© I. G. SVANIDZE, T. A. KREMLEVA, A. V. SOROMOTIN
svaigor@mail.ru, kreml-ta@yandex.ru, asoromonin@mail.ru

UDC 556.535.8

*INFLUENCE OF THE ARTESIAN BASIN GROUNDWATER OF WEST SIBERIA ON THE MIGRATION OF MACRO- AND MICROELEMENTS IN MINOR RIVERS**

SUMMARY. This paper presents peculiar properties of macro- and microelement composition of artesian waters, flowing out from expendable well No. 36-RG in the Tobolsk district, and further migration of chemical elements in the minor river Aremzyanka due to the inflow of the artesian water stream. The migration of Cl, Br, B, Se, Na, As, Sr, Ba, Te is discovered to be more intensive in the artesian waters, while Ca, Mg, Al, Si, P, S, Mn, U migrate more in the baseline river waters. It is demonstrated that, due to the inflow of the artesian water stream into the downstream of the Aremzyanka River, the mobility of the high-intensity oxygen migrants (Cl, Br, B, Na, Sr, F) and the medium-intensity migrant (Ba) increases. On the contrary, the mobility of the main river water macroelements (Ca and Mg) slightly decreases due to the change in the ion water composition. The increase in the mobility of other macro- and microelements is not registered.

KEY WORDS. Flowing wells, thermal waters, water microelements, water macroelements, minor rivers, water migration.

Introduction. In recent years, the problem of the artesian water influence on the environment in the Tyumen Region has become increasingly significant, due to the flowing of old expendable wells that were drilled in 1950s-1960s within the large-scale oil and gas exploration. These wells were considered unpromising and conserved after drilling. Nowadays, these wells are pouring out the thermal waters of the West-Siberian artesian megabasin as a result of the mouth outbreak. Since in 1950s-1960s the transport and load-lifting facilities were rather limited and it was impossible to move far from the main waterways, many exploration wells were drilled near the rivers. Thus, the majority of the wells of uncertain ownership pouring out the flows of mineralized waters are located on the terrace above the flood-plain and overflowed plains of both major rivers and minor streams in the south of the Tyumen Region. The total number of such wells is 22, and 13 of them are situated in the Tobolsk district [1].

The analysis of earlier publications demonstrated that the aquifers of the flowing oil wells of the Tobolsk area are the Hauterivian-Barremian and Valanginian layers of lower Cretaceous, as well as the Jurassic and even Paleozoic sediments [2], [3], [4]. According to the schematic hydrogeochemical map of the West-Siberian artesian

* This research was financially supported by the Government of the Russian Federation, Resolution No. 220 (grant No. 11G34.31.0036), *Formation of water quality and ecosystems in the conditions of the anthropogenic load and climate change in West Siberia*

basin [5], the artesian waters of the Neocomian-Jurassic Age of the Tobolsk area belong to the internal hydrogeochemical zone with low mineralization, sodium chloride ion composition. The content of microelements is higher even in comparison with the waters of the World Ocean [5]. However, in spite of the urgency and scale of the problem, geochemical influence of the Neocomian-Jurassic waters on the environment as a result of the oil well blowing has not been studied yet.

The purpose of this paper is to study the geochemical influence of the artesian waters on the minor streams during the migration of macro- and microelements and the river pollution caused by this influence. For this research we have chosen a model territory near Cherkashinsk Well No. 36-RG that is situated on the second terrace above the flood-plain of the Aremzyanka River (i.e. in the superaqual position).

The data and methods of the research

The description of the object. Cherkashinsk Well No. 36-RG was drilled in the Tobolsk district in 1965 1 km south-westward from the village of Shestakovo during the additional exploration of the Cherkashinsk deposit of iodide-bromine waters [3]. The well is located on the second terrace above the flood-plain of the Aremzyanka River and it is blowing out high-pressure thermal water. The age of the water-bearing strata is the Hauterivian-Barremian Stage (1730-1784 m and 1830-1842 m), and the Valanginian Stage (1862-1882 m). The water temperature is +90°C. The blow height is 7-8 m. The well capacity is 1,000 m^3 per day [3]. During drilling water was not investigated and macro- and microelement composition was not determined [3].

The methods of research. The macro- and microelement composition of the artesian and river waters was analyzed by the testing method. The samples were taken upstream (2,000 m and 1,000 m) and downstream (100 m, 300 m, 500 m, 1,000 m and 2,000 m) from the source of pollution and in the mouth of the Irtysh River (9,000 m). The sampling was carried out in the most significant low-water season — the summer dry-weather period (mid-July, 2012).

