UDC 556.314:556.388
DOI https://doi.org/10.32846/2306-9716/2022.eco.5-44.10

HYDROGEOCHEMICAL FEATURES OF CHANGES IN THE F^- CONTENT IN THE GROUNDWATER CHEMICAL COMPOSITION OF BUCHAK-KANIV AQUIFER TO INCREASE THE ECOLOGICAL SAFETY OF POPULATION DRINKING WATER SUPPLY

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The article solves a strategically important ecological problem of region – the key role of man-made component (intensification of water withdrawal, extension of water intakes network) in the existing tendency to increase the F^- content in the operation of region's water intakes was proved. The geological and ecological factors of increased F^- content in drinking groundwater of buchak-kaniv aquifer (BKA) at the water intakes of Eastern Ukraine were considered. It was determined that the predominant factor in the formation of BKA groundwater chemical composition at the present stage is natural phenomena (dissolution of phosphorite layer in the top of aquifer), activated by the man-made component (expansion of water intakes network and intensification of water withdrawal on them) and deep hydrogeomigratory processes (upward migration of unconditioned waters through tectonic faults associated with salt diapirs; upward and downward diffusion of mineralized pore solutions of waterproofs to BKA waters).

The average geological base content (GBC) of chemical element at the beginning of period of active man-made pressure on the geological environment was determined. It is inherent in the waters of territories within which there is no influence of studied factors.

It was determined that in the process of active operation of powerful water intakes, the F^- content increases. Territories with indicator content that is critically threatening to the health of population (from 4 to 8 mg/dm^3) were identified. These areas are characterized by the "overlapping" of all the natural and man-made factors investigated in the paper.

According to the correlation analysis results, a direct positive relationship between the change in element content and the volume of drinking groundwater in the influence zone of tectonic faults associated with salt diapirs was determined. It was during the period of maximum technogenesis – 1976-1995 – that the chemical composition of waters undergone the greatest changes.

The approach proposed by the author is recommended to be used when developing recommendations on the intensity of operating conditions of water intakes in Eastern Ukraine to increase the environmental safety of population drinking water supply. *Key words:* drinking groundwater, pollution, F^-, buchak-kaniv aquifer, ecological safety.

Гідрогеохімічні особливості зміни вмісту F^- у хімічному складі підземних вод бучацько-канівського водоносного комплексу для підвищення екологічної безпеки питного водопостачання населення. Левонюк С. М.

У статті розв'язано стратегічно важливу екологічну проблему регіону – доведено ключову роль техногенної складової (інтенсифікація водовідбору, розширення мережі водозаборів) у наявній тенденції до збільшення вмісту F^- у процесі експлуатації водозаборів регіону. Розглянуто геологічні та екологічні фактори підвищеного вмісту F^- у питних підземних водах бучацько-канівського водоносного комплексу (БКВК) на водозаборах Східної України. Визначено, що превалюючим чинником формування хімічного складу підземних вод БКВК на сучасному етапі є природні явища (розчинення фосфоритового шару у покрівлі водоносного комплексу), активізовані техногенною складовою (розширення мережі водозаборів та інтенсифікація водовідбору на них) та глибинними гідрогеоміграційними процесами (висхідна міграція некондиційних вод крізь тектонічні порушення, пов'язані з соляними діапірами; висхідна та низхідна дифузія мінералізованих порових розчинів водотривів до вод БКВК).

Визначено середній геологічний фоновий вміст хімічного елемента на початку періоду активного техногенного навантаження на геологічне середовище. Він притаманний для вод територій, у межах яких відсутній вплив досліджуваних факторів.

Визначено, що в процесі активної експлуатації потужних водозаборів вміст F^- зростає. Виділено території із критично загрозливим для здоров'я населення вмістом показнику (від 4 до 8 мг/дм^3). Даним ділянкам притаманне «накладання» усіх досліджених у роботі природних і техногенних факторів.

Відповідно до результатів кореляційного аналізу, визначено прямий позитивний зв'язок зміни вмісту елемента від об'єму водовідбору питних підземних вод у зоні впливу тектонічних порушень, пов'язаних із соляними діапірами. Саме у період максимального техногенезу – 1976-1995 рр. – хімічний склад вод зазнав найбільших змін.

