed instrumental in acquiring objective and precise information regarding the present hydrochemical state and the quality of transboundary waters (Fig. 2).



Figure 2 – Hydrochemical research area of Syr Darya river within Kazakhstan territory

3. HYDROCHEMICAL STUDIES RESULTS AND DISCUSSION

Under various factors influence the average annual values of river runoff tend to change over time. Fluctuations in river runoff tend to form a group of high-water and low-water years. This trend is usually called the cyclicity of runoff fluctuations.

The identification of runoff cyclicity and the dynamics of long-term changes in the water content of the transboundary waters of the Syrdarya River is clearly demonstrated by the so-called integral curve of modulus coefficients (Fig. 3). It is built on the basis of measured water discharges for the period from 1910 to 2020 at the Kazaly hydrological station. The modulus coefficient as a statistical characteristic of flow parameters defined as:

$$K = Q_i/Q^-$$

 Q_i long-term average value of water discharge for the entire observation period, Q^- discharge of the i-th year.

The coefficient of variation (C_v) is -0.56 – (dispersion distribution).

An analysis of the curves shows that the natural high-water period on the Syrdarya River is observed until the 1960s. Then there are turning points, from 1962 to 1970 a special period of fluctuation is fixed, singled out as a "transitional", which corresponds to the average water content of the year. Then the curve drops sharply down as modulus coefficient reacts to a dry period. These conclusions are consistent with previous studies (Shi, et al., 2019). This period lasts from 1975 to 2020, corresponding to the 35-year water cycle. Within this large cycle, there is a time interval with a clear 11-year period, which probably corresponds to 11 summer solar cycles (1975-1986; 1986-1997; 1997-2008 and 2008-2020).

During the 1960s, the annual Syr Darya river flow within Kazakhstan territory exceeded 20 km³ (Burlibaev, et al., 2004).

However, between 1950 and 1978, significant changes occurred in the basin due to the construction and operation of five large reservoirs. These structures completely regulated the river flow but had adverse effects on water flow. Notably, the construction and filling of reservoirs coincided with the high-water period of a 35-year cyclic fluctuation in flow (Fig. 3).

The reservoirs, mainly located in the flow formation zones and the transit section, include Kairakkum reservoir in Tajikistan, with a capacity of 4.20 km³, and Toktogul reservoir in Kyrgyzstan, with a capacity of 19.5 km³. The reservoirs demonstrated a discharge efficiency of approximately 75% in terms of releasing water downstream whereas the volume of stored water in all reservoirs reached up to 8.6 km³.

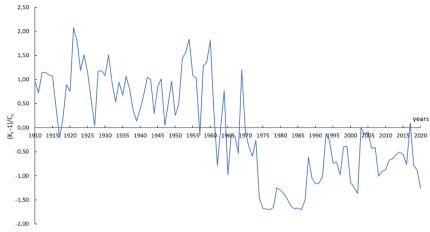


Figure 3 – The curve of modular flow coefficients. Syr Darya river, (Kazaly gauging station data)

The solar radiation impact on river runoff can be represented as:

Solar radiation (cycles, activity) \rightarrow climate (meteorological factors) \rightarrow water (river) runoff

However, further analysis reveals the following feature. Coincidentally, during the transition period (1962-1970) in the Syrdarya river basin, construction and commissioning of 5 large engineering structures began, which radically distorted the river flow. Engineering structures are located mainly in the areas of flow formation and the transit part, among them: Kairakkum (Tajikistan) with a volume of 4.20 km³, Toktogul (Kyrgyzstan) with a volume of 19.5 km³, Shardara (Kazakhstan) with a volume of 5.20 km³ and Sharvak (Uzbekistan) with a volume of 2.00 km³.

Moreover, the efficiency of water returns of these reservoirs amounted to about 75%, and the unproductive value of the volume reached up to 8.6 km³. It was these factors that contributed to the drop in the runoff curve on the graph.

Thus, the transboundary flow of the Syrdarya River at the site of the Kazaly hydrological station (Kazakhstan), which in 1960 was more than 20 km³ per year, decreased to 1.0 km³ (1984) and less in 1990, and in some periods the river flow to the Aral Sea practically stopped.

Consequently, it was the anthropogenic factor that turned out to be prevailing in the change in the water content of the Syrdarya River. As a result, these consequences were expressed in the form of a large-scale ecological catastrophe in the Aral Sea region.

What is the situation with the hydrochemistry of transboundary waters?

