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Satbayev University

# Х А Б А Р Л А Р Ы

# ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
Satbayev University

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# FEATURES OF THE ISOTOPIC COMPOSITION OF GROUNDWATER IN THE MANGYSTAU REGION

**Abstract.** This paper presents data on the isotopic composition of fresh and mineral groundwater in the Mangystau region.

The least studied component of the hydrologic cycle is groundwater involvement. Isotopes of natural origin are used as indicators to find out whether groundwater is replenished, its genesis, how it moves, whether it is at risk of pollution, and whether it is susceptible to changing climatic conditions. Waters of different genesis have specific isotopic signatures that leave a unique "footprint". This is used to track the movement of water throughout the entire hydrologic cycle - evaporation, burial, infiltration, runoff, evapotranspiration, etc.

This paper presents the results of a study of groundwater genesis using a comprehensive approach that would be relatively inexpensive and not require long observation cycles. In this case, to study the rates of water exchange and groundwater formation conditions in the Mangystau region used data on the chemical and isotopic composition of water ($^{18}O$, $^{2}H$), and the concentration of tritium ($^{3}H$), obtained by sampling in September 2021 The sampled areas are located within the Mangystau-Ustyurt hydrogeological basin, which occupies the southwestern part of the vast Turan plate and is located south of the Caspian hydrogeological basin.

Analysis of isotopic compositions (contents of deuterium, oxygen-18 and tritium) of water samples was performed at the Institute of Radiation Safety and Ecology (National Nuclear Center of the Republic of Kazakhstan) on a high-sensitivity laser spectrometer LGR 912-0008. VSMOW standards were used as reference standards, Measurement of radionuclide $^{3}H$ was carried out on liquid scintillation beta spectrometer TRI-CARB 2900TR.

**Key words:** groundwater, Mangystau region, isotope research methods, deuterium, tritium, oxygen-18.

**Introduction.** The efficiency of using isotope methods for solving hydrogeological problems has been demonstrated by a large number of studies [1-14]. Convenience of application of isotope methods comprises that the wide range of qualitative and quantitative parameters can be estimated on the basis of sufficiently small volumes of one-time sampling.

The share of groundwater in the total water consumption balance of Mangystau Region is about 360 thousand cubic meters/day, which is one of the smaller indicators for the regions of Kazakhstan [15, 16].

To study the rates of water exchange and conditions of formation of groundwater of Mangystau Region used data on the chemical and isotopic composition of water ($^{18}O$, $^{2}H$), and the concentration of tritium ($^{3}H$), obtained by sampling the groundwater of Mangystau Region in September 2021 (Fig.1). Studies of oxygen and hydrogen isotopes in the studied groundwater allowed to determine their genesis, and tritium concentrations to estimate the rate of water exchange. The obtained data are shown in table 1 and figure 2.

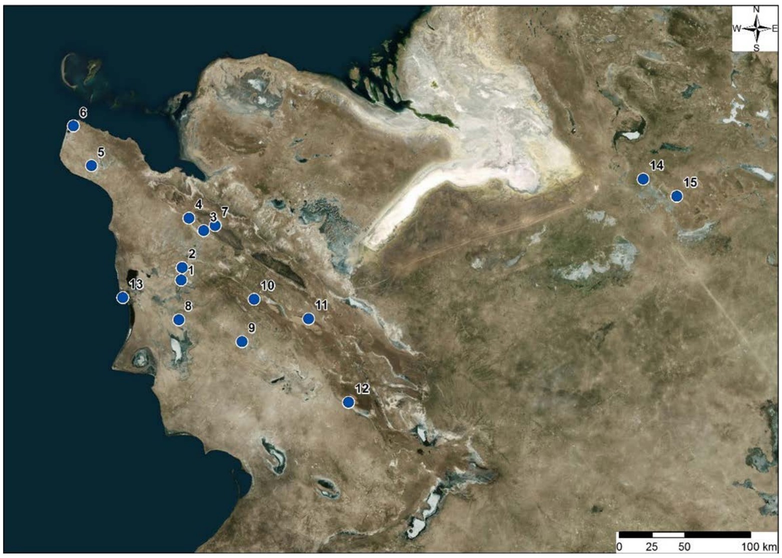


Figure 1. Groundwater sampling points. 1 - Kuiylys, 2 - Kuiylys 2, 3 - Zhyngyldy, 4 - Ulanak, 5 - Saubet, 6 – Sad - Dubskogo, 7 - Moinak, 8 - Prohlada, 9 - Asar, 10 - Baskudyk, 11 - Sauskan, 12 - Tuesu, 13 - Shagala, 14 - Beineu, 15 - Sam