Запропонований автором підхід рекомендується використати при розробці рекомендацій з інтенсивності умов експлуатації водозаборів Східної України для підвищення екологічної безпеки питного водопостачання населення. *Ключові слова:* питні підземні води, забруднення, F^-, бучацько-канівський водоносний комплекс, екологічна безпека.

Formulation of the problem and the relevance of research. Buchak-kaniv aquifer (BKA) is the one of strategic sources of drinking groundwater in Eastern Ukraine. There is about 50 % of the total water supply here is exactly the water from this aquifer.

Current F^- content in the BKA groundwater within the region of research has threatening proportions. In accordance with our research, an exceeding of parameter concentrations of permissible WHO drinking water quality standard (1,5 mg/dm^3) can be traced within about

80 % of research territory. Its average content is more than 3 mg/dm^3, it reaches values of 5 maximum permissible concentrations (MPC) [1].

A presence of stable relationship between the fluoride intoxication and rising of population level morbidity in the studied territories has been clinically proven. But the problem of high F^- content in BKA waters is not fully investigated. Author can expand knowledge about these processes. This is especially relevant because of necessity of ecological safety increasing of Eastern Ukraine.

Analysis of recent researches and publications. There are a lot of publications of Ukrainian and foreign scientists, that devoted to the study of F^- geochemical features in natural waters and causes of element increased content.

V. G. Suyarko [2] has been considered the hydrogeochemical features of F^- in Donbass groundwaters. He has identified the technogenic and natural sources of its migration into the underground hydrosphere. Some aspects of element influence on non-infectious population diseases within the territory also have been studied.

V. V. Yakovlev [3] has studied the peculiarities of F^- content at some water intakes of Eastern Ukraine. It has been proven that the source of component in groundwater is the phosphorite layer, which lies in the reservoirs of interlayer aquifers. It is also shown that there is a relationship between the intensity of water withdrawal at powerful water intakes and change in the F^- content in water.

E. Ya. Zhovynsky, N. O. Kriuchenko et al [4, 5] have studied the geochemistry of halogens (including F^-) in the groundwaters of Dnipro-Donetsk artesian basin, especially Poltava region. Geochemical dependencies of basic indicators of water qualitative composition and F^- content have been traced. The possible sources of component migration to the BKA waters have been indicated.

The papers by T. Chernet, D. V. Reddy et al [6, 7-10] have been dedicated to the local problems of F^- increased content in groundwater. These studies have been conducted in African and Asian countries where these ecological problems are threatening.

As a conclusion, most researchers believe that the problem of increased F^- content in the BKA waters of Eastern Ukraine has purely natural character. Scientists distinguish 3 factors. First, it is the lithological composition of water-bearing and overlying rocks [3, 4]. Secondly, the geochemical prerequisites for the intensification of solid phase solubility in the natural "solution-rock" system due to the change in the waters chemical composition under the influence of natural (deep) factors [3, 4, 6, 7]. Thirdly, additional migration of an element of purely deep origin is possible [5, 10].

But these papers did not consider such an issue as the man-made influence on changes in the F^- content in drinking groundwater. This could help to develop measures to stabilize the component content, which would increase the ecological safety of population drinking water supply of this region.

Description of the study. At the first stage, data on the genesis of component increased content in groundwater was integrated and the main geoecological factors affecting these processes were determined.

The author systematized available literature data on the natural mechanism of F^- enrichment of groundwater, including at water intakes in Eastern Ukraine. The mechanism consists of 3 factors [1].

1) Lithological composition of water-bearing rocks. According to the results of drilling wells in the region, the presence of regional layer of phosphorite nodules with a gross F^- content of up to 1,5% was established in the upper part of BKA.

2) As a result of active influence of salt-dome tectonics, processes of discharging of deep highly mineralized groundwater into drinking water of active water exchange zone are characteristic for this region. Migration zones are numerous faults within tectonic structures, mainly associated with salt diapirs. As a result, there is a gradual change in the chemical composition of BKA waters to the chloride-sodium type, the salt content increases, relative content of Ca^{2+} and Mg^{2+} decreases. The change in waters chemical composition creates geochemical prerequisites for the intensification of solid phase solubility of above-mentioned phosphorite layer and an increase in the F^- content in these waters. Schematically, these chemical reactions look as follows:

a) $Ca_5(PO_4)_3F$ (*fluorine apatite*) + Ca / Mg (*high content*) + Na (*low content*) + … → CaF^+ / MgF^+ (*inactive forms of F$^-$, precipitation and transition to the solid state*) + … – low F^- content in waters;

b) $Ca_5(PO_4)_3F$ (*fluorine apatite*) + Na (*high content*) + Ca / Mg (*low content*) + … → NaF^+, F^- (*the most active forms of F$^-$, active migration of element*) + … – increased F^- content in the waters.