Prior to the large-scale development of the transboundary Syr Darya river basin, significant differences in the mineralization and qualitative composition of the river

water along its course were not observed, as noted by numerous researchers. The assessment of water pollution levels has designated the Syr Darya river's quality as belonging to class 2, indicating a state of cleanliness. However, within the context of future development, a noticeable escalation in mineralization along the river's course has emerged as a discernible phenomenon. As a result, the quality of the river water is now categorized into two distinct stages, surpassing the limits of class 4, (Water Code of Kazakhstan, 2003). Intensive treatment of the water is imperative for its suitability for domestic and drinking purposes, whereas its use for recreational activities is not recommended. Notably, the average mineralization level of the Syr Darya river's water downstream at the «Kazaly» gauging station (Kazakhstan) exceeds the mineralization level recorded upstream the Uchkurgan gauging station (Kyrgyzstan) of over 2.3 times, as presented in (Table 1).

Table 1. Transboundary Syr Darya river mineralization

River	Gauging Station	Country	mg/L
Naryn (Syr Darya tributary)	Uchkurgan	Kyrgyzstan	400
Karadarya (Syr Darya tributary)	Uchtepe	Uzbekistan	640
Syr Darya	Kazaly	Kazakhstan	938

Over the course of a 100-year comparison, the Syr Darya river underwent notable transformations in the chemical composition of its water, leading to a substantial metamorphosis (Table 2). The average annual water mineralization value experienced a remarkable 3.9-fold increase.

Table 2. Syr Darya river average annual mineralization changes according the 'Kazaly' gauging station data.

Years	1910	1938	1952	1960	1970	1980	1990	2000	2010	2020
mg/L	440	471	570	677	776	998	1553	1158	974	1720

Preceding undisturbed (natural) period of flow regime, the water mineralization composition was primarily dominated by hydrocarbonate ions (HCO_3^-) and calcium cations (Ca^{2+}) .

However, as the disturbed (anthropogenically) period begins, with a notable shift in the dominant ions (SO_4^{2-}) within the water mineralization composition. Sulfate ions progressively become the prevailing species, superseding the previously dominant hydrocarbonate ions (HCO_3^{-}) and calcium cations (Ca^{2+}) . Furthermore, $(K^+ + Na^+)$ cations exhibit an increasing presence, while calcium ions (Ca^{2+}) assume a subordinate role. Concurrently, the concentration of chloride anions (Cl^-) initiates to increase (Table 3).

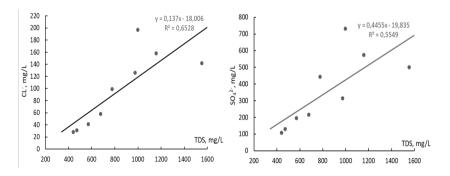
Years	1910	1938	1952	1960	1970	1980	1990	2000	2010
Ions	mg/L								
Ca ²⁺	60,4	64,2	76,1	86	98	112	101,5	123	92
Mg ²⁺	23,4	27,3	24,2	30	57	87	82,5	66,3	28
$K^+ + Na^+$	32,8	31,6	63,4	88	130	253	158	138	214
HCO ₃	187	186	170	198	170	173	174	98	200
SO ₄ ²⁻	108	131	195	217	444	731	500	575	314
cl-	28,4	31,3	41,4	58	99	197	142	158	126

Table 3. Syr Darya river qualitative (ionic) water composition 1910-2010

The absolute quantity $(K^+ + Na^+)$, and Ca^{2+} , as well as (Cl^-) and (SO_4^{2-}) anions, continuously increases with progressive elevation of mineralization, with a rapid increase of (Cl^-) , $(K^+ + Na^+)$, and (SO_4^{2-}) . This consistent trend is also corroborated by previous research (Lezin, Lakes of Central Kazakhstan. Alma-Ata, 1982). The predominance of Mg^{2+} ions in the chemical composition is observed at mineralization levels (TDS) ranging from 770 to 1550 mg/L, subsequently, the level decreases. The (SO_4^{2-}) sulfate ion takes a stable position at water mineralization (TDS) up to 550 mg/L, however, beyond this threshold, its concentration exhibits an upward trend.

The (HCO_3^-) hydrocarbonate ions exhibit a relatively stable equilibrium state across all levels of mineralization.

Correlation analysis indicates that with the increasing of (Ca^{2+}) , $(K^+ + Na^+)$, (SO_4^{2-}) , (Mg^{2+}) , and (Cl^-) ions in the chemical composition, the linkage between these components and the overall water mineralization increases. (Fig. 4). The correlation coefficient - (r) varies between -0.82 to -0.97.