The macro- and microelement composition of the waters was analyzed in the Tyumen State University laboratories and in V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Science. The analytical program included the determination of macroelements (Cl^-, Ca^{2+}, Mg^{2+}, K^+, Na^+) and complex water ions (HCO_3^-, SO_4^{2-}), and it was implemented by the ICS-1100 and ICS-2100 ion chromatographs. The trace water analysis was carried out by ICP.

Since the microelement concentration in water does not give an idea of microelement migration ability, basing on the data obtained for all macro- and microelements of the river and artesian waters, the coefficients of water migration K_x were calculated according to the formula proposed by A.I. Perelman (1975) [6]:

$$K_x = \frac{m_x * 100}{a * n_x}$$

where m_x is the element content in the water (mg/l); a is the mineralization (mg/l); n_x is the lithosphere Clark (%). To calculate K_x, the Clarks of chemical elements in the lithosphere according to A.P. Vinogradov (1967) were used. The intensity of water migration was estimated according to the gradation for oxygen and thermal waters [7].

Results and Discussion

The comparative analysis of macro-and microelement composition of the artesian and river waters. The macro- and microelement composition of the artesian water from Well No. 36-RG and the baseline river water is presented in Fig. 1.

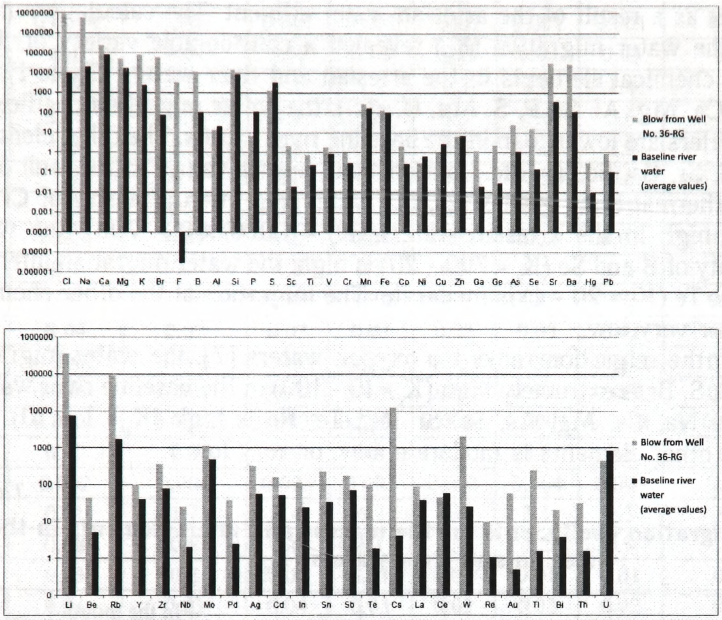

Fig. 1. The macro- and microelement composition of the thermal waters from the blow of Well No. 36-RG and the baseline river waters (a — μg/l, b — ng/l).

According to the ion composition, the artesian water is chloride-sodium. According to the anion concentration, Cl^- (8,788 ± 879 mg/l) is the highest, HCO_3^- (505.4 mg/l) and SO_4^{2-} (54.2 ± 5.4 mg/l) are the next. According to the cation concentration, Na^+ (5,747 ± 575 mg/l) is the highest, Ca^{2+} (255 ± 26 mg/l), K^+ (83.6 ± 8.4 mg/l), and Mg^{2+} (53.3 ± 5.3 mg/l) are the next. According to the venetian system, the artesian water falls in the brackish mesogaline water category (5-18 d) with the ion sum of 15,486 mg/l (i.e., more than 15 d). All above- mentioned values considerably exceed the basic ion concentration in the baseline water of the Aremzyanka River.

The river water had the following ion composition (average values): HCO_3^- (348 mg/l), Cl^-(9.5 mg/l), SO_4^{2-} (10.6 mg/l), Ca^{2+} (79.9 mg/l), Na^+ (19.5 ± mg/l), Mg^{2+}(17.4 mg/l), K^+(2.5 mg/l). These waters are included into the hydrocarbonate class, the calcium group, and are low-mineralized. The mineralization of the baseline water was 484.4 mg/l that is correlated with the published data for the summer dry-weather period [8].