The sampled areas are located within the Mangystau-Ustyurt hydrogeological basin, which occupies the southwestern part of the vast Turan plate and is located to the south of the Caspian hydrogeological basin. Four structural-geomorphological types of relief are quite clearly distinguished within it: the North Mangystau Lowland (Bozashi Peninsula), the Mountain (Central) Mangystau, the South Mangystau Plateau and the Ustyurt Plateau.

The North Mangystau Lowland (Bozashi) is a marine accumulative plain. Its plain surface occupies absolute marks from minus marks near the sea and within the saline lands of Dead Koltuk and Kaidak, and in the south-west and the northern slope of North Aktau, and the downdraft plain in the central part to the absolute mark of zero to 80-100 m. The surface of the latter is complicated by salt depressions (Ulkensor, Kyzylsor, Myasteksor, Kyzansor, etc.) and small massifs of aeolian sands (Kyzylkum, Shol-Shagyl, Uakkum, Zhinishke, etc.). To the south and south-west of the Mangystau Mountains stretches the South Aktau Upland, the southern slope of which gradually turns into the South Mangystau Plateau. The latter in the northwest direction includes the Tupkaragan Plateau, which with the South Mangystau Plateau itself forms a single uniform type of relief. Their flat surface is composed of Neogene and Upper Cretaceous limestones. The North Aktau elevation forms a similar relief type in the north of the Mangystau Mountains. Its surface slopes more steeply towards the Bozashi depression, in the North Mangystau, from 250-280 m to 50-30 m, in the south-west the slope of the North Aktau Upland passes into the Prikaratau Valley and the Caspian Sea depression with a sharply steep precipice. The northern and central parts of the South Mangystau Plateau are complicated by deep drainless depressions (Karagiya, Kaundy, Basgurly and Zhazgurly, Uzen). The large Karinzharyk depression separates this plateau in the east from the Ustyurt plateau. In the northeast of the South Mangystau plateau are the Sauskan, Bostankum and Tuyesu sand massifs. To the east and northeast of the Mangystau plateaus and the Bozashi lowlands, separated from them by a steep scarp - chink, 100-200 m high, extends the Ustyurt plateau. Its flat and armored surface with Neogene limestone-shells is complicated by rare enclosed hollows, sinkholes and sand massifs in the north (Sam and Mataykum) and elevated sublatitudinal rampart - in the central part.

The climate of the territory is deserted, the average annual atmospheric temperature varies from north to south: January from -10 to -3$^{o}$C and July from 27 to 38$^{o}$C, and the average annual precipitation from 100-120 mm in the south to 200 mm in the north. The aridity of the climate determines the complete absence of surface water sources in the region.

There are three major structural-tectonic zones in the basin: the Central Mangystau-Ustyurt dislocation system, the Bozashy-Severustyurt and South Mangystau-Ustyurt deflection zones. Ancient formations involved in the geological structure of the region are Permo-Triassic folded rocks and the Jurassic blanket deposits, which come to the day surface in the central (mountainous) part of the region. They are exposed within the Prikaratau valley framing Karatau mountain massifs and Alb Cenomanian deposits, which further in the territory of the South Mangystau and Ustyurt plateau, as well as in the North Mangystau depression sink to a depth of 50-100 m, and in the Prekaratau valley to 700-800 m and more. They are overlapped by Upper Cretaceous, Paleogene and Neogene sediments, the upper part (Upper Miocene-Pliocene) of which composes the daily surface of the Southern Mangystau and Ustyurt plateaus. In some areas, in particular, in the North Mangystau depression there are sand massifs.