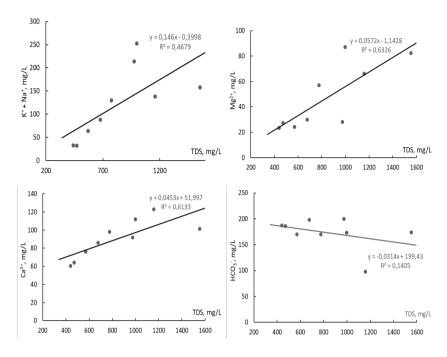


Figure 4 – Syr Darya river major ions and total dissolved solids (TDS) correlation.

The (Ca^{2+}) , (SO_4^{2-}) and (Cl^{-}) ions exhibit the strongest correlation with water mineralization (TDS). The correlation coefficient – (r) for these components – 0.95, 0.97, 0.97 respectively, which indicates a strong correlation between the ions content and their sum, as evidenced by the high approximation confidence factor (R²), which is acceptably in agreement at a minimum threshold of 50%. However, bicarbonate ions (HCO_3^{-}) exhibit a contrasting behavior with a negative correlation (r = -0.59). This indicates that the proportion of bicarbonate ion content is not associated with an increase in total water salinity (TDS).

The calculated data of salt flow in transboundary waters convincingly demonstrate significant variations in ion flow values across individual years (Table 4). Therefore, sulfate ions (SO_4^{2-}) constitute a significant proportion of the overall ion flow. Their contribution varies depending on specific yearly conditions, with an average range of approximately 45%, and occasionally reaching levels as high as 70%. In natural conditions, sulfate ions typically do not exceed 30%. The lowest contribution to the ion flow is observed for (Mg^{2+}) ions, which, on average, constitute no more than 5.0%. However, in certain years, their proportion can reach up to 9.0%.

The observed elevation in sulfate concentration in the residual water bodies of the Northern (Small) Aral Sea, which solely receive transboundary waters from the Syr Darya, has also been confirmed by other studies (Andreulionis et al., 2022).

No	Years	River flow, km ³	Ion flow, 1000 t	Salinity/water discharge ratio
1	1910	16,0	7040,0	1/0,44
2	1938	12,5	5887,5	1/0,47
3	1952	18,8	10716,0	1/0,57
4	1960	21,0	14217,0	1/0,68
5	1970	9,83	9810,3	1/1,00
6	1980	2,82	4379,5	1/1,55
7	1990	3,60	4168,8	1/1,16
8	2000	2,43	2814,0	1/1,15
9	2010	5,30	5162,2	1/0,97
10	2020	3,00	5160,0	1/1,72

Table 4. The Syr Darya River's long-term ion flow

However, a more precise understanding of the quantitative relationship between ionic and water flow can be achieved through the use of utilizing a specific metric – (1000t/km³). During the undisturbed (natural) period of the flow regime, the average ionic flow was 554.0 thousand tons per km³ of water, while during the disturbed (anthropogenically disturbed) period, the average was 1170 thousand t/km³.

Considering the average long-term mineralization values for different periods and treating them as relative norms, the following general observations can be made. In the undisturbed (natural) period, the mineralization rate was 540 mg/L, whereas in the disturbed (anthropogenically disturbed) period, the rate was 1200 mg/L. This represents an excess of 2.2 times.

Regarding the distribution of mineralization in river water during the disturbed period, prior to the commencement of the "vegetation period", the relative standard is 572 mg/L. The results of the comparative analysis show a mere 6% increase in mineralization, indicating nearly equal proportions with the values observed during the undisturbed (natural) period.

The systemic analysis of ion flow dynamics reveals a distinct pattern, qualitatively reflecting the development rates of the agro-industrial complex throughout the entire Central Asian region (Uzbekistan, Kyrgyzstan, Tajikistan, Kazakhstan):

- I Period (1910-1950): 455.0 thousand tons of ion flow/km³ of water flow;
- II Period (1950-1970): 702.0 thousand tons of ion flow/km³ of water flow;
- III Period (1980 to present): 1276.0 thousand tons of ion flow/km³ of flow.

This can be explained by:

The rapid exploitation of water resources in the basin, leading to increased ion flow in river water.

The deceleration of agro-complex development, primarily associated with the economic conditions of the countries and a decline in production, resulting in reduced ion flow.

In the first case, excessive increases in water withdrawal for irrigation purposes and large volumes of wastewater discharge back into the river system are key factors. In the second case, reduced water withdrawal from the river system and consequently lower volumes of discharged water play a role.

