Comparative Hydrogeochemical Assessment of Groundwater in Rural Settlements With Different Types of Anthropogenic Loads

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Abstract. The interrelation between surface and groundwater is of particular importance in agroindustrial regions where intensive exploitation of aquifers occurs, both for economic and drinking water supply, and for water drainage in mining areas. Belgorod Oblast is one such region, where a comparative ecological and hydrogeochemical assessment of groundwater was conducted in two contrasting rural settlements: one with significant anthropogenic pressure, including the impact of mining complexes, and a background territory dominated by agroindustrial production. The empirical basis of the study was provided by groundwater samples collected from water wells, boreholes, and water towers, followed by the determination of macro- and microelement content to assess the ecological state of groundwater. The Upper-Lower Cretaceous aquifer complex, characterized by hydrocarbonate-sulfate calcium composition with mineralization of 0.5-0.6 g/L, is most widely used for water supply to industrial enterprises, cities, rural settlements, and livestock complexes. It was established that the water from this complex in the background territory has microelement indicators that do not exceed the maximum permissible concentrations set for drinking water. In contrast, in the territory with strong anthropogenic pressure, the main contaminants are lead, cadmium, and copper. The influence of different types and intensities of anthropogenic loads is reflected in changes to the natural regime of aquifers and the rate of leaching and further contamination processes. This study highlights the need for developing and implementing differentiated sets of measures to maintain groundwater quality, taking into account the specific anthropogenic pressures in different areas.

INTRODUCTION

Groundwater is a key natural resource, playing a significant role in the economy, but most importantly, it serves as the primary source of drinking water for more than two billion people globally [1]. The Central Black Earth region is a water-scarce area of Russia, and with the minor role of surface water resources, monitoring the replenishment and use of groundwater becomes critically important. A regional feature of water use in the Kursk Magnetic Anomaly territory, which contains at least two-thirds of Russia's iron ore reserves [2, 3], is the intensive exploitation of aquifers near industrial centers for economic and drinking water supply, as well as significant changes in the hydrogeological regime and qualitative state of groundwater [4, 5]. In the Belgorod region, the main area of the Kursk Magnetic Anomaly, 250 freshwater groundwater deposits have been explored, which can be used for economic, drinking, industrial, technical, and agricultural water supply. Although the region uses 95% of all water resources from groundwater to meet the drinking needs of the population, only 47% of the total water withdrawal is consumed by economic and drinking water supply systems, while 40% of the withdrawn water consists of drainage waters from four operating mining enterprises (OJSC Lebedinsky GOK, OJSC Stoilensky GOK, OJSC "KMAruda Combine" and LLC "Metal-group" Yakovlevsky mine) [6]. Therefore, this region also has a complex of problems actively discussed in the world literature: the influence of the discharge of mine water on the surface water quality and the prospects of

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using Managed Aquifer Recharge (MAR) technology within the mining industry [7,8]. Because the main sources of economic and drinking water supply are the Turonian-Maastrichtian, Bathonian-Callovian aquifer complexes, the Albian-Cenomanian aquifer, and in the area of iron ore enterprises, groundwater is already extracted from the Carboniferous and Archean-Proterozoic aquifer complexes, all zones of active, slow, and hindered water exchange in the Earth's crust experience intense anthropogenic pressure.

The active agricultural development of the region's territory (the share of arable land is 60%), as well as the imbalance of erosional soil losses with the rate of soil formation, leads to the degradation of surface water bodies, especially the upper reaches of rivers [9, 10]. In this regard, within the identified groundwater flow basins, it is necessary to determine the quantitative and qualitative characteristics of the state of rivers, water bodies, and groundwater, followed by identifying areas of interaction between surface and groundwater [11]. Currently, with significant attention to the ecological and economic sustainability of rural settlements, a key aspect of this development is ensuring quality water supply [12, 13]. Often in rural areas, water supply is provided by single wells. It is necessary to consider that groundwater can be contaminated, and the list of pollutants is closely related to the municipality's belonging to a particular specialization sector (mining, agricultural, etc.). In this regard, it is advisable to develop environmental protection measures based on a comparative assessment of the ecological and hydrogeochemical situation. This approach will allow forming a typical list of measures to ensure the safety and quality of drinking water for residents of rural settlements.

The aim of this study was comparative ecological-hydrogeochemical assessment of groundwater in the territory of two rural settlements, which differ in economic activity profiles (mining and agro-industrial complexes), to improve measures for maintaining groundwater quality.