The concentration of most of the artesian water elements exceeds the concentration of the river water elements, except for Al, P, S, Ni, Cu, Zn, Ce, U (Fig. 1, a, b). The high non-metal contents were registered: Br (59,200 μg/l), Si (14,667 μg/l), B (11,900 μg/l), F (3,450 μg/l), as well as the high alkaline-earth metal contents: Sr (33,389 μg/l), Ba (26,978 μg/l).

According to the acid-base conditions, the artesian water had the neutral reaction (pH = 7.03 ± 0.2), the river water generally had the low-alkaline reaction (pH = 8.16-8.28 ± 0.2).

The increase in the water migration coefficients for the macro- and microelements in the river water as a result of the artesian water effluent. The calculation of the coefficients for the water migration (K_x) revealed a considerable variety of these values for many chemical elements in the artesian and river waters (Table 1). For some elements (Ca, Mg, Al, Si, P, S, Mn, U, etc.), the water migration coefficients in the artesian waters are lower than in the baseline river waters. The other elements (Cl, Br, B, Na, F, Sr, Ba, Se, Te, etc.) demonstrate higher values in the well blow. In terms of the thermal brine grades [7], the water migration intensity of Cl and Br is extremely high in the artesian waters (K_x = 1,000,000 - 700); the water migration intensity of B and Se (K_x = 700 - 20) is high; the water migration intensity of Na, As, Sr, Ba, Te (K_x = 20 - 1) is moderate. The migration of the other chemical elements is low or very low.

According to the migration ranks for oxygen waters [7], the water migration intensity of Cl, B, S, Br is extremely high (K_x = 10 - 100) in the baseline river waters. The migration of Na, Ca, Mg, As, Se, Sr, Ag, Te, Re is high (K_x = 1 - 10). The migration of the other elements is moderate, low, or very low.

Table 1

The water migration coefficients for the macro- and microelements in the artesian and river waters (K_x)

	Blow from Well No. 36-RG	Baseline river water (average values)	100 m down-stream	300 m down-stream	500 m down-stream	1,000 m down-stream	2,000 m down-stream	In the mouth of the confluence into the Irtysh River	River Water (average values)
Cl	3,338.0	114.7	1084.1	780.4	595.2	444.1	428.9	543.9	570.2
Na	14.8	1.6	5.9	4.4	3.6	2.9	2.8	3.4	3.5
Ca	0.6	5.5	4.1	4.5	4.8	5.0	5.0	4.8	4.8
Mg	0.2	1.9	1.4	1.5	1.6	1.7	1.7	1.6	1.6
K	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Br	1,820.3	77.1	602.6	428.2	335.0	247.1	209.4	270.5	310
F	0.3	0.00000001	0.03	0.11	0.03	0.03	0.02	0.03	0.03
B	64.0	16.5	28.6	23.9	20.6	18.5	16.6	19.1	20.6
Al	0.00001	0.0006	0.001	0.0004	0.001	0.001	0.001	0.001	0.001
Si	0.003	0.06	0.04	0.05	0.05	0.06	0.05	0.04	0.1
P	0.0005	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2
S	0.18	15.2	10.0	11.6	12.7	14.0	13.9	12.8	12.9
Sc	0.01	0.004	0.003	0.003	0.004	0.004	0.004	0.004	0.004
Ti	0.00001	0.0001	0.0004	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
V	0.001	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Cr	0.001	0.007	0.01	0.01	0.01	0.01	0.01	0.01	0.006
Mn	0.02	0.3	0.2	0.3	0.3	0.3	0.3	0.2	0.3
Fe	0.0002	0.005	0.004	0.003	0.004	0.004	0.004	0.003	0.004
Co	0.008	0.03	0.03	0.03	0.03	0.04	0.03	0.03	0.03