Aquifers, aquifer systems and other groundwater data are mapped in Kazakhstan on the maps taking into account the requirements for displaying geographical objects on digital hydrogeological maps [17-22]. The main aquifer complexes and horizons of the region containing low-salinity water are the following sediments: Alb-Cenomanian, Upper Cretaceous, Upper Miocene-Pliocene and eolian sands. Groundwater of Alb-Cenomanian deposits is the most widespread and water-bearing among all aquiferous deposits in the basin and represented by different-grained sands and sandstones with interlayers of clay sediments, and come out to the day surface in Prekaratau valleys and in bottoms of some drainless depressions. Depth of occurrence of underground water complex in the basin as a whole varies from absolute levels of 100-150 m in the Prekaratau valleys to minus 800 m in the South Mangystau and Ustyurt. In the zones of outcrop of water-bearing rocks the discharge of springs does not exceed 1.5-2 L/sec. With dipping of the stratum and with the increase of groundwater head their productivity increases: in Prekaratau valleys self-discharge well flow rates are 5-40 L/sec, in the south and north of Mangystau reach 40-55 L/sec. Water-bearing complex of Upper Cretaceous deposits containing groundwater of marl-chalk sediments with mineralization up to 5 g/L is spread in the region on the limited area. Such waters are uncovered within the North and South Aktau monoclines. Flow rates of water points do not exceed 1-1.5 L/sec under small drops in water level. Here their salinity is 1.5-5 g/L. Water-bearing complex of Quaternary sediments with salinity up to 5 g/L is connected mainly with uncemented and weakly cemented sand massifs and in some limited in area sections of marine Quaternary sediments in the form of lenses and interlayers in clay strata. Weakly mineralized groundwater is established in the northern part of Ustyurt, in the northwest of the South Mangystau plateau, as well as in different parts of the Bozashi Peninsula. The Sam sand massif is the largest with a total area of 2320 km$^2$ in the northern part of Ustyurt. The sand massifs of the northwestern part of Southern Mangystau (Sauskan-Bostankum, Tuyesu, Baskudyk) and the Bozashi Peninsula (Kyzylkum, Zhilimshik, etc.) have small areas (150-500 km$^2$ each). The productivity of wells, laid especially in the sands in the north-west of Southern Mangystau and Sam massif, varies from 0.2 to 6 L/sec at lowering the water level by 1.5-10 m. Mineralization of water in the most part of massifs is mainly 0.2-1 g/L, and in their marginal parts and near salt depressions increases from 1.5-3 to 5 g/L. Weakly mineralized groundwater of marine Quaternary deposits in some parts of the central upland part or in flat depressions of the relief, near lake and other depressions is revealed only in the South and Central Peninsula Bozashi [23].

**Materials and methods.** Fifteen groundwater samples from wells in the Mangystau region were collected for studies (Fig.1). For isotopic analysis, samples were taken only from self-discharging wells, and wells operated by submersible pumps. This somewhat narrowed the range of observed water points, but also sharply reduced the possibility of accidental influence of anthropogenic, seasonal, and other factors on the sampling results [24].

The results of the isotope analysis are presented in Table 1. Stable isotope ratios of $^2H/^1H$ and $^{18}O/^{16}O$ in the measured sample were measured on a high-sensitivity laser spectrometer LGR 912-0008. Water samples calibrated against the International Standard VSMOW (IAEA) were used as internal standards. The accuracy of $^2H$ and $^{18}O$ measurements was ± 1 ‰ and 0.5 ‰, respectively.

Table 1. Measured values of indicators of chemical and isotopic composition of groundwater