3) Additional migration of an element of deep origin is also possible during the processes described in the previous point.

To activate these processes, it is necessary to have a stable inflow of chloride-sodium highly mineralized groundwater with a low content of Ca^{2+} and Mg^{2+} into the waters of target aquifer. But these geological processes in natural conditions are not typical for the waters of active water exchange zone within the study area. The author connects this with modern active processes of technogenesis of geological environment, namely [1]:

– intensification of groundwater withdrawal;

– changes in the hydrodynamic conditions of operational aquifer due to an increase in the network of water intakes;

– the formation of regional depression funnels of operational aquifers, the overlap of which creates a synergistic effect.

In order to establish this relationship, the dynamics of changes in the F^- content in the BKA waters during the period of active man-made pressure on the geological environment – 1960-2020 – was been traced. The average geological base content (GBC) of component

was determined – about 2 mg/dm^3.

The spatio-temporal changes of indicator before the beginning of period of active technogenesis and now are studied. In 1960-1975, the content of component corresponded to 2 intervals of values: up to 1 GBC – within the territories with less active tectonic processes (northern and southern parts of region); from 1 to 2 GBC – within the area with the active influence of salt-dome tectonics (central part of territory).

Currently (as of 2005-2020), in addition to the reduction of areas containing up to 1 GBC, territories containing more than 2 GBC (up to 4 inclusive) have appeared, which is critically threatening to population health (Figure 1). Their area is about 20% of the total.

Based on available clinical studies within the region [11-13], a connection between these processes and some serious diseases was established:

1) children's endemic fluorosis (from 74% to 95% of children within the territory with a critical F^- content suffer from it);

2) diseases of the thyroid gland (during the period 1990-2005, the number of various diseases of thyroid gland in the population of this territory increased by 2-9 times);

3) congenital defects (occurring here 1,5 times more often than background values).

Within the established zone of F^- content critical values, there was an "overlay" of particularly active manifestations of technogenesis (water intake networks of Poltava city and some less powerful ones) on tectonic structures associated with salt diapirs of central part of Dnipro-Donetsk depression. The latter are actively divided into blocks by faults, which act as migration paths for the intensive upward flow of deep, highly mineralized waters to the operational aquifers.

The dynamics of F^- content changes at typical powerful water intakes of region (water intakes of Poltava, Lubny, Khorol, Karlivka, Krasnograd, Reshetylivka cities and some others) were also traced. In the process of active operation of these water intakes, the content of F^- increases. Over the 60-year period, the number of values corresponding to more than 1 GBC increased from 38% to 63%.

In order to establish and quantify the relationship between one of the main components of underground water technogenesis – the water withdrawal indicator – and the dynamics of F^- content changes, these processes at the Poltava city water intakes, which are strategically important within the region, were studied in more detail.

On the example of these water intakes, based on the results of correlation analysis, a linear positive relationship between the F^- content change and the amount of water withdrawal in the influence zone of tectonic faults associated with the Poltava salt diapir was established (the distance between water intake objects and faults is from 0,5 to more than 5 km).

A direct positive relationship between these indicators was established, the following correlation coefficients were calculated:

– distance to faults 0,5 km = 0,84;