In practice, water withdrawal in the river basin exceeds 35.0 km³/ year. As a result, approximately 20.4 km³ of collector-drainage water are generated annually in the Syr Darya river basin. About 60% of this water consists of return flows, which are discharged back into the river network without proper purification, while the remaining portion is lost in natural depressions. The mineralization of these discharged (irrigation) waters reaches values ranging from 1.0 mg/L to 3.0 mg/L or higher. These findings are consistent with previous studies (Rubinova and Kuropatka, 1980; Omarov, 2003), highlighting the prevalence of return (discharged) wastewater in altering the chemical composition of river water. Various elements, including toxic salts, heavy metals, and pesticide residues, are present in the chemical composition of Central Asian river water. Consequently, up to 20% of the total applied fertilizers are lost with the discharged water in irrigated fields, and some modern compounds exhibit greater persistence in the aquatic environment. For instance, herbicides widely used in rice cultivation can persist in soil, irrigation water, and drainage water for approximately three months (Fundukchiev and Belyalova, 2004). Analysis of certain elements in the water-salt balance of irrigated areas indicates that the most severe meliorative conditions occur in the lower parts of the Syr Darya river basin. These observations confirm that the downstream areas of the transboundary Syr Darya river serve as an accumulation zone not only for saline (ionic) flow but also for chemical pollutants.

Risks imposed by climate change to irrigated agricultural production include increased water scarcity, unpredictable weather patterns, and heightened vulnerability to extreme events, such as floods and droughts. These challenges threaten food security and necessitate adaptive strategies and sustainable practices in farming (Leman et al., 2017).

Hydrochemical toxicity of river water salts significantly increases or deteriorates as the water flow moves from the formation zone to the dispersion (accumulation) zone, i.e., along the length of the transboundary watercourse.

Conclusion. Over the compared long-term observation period in the transboundary waters of the Syr Darya river, indicating significant metamorphosis processes of chemical composition. Absolute content of ions $(K^+ + Na^+)$, and Ca^{2+} , (Cl^-) continuously growing with increasing water mineralization level.

The (Ca^{2+}) , (HCO_3^-) and (Cl^-) ions exhibit the strongest correlation with water mineralization (TDS). The correlation coefficient - (r) for these components – 0.95, 0.97, 0.97 respectively, which indicates a strong correlation between the ions content and their sum. (HCO_3^-) ions have a negative correlation (r-0.59).

Relatively major ion flow is accounted for by sulfate ions (HCO_3^-) , depending on the specific year conditions, is on average in within 45% of the total amount, and in some years reach up to 70%. In natural conditions (undisturbed mode

period) sulfate ions did not exceed 30%. The minimum ions value corresponds to magnesium ions, which does not exceed 5.0% riches up to 9.0% in some years.

Magnesium ions predominance is observed with mineralization from 770 to 1550 mg/L, then decreases. Sulfate ions with water salinity up to 550 mg/L takes a stable position, above 550 mg/L – increases. Bicarbonate ions at any values of mineralization occupy a more or less balanced position.

Hydrochemical analysis for the long-term observation period and calculation convincingly demonstrates that an ion flow increase is not always proportional to an increase of water flow. The ionic composition of the researched transboundary river changed from hydrocarbonate-calcium (inherent in natural waters) to sulfate-sodium class. In the qualitative composition of water, the predominant main ions become sulfates (SO_4^{2-}) and cations $(K^+ + Na^+)$, but chlorine anion (Cl^-) , which occupied the subordinate state in the undisturbed flow regime began to increase, which is associated, firstly with an increase of wastes into the transboundary Syr Darya river basin. The water runoff for the disturbed (anthropogenically disturbed) period relative to the undisturbed (natural) period decreased on average by almost 70%. A comparative assessment of the water content of the transboundary Syr Darya river indicates the state of depletion of the water resources of the basin.

For each km³ of water runoff in the undisturbed (natural) period of the flow regime, there was an average of 554.0 thousand tons of ionic flow, while in the disturbed (anthropogenically disturbed) period – 1170 thousand t/km³. of ionic flow.

In the ion flow dynamics of transboundary waters, a certain regularity can be traced in the characteristic developmental changes of Central Asian countries. System analysis shows that:

- 1) With the rapid rates of water resource utilization in the basin, the ion flow in river water increases;
- 2) With the deceleration of agricultural sector development and a decline in production rates. The statistical method of data analysis reveals that at least 50% of the ion flow, which in the average long-term period is about 620.0 thousand t/km³, is brought exclusively by water runoff during the «vegetation period».

The determination of changes in hydrochemistry of the Syr Darya river flow is anthropogenic activity, i.e. due to anthropogenic origin. The current trend of decreasing water quality and transboundary waters mineralization growing is progressing.

Data Availability. All study data are included in the article.

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