| **Sample no.** | **Location of the water point** | **Coordinates** | | **Aquifer** | **Mineralization** | **δ$^{18}$O** | **δ$^2$H** | **$^3$H** | **pH** |
|---|---|---|---|---|---|---|---|---|---|
| | | NL | EL | | mg/l | ‰ | ‰ | Bq/l | |
| 1 | Kuiylys | 43$^0$ 50' | 51$^0$ 38' | $K_2$, marls | 2119 | -14.1 | -106.5 | | 8.43 |
| 2 | Kuiylys 2 | 43$^0$ 55' | 51$^0$ 37' | $K_2$, marls | | -14.5 | -107 | < 7 | 8.1 |
| 3 | Zhyngyldy | 44$^0$ 11' | 51$^0$ 42' | K, sands, sandstones | 5117 | -12.7 | -94.5 | | 7.53 |
| 4 | Ulanak | 44$^0$ 14' | 51$^0$ 32' | K, sands, sandstones | | -6.4 | -62.8 | | - |
| 5 | Saubet | 44$^0$ 22' | 50$^0$ 33' | K, sands, sandstones | 4107 | -12.3 | -93.6 | | 7.32 |
| 6 | Sad-Dubskogo | 44$^0$ 35' | 50$^0$ 17' | K, sands, sandstones | 8739 | -12.3 | -94.5 | | 7.91 |
| 7 | Moinak | 44$^0$ 14' | 51$^0$ 47' | Triassic | 811 | -9 | -69.7 | < 6 | 8.24 |
| 8 | Prohlada | 43$^0$ 34' | 51$^0$ 43' | K, sands, sandstones | 7503 | -11.5 | -95.1 | | 7.44 |
| 9 | Asar | 43$^0$ 33' | 52$^0$ 19' | K, sands, sandstones | 10451 | -12.1 | -100.6 | | 7.59 |
| 10 | Baskudyk | 43$^0$ 51' | 52$^0$ 19' | Q, sands | 475 | -7.7 | -66.6 | | 8.24 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 11 | Sauskan | 43⁰49' | 52⁰51' | Q, sands | 494 | -7.8 | -68.1 | < 6 | 7.94 |
| 12 | Tuesu | 43⁰22' | 53⁰24' | K, sands, sandstones | 1008 | -7.6 | -66.9 | < 7 | 7.94 |
| 13 | Shagala sanatorium | 43⁰37' | 51⁰11' | K, sands, sandstones | 8325 | -5.5 | -54 | | 7.79 |
| 14 | Beineu | 45⁰17' | 55⁰31' | Q, sands | | -11.1 | -92.5 | | - |
| 15 | Sam | 45⁰14' | 55⁰52' | Q, sands | 395 | -9.5 | -80.6 | < 7 | 7.38 |

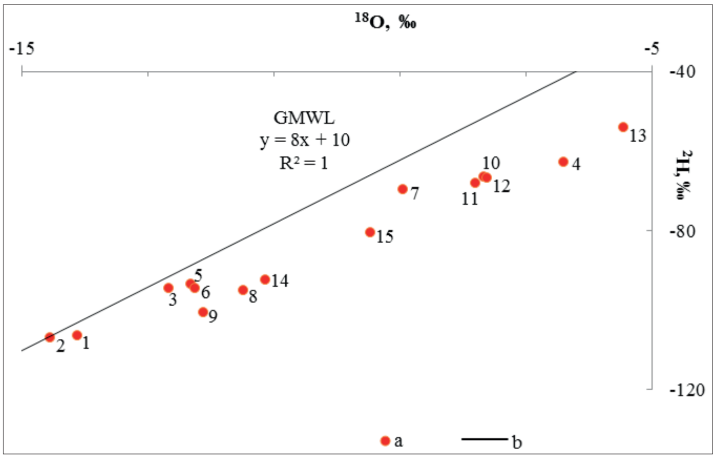


Figure 2. Isotopic composition of groundwater in the Mangystau region.
a - groundwater, b - global meteoric water line

*Tritium* is an ideal tracer to study water circulation in the zone of active water exchange [25, 26]. Natural concentrations of cosmogenic tritium in atmospheric precipitation are estimated to be about 1-5 TU (0.12-0.6 Bq/L), and during fusion charge testing in 1952-1964 its maximum concentrations in atmospheric precipitation reached $10^4$ TU. Given the half-life of tritium $T_{1/2}$ = 12.26 years, we can assume that the tritium that entered the groundwater in the pre-nuclear era to the present time has decayed completely, it allows us to easily diagnose the contribution of modern waters in the structure of groundwater resources.

Concentrations of *deuterium and oxygen-18* in natural waters experience the most significant, in comparison with other substances, changes in isotopic composition due to fractionation during evaporation, condensation, and freezing [27-29]. The regularity is strictly observed – the heavy isotope accumulates in the more condensed phase. It should be emphasized that fractionation usually does not occur during water melting due to too low diffusion rates of water molecules in ice. The isotopic composition of water is expressed in relative units, using the Vienna standard of average ocean water as a reference:

$$\delta X = (Rsample/Rst — 1) \times 1000, ‰$$

where R = $^2H/^1H$ or $^{18}O/^{16}O$ – atomic ratio of hydrogen and oxygen isotopes in the sample and the standard (indices sample and st, respectively).

For the analysis of natural groundwater formation conditions, the results of measurements were plotted on the $\delta^{18}O \div \delta^2H$ diagram, which reflects the regular distribution of isotopic composition of atmospheric precipitation, the so-called global meteoric water line (Figure 2). Global line of meteoric waters is a relation between mean annual air temperature and mean annual precipitation isotopic composition according to different meteorological stations of the Earth – from tropical latitudes to Greenland and Antarctica.