The end of Table 1

Ni	0.0003	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Cu	0.001	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Zn	0.005	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Ga	0.0044	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Ge	0.1	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.03
As	1.0	1.4	1.1	1.2	1.3	1.4	1.4	1.2	1.3
Se	22.0	6.2	4.4	5.0	5.3	5.6	5.6	5.4	5.4
Sr	6.3	2.3	3.3	2.7	2.6	2.6	2.5	2.4	2.6
Ba	2.7	0.4	0.8	0.7	0.6	0.5	0.5	0.5	0.6
Hg	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Pb	0.004	0.01	0.02	0.01	0.02	0.02	0.01	0.01	0.01
Li	0.7	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Be	0.001	0.003	0.003	0.002	0.002	0.002	0.004	0.002	0.003
Rb	0.04	0.02	0.03	0.03	0.03	0.03	0.02	0.02	0.03
Y	0.0002	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003
Zr	0.0001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Nb	0.0001	0.0002	0.0003	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Mo	0.07	0.9	0.7	0.8	0.9	0.8	0.8	0.8	0.8
Pd	0.002	0.004	0.003	0.003	0.003	0.004	0.004	0.003	0.003
Ag	0.31	1.7	1.4	6.2	1.4	1.1	1.3	0.9	2.0
Cd	0.08	0.8	0.8	1.1	1.1	1.2	0.9	1.0	1.0
In	0.03	0.2	0.01	0.01	0.01	0.01	0.01	0.01	0.04
Sn	0.01	0.03	0.04	0.03	0.02	0.02	0.02	0.01	0.03
Sb	0.02	0.3	0.3	0.4	0.5	0.5	0.4	0.3	0.4
Te	6.7	3.9	2.2	2.5	2.7	2.8	2.8	2.7	2.8
Cs	0.2	0.002	0.04	0.03	0.02	0.01	0.01	0.005	0.017
La	0.0002	0.003	0.004	0.003	0.003	0.003	0.003	0.003	0.003
Ce	0.00004	0.002	0.003	0.002	0.002	0.002	0.002	0.002	0.002
W	0.1	0.04	0.03	0.04	0.03	0.04	0.03	0.03	0.03
Re	0.9	3.2	3.3	2.8	4.8	3.3	3.7	4.2	3.6
Au	0.9	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Tl	0.02	0.003	0.01	0.01	0.005	0.005	0.005	0.004	0.005
Bi	0.15	0.9	0.7	0.6	0.7	0.8	0.6	0.7	0.7
Th	0.0002	0.0003	0.0005	0.0003	0.0003	0.0004	0.0003	0.001	0.0004
U	0.01	0.7	0.5	0.7	0.7	0.7	0.6	0.6	0.63

Br, Cl, and B input with the artesian water results in a considerable growth of the water migration coefficients (Table 1, Fig. 2); it can be explained by the extremely high level of their water migration intensity in any conditions [7]. The most considerable jumps of the migration coefficients were registered for Cl and Br. K_{Cl} coefficient increases from 114.9 to 1,084 (100 m downstream from the source of pollution); it is 9 times higher than the baseline values. K_{Br} coefficient increases from 77.2 to 602.6. While the distance from the source of pollution downstream is increasing, the values of the coefficients are gradually decreasing, but they remain higher in all the test points to the mouth of the Aremzyanka confluence into the Irtysh River. In general, the values of Cl migration coefficients are 4-9 times higher, the values of Br migration coefficients are 3-8 times higher than the environmental level. Full returns to the environmental level are not observed. K_B coefficient increases from 16.6 to 28.6 and returns to the environmental level 2 km downstream from the source of pollution.

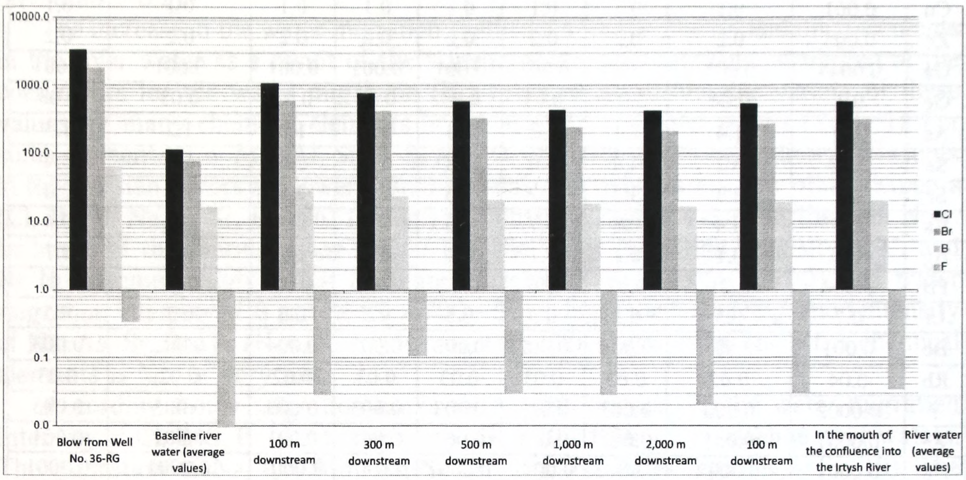

Fig. 2. The changes in the water migration coefficients for non-metals downstream the Aremzyanka River

We should mention that in the mouth of the confluence of the Aremzyanka into the Irtysh, Cl, Br, B, F, and Na migration coefficients increase again; it is caused not only by the high mobility of migrants, but also by the high mineralization of the Irtysh River, its flow is mainly formed in the steppe and forest-steppe zones with saline lands in a large area [9].