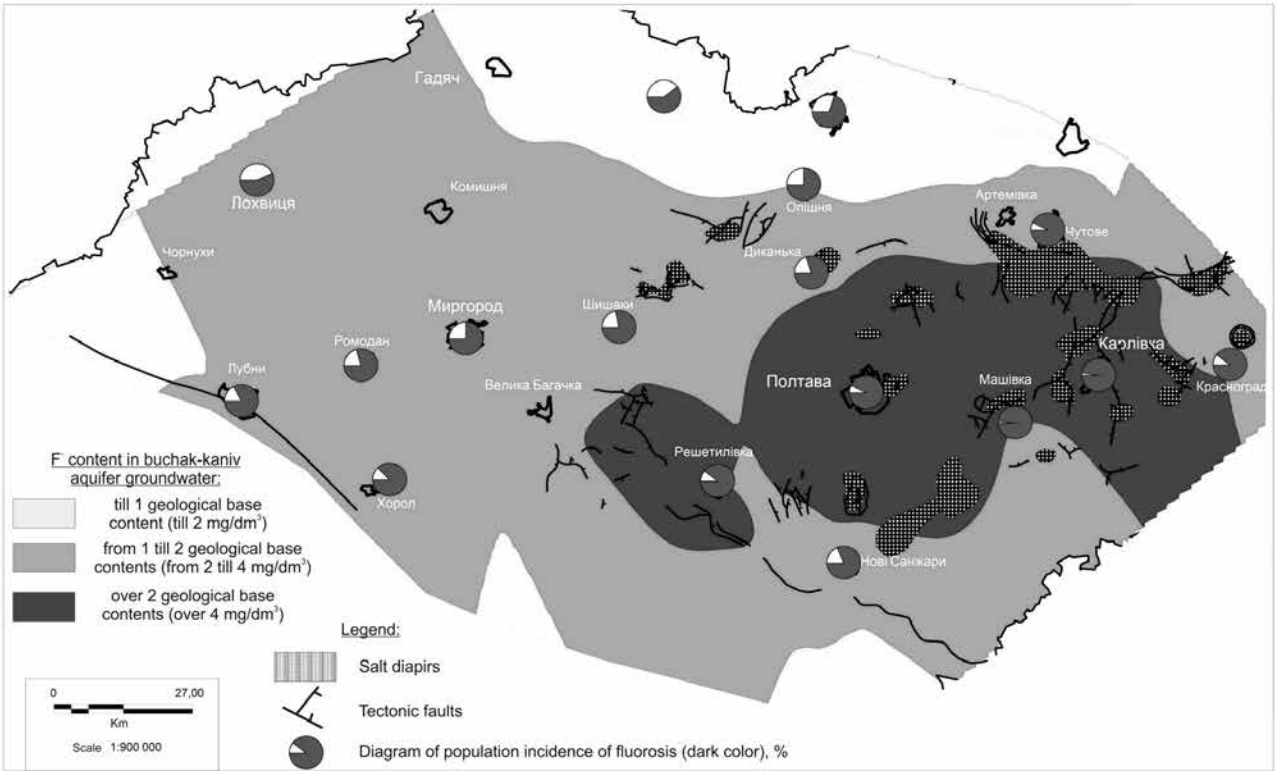

Fig. 1. Map-scheme of F^- content in BKA groundwater within the studied region as of 2005-2020

– distance to faults 1 km = 0,61;
– distance to faults 2 km = 0,65;
– distance to faults about 4 km = 0,5;
– distance to faults more than 5 km = 0,57.

That is, it has been established that one of the main conditions for the activation of BKA groundwater F^- enrichment natural mechanism is the presence and nature of man-made pressure on the drinking groundwater of territory. At the water intakes of Poltava city, activation took place during the period of maximum technogenesis – 1976-1995.

Main conclusions. Strategically important ecological problem of region – the key role of technogenic component (intensification of water withdrawal, extension of water intakes network) in the current tendency to increase the F^- content in the operation of region's water intakes have been considered in the article.

The author has determined the geological base content (GBC) of element (about 2 mg/dm^3) at the beginning of active man-made period. It is inherent to the waters of areas, within which there is no influence of investigated ecological and geological factors of increased F^- content.

It has been identified that F^- content increases in the process of active operation of powerful water intakes. It has been determined that the areas with critical for population health content (from 2 to 4 GBC) have appeared now. «Overlay» of all the studied in paper natural and technogenic factors is inherent to these territories.

On the example of Poltava water intakes network, it has been shown that the explored natural mechanism of groundwater F^- enrichment is activated by an influence of technogenic component (intensification of underground water withdrawal, extension of water intakes network, hydrodynamic changes). During the period of maximum technogenesis – 1976-1995 – the water chemical composition undergone the greatest changes (an increase in F^- content from 81 % to 90 % of the total).

According to the results of correlation analysis, a direct connection between the changes in F^- concentrations and the value of water withdrawal in zone of influence of tectonic faults associated with salt diapir has been established (correlation coefficient = 0,84).

Prospects for the use of research results. After determining the hydrogeochemical features of changes in the F^- content in the groundwater chemical composition of buchak-kaniv aquifer and the main causes of these processes, the next step will be the development of measures to increase the ecological safety of drinking water supply for the population of these territories.

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