The fractionation of the isotopic composition of water, which takes place during phase transformations, is also shown in relation to the global line of meteoric waters. In this case, the rule is strictly observed – during evaporation, the isotopic composition of water changes in accordance with the evaporation line, where the residual water is isotopically weighted, and the evaporated steam is lightened. In the process of freezing, the forming ice is isotopically weighted and the residual water is lightened.

The content of stable isotopes in water samples of Mangystau region changes in the following limits: from -14,5‰ to -5,5‰ for $^{18}O$; from -107,0‰ to -54,0‰ for $^2H$.

Tritium radionuclide $^3H$ was measured on liquid scintillation beta spectrometer TRI-CARB 2900TR produced by Hewlett Packard company and designed for determination of specific activity of $^3H$.

According to the results of β-spectrometric analysis it was established that in the analyzed samples the concentration of man-made radionuclide is less than the detection limit of < 7 Bq/L in water. In the 50s and early 60s, large amounts of tritium were released into the atmosphere as a result of atomic bomb testing. Thus, the sediments were labeled [6, 30], and if the groundwater sample does not contain significant amounts of tritium, it definitely indicates that the water has not been fed for the last two or three decades.

**Results and discussion**. Figure 2 clearly shows that the isotopic composition of groundwater of Mangystau region is enriched by the heavy isotope $\delta^{18}O$ relative to the generally accepted meteoric water line. This is probably caused by evaporation concentration, during which the light isotope $\delta^{16}O$ is removed from water, thus enriching water with heavier isotope $\delta^{18}O$.

The exception is the samples taken from two wells of Kuiylys, which have relatively identical "light" isotope composition and are not subject to changes caused by hydrogeological processes (evaporation processes and weak water exchange). This may be due to the fact that these waters lie relatively deeper and are localized in an impermeable aquifer, which excludes ingress of surface water and atmospheric precipitation.

Detection of light by composition groundwater (Kuiylys) $\delta^2H < -107$ and $\delta^{18}O < -14$ ‰, suggests that these groundwaters were formed in cold climatic conditions, with average annual temperature below 0° C [6].

In all other cases, groundwater is subject to change in isotopic composition. The samples taken from the wells Sad-Dubskogo (thermo-mineral waters) and Saubet have a characteristic relationship, indicating one source of formation and hydro-geological relationship. The opposite picture is observed on the samples of Zhyngyldy, Ulanak and Moinak. Despite the fact that Zhyngyldy, Ulanak and Moinak are located next to each other by coordinates, the waters from these points have a completely different isotopic composition. The isotopic ratios indicate that the waters are taken from different aquifers without any correlation. Also, the water from the village of Sam has no correlation in isotopic composition with the waters of Beineu, which is located nearby. According to the comparative isotopic analysis, the waters of Sam are strongly subject to the process of evaporation compared to the waters of Beineu, which indicates different aquifers.

**Conclusion.** Waters sampled from the Shagala Sanatorium (Aktau) are characterized by the "heaviest" isotopes, perhaps these waters are subjected to an intense process of evaporative concentration.

Isotopic researches of underground fresh and low-saline waters spread in Mangystau region have allowed to draw the following conclusions:

1. Ratios of stable isotopes $\delta^{18}O$ and $\delta^2H$ in groundwater of the region show a single atmogenic origin.

2. Tritium concentrations were measured in order to establish the rate of water exchange in the fields. For the groundwater of the study area, tritium concentrations are less than the detection limit <7 Bq/l in water, indicating difficult water exchange and lack of connection with surface water.

In conclusion, we note that for reliable determination of stable isotope ratios, seasonal sampling of groundwater from the same sites throughout the year is necessary. The same should be used data on the isotopic composition of atmospheric precipitation of Mangystau region. Global lines of meteoric waters are obtained by interpolation cannot be considered reliable for the Mangystau region, as the nearest network stations GNIP (Global Network on Isotopes in Precipitation) are at a considerable distance and near the Caspian Sea, which affects the precipitation.

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## МАҢҒЫСТАУ ОБЛЫСЫНДАҒЫ ЖЕРАСТЫ СУЫ ИЗОТОПТЫ ҚҰРАМЫНЫҢ ЕРЕКШЕЛІКТЕРІ

**Аннотация.** Бұл мақалада Маңғыстау облысындағы тұщы және минералданған жерасты суының изотоптық құрамы туралы айтылады.