In addition to the above-mentioned elements, F inputs into the river with the artesian waters; it is a high-intensity migrant in the oxygen waters according to Perelman's migration ranks [7]. Nevertheless, the concentration of this element in the baseline river water is insignificant, the migration is very low. The input of the element results in the increase in K_F coefficients to 0.02-0.03 downstream the river and even 0.11 300 m downstream from the source of pollution (Table 1, Fig. 2). F migration intensity changes from an extremely low intensity to a low one. Full returns to the environmental level do not occur.

Another regularity of the artesian water influence is the increase in Na migration coefficients downstream the river from the source of pollution. K_{Na} coefficient increases from 1.6 to 5.9 100 m downstream (Table 1, Fig. 3). At this point, Na over Ca excess of the migration coefficients (5.9 and 4.1) and the change of the calcium group of the river waters into the sodium group were registered. Further downstream, the values of K_{Na} coefficients are decreasing, K_{Ca} is over K_{Na} at all the test points; the return of the river water to the calcium group occurs, but the return of the migration coefficients to the environmental level does not occur, the coefficients are 2-3 times higher up to the confluence into the Irtysh River.

The considerable increase in Cl and Na mobility in the river waters results in the river mineralization increase downstream, the change in the composition and ratios of the basic cations and anions in the river waters, the change of the calcium group into the sodium group near the source of pollution while the hydrocarbonate class retains throughout the river up to the confluence into the Irtysh River.

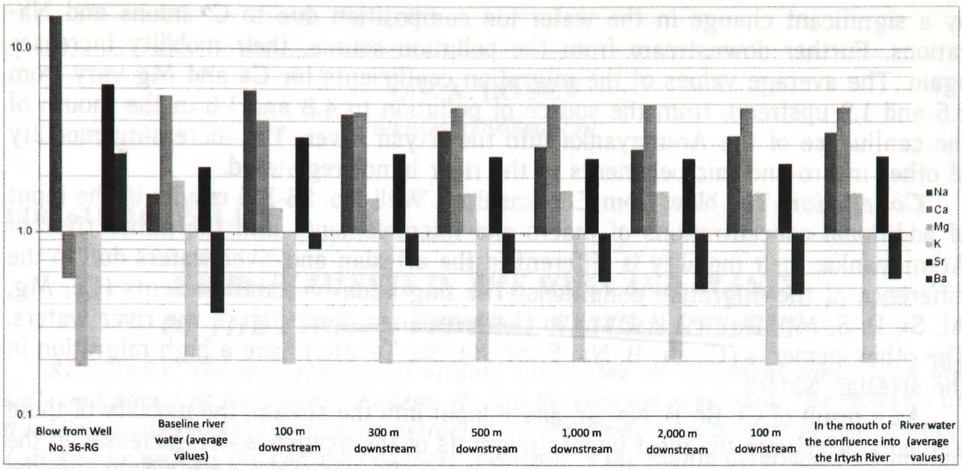

Fig. 3. The changes in the water migration coefficients for alkaline and alkaline-earth metals downstream the Aremzyanka River

Other alkali and alkaline-earth metals of high-intensity water migration (macroelements of the river water: Ca, Mg, and K, medium intensity migrant [7]), run into the river together with the artesian waters in high concentration. Nevertheless, the increase in the migration coefficients for K_{Ca}, K_{Mg}, K_K, main macroelements of the river water, due to their input together with the artesian waters, was not registered. On the contrary, Ca and Mg migration coefficients slightly decrease downstream, and they increase again further downstream from the source of pollution (Table 1, Fig. 3). If the average K_{Ca} and K_{Mg} values upstream the river were 5.5 and 1.9, respectively, the average values downstream the river were 4.8 and 1.6. This phenomenon can be obviously explained by the strong change in the ion composition of the river waters in connection with the input of Cl-anions and Na-cations.

The increase in the water migration coefficients is registered for the alkaline-earth metals, which are microelements of the river water: Sr and Ba (Table 1, Fig. 3). Sr is a high-intensity migrant in the oxygen waters, and Ba is a moderate-intense migrant [7]. Downstream from the source of pollution (100 m), K_{Sr} coefficient changes from 2.3 to 3.3; and further downstream, it is slightly above the environmental level. K_{Ba} coefficient also increases from 0.4 to 0.8 100 m downstream the river and gradually decreases to the environmental level.

Thus, as a result of the input of macro — and microelements together with the artesian water flow downstream the Aremzyanka River, the mobility of the high-intensity migrants of the oxygen waters (Cl, Br, B, Na, Sr, and F) increases. The mobility of the moderate-intensity migrant (Ba) also increases. According to the average values of the water migration coefficients, after the input from the well into the river, the elements arranged in the descending order: Cl (570.2), Br (310), B (20.6), Na (3.5), Sr (2.6), Ba (0.6), and F (0.03). The same elements before the input had the following average values: Cl (114.7), Br (77.1), B (16.5), Na (1.6), Sr (2.26), Ba (0.36), and F (0.00000001). The mobility of the main macroelements of the river water (Ca, Mg), despite the input of these components into the river with the artesian water, slightly decreases near the well, which can be evidently explained by a significant change in the water ion composition due to Cl-anions and Na-cations. Further downstream from the pollution source, their mobility increases again. The average values of the migration coefficients for Ca and Mg vary from 5.5 and 1.9 upstream from the source of pollution to 4.8 and 1.6 in the mouth of the confluence of the Aremzyanka into the Irtysh River. The increasing mobility of other macro-and microelements in the river is not registered.

Conclusion. The blow from Cherkashinsk Well No. 36-RG results in the input of additional concentrations of macro-and microelements into the minor river of Aremzyanka; their mobility is different in the artesian and river waters due to the difference of the migration conditions. The migration of some elements (Ca, Mg, Al, Si, P, S, Mn, U, etc.) is lower in the artesian waters than in the river waters. The other elements (Cl, Br, B, Na, F, Sr, Ba, Se, Te, etc.) have a high migration in the artesian waters.

As a result of Cl, Br, B, Na, Sr, and F input into the stream, the mobility of these elements, which are the most intense migrants of the oxygen water, increases in the river waters; it occurs even in the mouth of the confluence of the Aremzyanka into the Irtysh River. The mobility of the moderate-intensity migrant (Ba) also increases.

The additional input of the main macroelements in considerable concentration (Ca and Mg) with the artesian waters into the river waters does not cause the increasing mobility of these elements in the stream; on the contrary, the mobility slightly decreases, due to the strong change in the ion composition of the river water, and the increase in Cl-anions and Na-cations.

The increasing migration of other macro- and microelements due to the input of the artesian water is not registered.

REFERENCES

1. Konovalov, I.A., Pak, I.V. Environmental Conditions of the Territories in the Areas of Exploration Wells of the Undistributed Resources Fund in the South of the Tyumen Region. The Environment and Environmental Management: Proc. of the International Conference. Tyumen: Publishing House of the Tyumen State University, 2010. P. 177-179.

2. Exploration Report on the Project «Inventory and Determination of Well Conditions for Fresh and Mineral Water, Drilled in the South of the Tyumen Region.» Report of the «Tyumengeomonitoring» Territorial Centre, 2008. P. 221.

3. Executing Report on the Project: "Development of the Conditions of the Resource Use and Preparing the Competition Information for the Extraction License for Geological Exploration (Research, Eatimation), Exploration and Extraction of the Underground Mineral Water for Balneal Use at the Shestakovsk Site in the Tobolsk District of the Tyumen Region in 2010". Resource Management Department of the Tyumen Region, «Tyumengeomonitoring» Territorial Centre. Tyumen, 2010. P. 122.

4. Document Set on the Sixth Competition for Extraction License in the Southern Districts of the Tyumen Region. Resource Management Department of the Tyumen Region, «Tyumengeomonitoring» Territorial Centre. Tyumen, 1999. P. 93.

5. Matusevich, V.M. Undergroundwater Geochemistry of the West Siberian Oil and Gas Basin. Moscow: Nedra, 1976. 157 p.

6. Perelman, A.I. Landscape Geochemistry. Moscow: Vysshaya Shkola, 1975. 342 p.

7. Perelman, A.I. Geochemistry of Natural Waters. Moscow: Nauka, 1982. 154 p.

8. Lezin, V.A. Rivers of the Tyumen Region (Southern Districts): Reference Book. Tyumen: Vector Book, 1999.

9. Babushkin, A.G., Moskovchenko, D.V., Piskunov, A.V. Hydrochemical Monitoring of Surface Waters of the Khanty-Mansi Autonomous Okrug — Yugra. Novosibirsk: Nauka, 2007. 152 p.