Гидрологиялық циклдің ең аз зерттелген компоненті жерасты суы екені белгілі. Табиғи түрде пайда болатын судың изотоптық көрсеткіштерін, жерасты суларының толығуын, оның генезисін, қалай қозғалатынын, ластану қаупі бар ма және құбылмалы климаттық жағдайларға бейімділігін анықтау мақсатында индикатор ретінде пайдалануға болады. Әртүрлі генезисті жерасты суларының өзіндік бірегей із қалдыра алатын ерекше изотоптық белгілері болады. Изотоптық анализдердің көмегімен судың бүкіл гидрологиялық циклдегі қозғалысын бақылауға болады: булануы, жойылуы, сүзгіленуі, ағыны және тағы сол сияқты.

Бұл жұмыста, салыстырмалы түрде арзан болып келетін және ұзақ бақылау циклдерін қажет етпейтін, кешенді тәсілді пайдалана отырып, Маңғыстау облысындағы жерасты суларының генезисін зерттеу нәтижелері ұсынылады. Бұл ретте, 2021 жылдың қыркүйек айында алынған сынамалардың химиялық, изотоптық құрамдары ($^{18}O$, $^{2}H$) және тритий концентрациясы ($^{3}H$) туралы деректерді, су алмасу жылдамдығын және судың қалыптасу жағдайларын зерттеу үшін пайдаланылғаны көрсетілген. Сынама алынған аймақтар Каспий маңы гидрогеологиялық ойпатының оңтүстігінде, үлкен ауқымды Тұран тақтасының оңтүстік-батыс бөлігіндегі, Маңғыстау-Үстірт гидрогеологиялық ойпатында орналасқан.

Радиациялық қауіпсіздік және экология институтында (ҚР Ұлттық ядролық орталығында) LGR 912-0008 жоғары сезімтал лазерлік спектрометрде су үлгілерінің изотоптық құрамдарына (дейтерий, оттегі-18 және тритий) талдау жүргізілді. Стандарт ретінде VSMOW стандарттары қолданылды, $^{3}H$ радионуклиді TRI-CARB 2900TR сұйық сцинтилляциялық бета спектрометрінде өлшенді.

**Түйінді сөздер:** жерасты суы, Маңғыстау облысы, изотопты зерттеу әдістері, дейтерий, тритий, оттегі-18.

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## ОСОБЕННОСТИ ИЗОТОПНОГО СОСТАВА ПОДЗЕМНЫХ ВОД МАНГИСТАУСКОЙ ОБЛАСТИ

**Аннотация.** Приведены данные по изотопному составу пресных и минерализованных подземных вод Мангистауской области.

Наименее изученным компонентом гидрологического цикла является участие подземных вод. Изотопы природного происхождения используются в качестве индикаторов, позволяющих выяснить, восполняются ли подземные воды, их генезис, как они движутся, подвержены ли они риску загрязнения и восприимчивы ли к меняющимся климатическим условиям. Воды различного генезиса имеют особые изотопные признаки, оставляющие уникальный «след». Это используется для отслеживания движения воды на протяжении всего гидрологического цикла - испарение, захоронение, инфильтрация, сток, эвапотранспирация и т.д.

В данной работе представлены результаты изучения генезиса подземных вод с использованием комплексного подхода, который является относительно недорогим и не требует проведения длительных циклов наблюдений. При этом для изучения темпов водообмена и условий формирования подземных вод Мангистауской области использованы данные о химическом и изотопном составе воды ($^{18}O$, $^{2}H$) и концентрациях трития ($^{3}H$), полученные в результате опробования в сентябре 2021 г. Опробованные участки расположены в пределах Мангистау-Устюртского гидрогеологического бассейна, который занимает юго-западную часть обширной Туранской плиты и находится южнее Прикаспийского гидрогеологического бассейна.

Анализ изотопных составов (содержаний дейтерия, кислорода-18 и трития) проб воды выполнялся в Институте радиационной безопасности и экологии (Национальный ядерный центр Республики Казахстан) на высокочувствительном лазерном спектрометре LGR 912-0008. В качестве эталонов использовались стандарты VSMOW, Измерение радионуклида $^{3}H$ проводилось на жидкостно-сцинтилляционный бета-спектрометре TRI-CARB 2900TR.

**Ключевые слова:** подземные воды, Мангистауская область, изотопные методы исследования, дейтерий, тритий, кислород-18.

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