MATERIALS AND METHODS

The objects of study were two municipal formations in Belgorod Oblast, characterized by contrasting natural and economic conditions. Bykovskoe rural settlement (RS) (area 58.1 km^2) is located in the center of Belgorod Oblast (Yakovlevsky district). This territory experiences high anthropogenic pressure associated with the activities of the Yakovlevsky mine complex (1.5 km from Bykovka village), proximity to the city of Stroitel, and the passage of high-traffic roads (14N-794 and E105) through this settlement. Additionally, the territory is characterized by active agroindustrial development. Novoukolovskoe municipal formation (area 210 km^2) in the Krasnensky district is located in the east of Belgorod Oblast. The anthropogenic load here is relatively low, as there are no major highways, and the main activity is agriculture (the share of agricultural land reaches 97%).

The sources for groundwater sampling were all-metal water towers, wells, and water intake boreholes of private households. In Bykovskoe and Novoukolovskoe rural settlements, 13 and 7 groundwater samples were collected, respectively. Groundwater samples were taken according to GOST R 59024-2020 "Water. General requirements for sampling", then they were analyzed in the accredited laboratory of the Research Institute of Geology for macrocomponents (Voronezh State University) and for microcomponents at Belgorod State National Research University using atomic emission spectrometric method on a Shimadzu ICPE-9000 parallel-action emission spectrometer with inductively coupled plasma. The assessment of the degree of chemical contamination was carried out using indicators developed in conjugate geochemical and hygienic environmental studies: concentration coefficient relative to Maximum Permissible Concentration (MPC):

$$K_{MPC} = \frac{C_i}{MPC}, \quad (1)$$

where C_i is the actual content of the *i-th* chemical element in the sample, mg/dm^3.

Concentration coefficient (K_{ci}) characterizes the intensity of the anomaly:

$$K_{ci} = \frac{C_i}{C_{bc}}, \quad (2)$$

where C_{bc} is the background content of the *i-th* chemical element in the sample, mg/dm^3.

Background values for the studied pollutants in groundwater were adopted in accordance with the average content in groundwater of the leaching zone (GWLZ) in temperate climates [14]. Stiff diagrams [15] were used for graphical representation of the macrocomponent composition of waters. The content of micro- and macroelements are the main parameters used to assess the ecological state of groundwater. Recognizing the immense role of global and regional strategies for controlling groundwater depletion, hydrogeology specialists call for assistance to promote the transition from regional to aquifer scale [1]. Pollution indicators of individual sources (wells, springs) were interpolated to the entire aquifer within the studied rural area.

RESULTS

The main exploited aquifer complexes for the Bykovsky RS territory are the modern alluvial complex (aIV), and for the Novoukolovsky RS territory - the Lower-Upper Quaternary alluvial complex (aI-III). Additionally, the combined Upper-Lower Cretaceous complex (K_{1-2}) plays an important role for both settlements. The aIV aquifer complex is associated with floodplains of small rivers and erosion networks. It is located on different layers of Paleogene and Upper Cretaceous. Sands of varying grain sizes form the basis of water-bearing rocks in river valleys. In the upper part of the section, layers of loam, clay, silt, and peat are often encountered. The average water table depth is about 15 m. The complex is used for water supply in rural areas through wells and for small-scale water supply. The locally weak Lower-Upper Quaternary alluvial aquifer complex (aI-III) is confined to terrace deposits and is distributed in the valleys of large and medium rivers. It lies on the Turonian-Maastrichtian aquifer complex and is the first from the surface. Water-bearing rocks are variously grained sands and sandy loams in the deposits of the first and second terraces, clays, loams, and sands with sandy loams in the sections of the third, fourth, and buried terraces. The water table depth is 2-10 m, with the greatest depth in the alluvial deposits of the third and fourth terraces (2-5 m). The waters of this complex are used for local water supply in rural areas.

The combined Upper-Lower Cretaceous complex (K_{1-2}) includes the Turonian-Maastrichtian terrigenous-carbonate aquifer complex (K_2t-m) and the Aptian-Cenomanian terrigenous aquifer complex (K_{1a-s}). Groundwater of the Turonian-Maastrichtian terrigenous-carbonate aquifer complex (K_2t-m) is found in the thickness of dense white chalk rocks and gray marls. The chemical composition of groundwater is hydrocarbonate-sulfate, calcium-magnesium with mineralization from 0.5 to 0.9 g/l. The complex is recharged through infiltration of atmospheric precipitation in watersheds and inflow from adjacent hydrogeological units. Discharge occurs within river valleys, where numerous springs are observed. The water abundance of the aquifer complex in the study area is low, as it is associated with the watershed. The yield is up to 500 m³ per day, and the transmissivity is 260 m². Waters of this horizon are widely used for water supply to livestock complexes, rural settlements, industrial enterprises, and cities.

The Aptian-Cenomanian aquifer complex (K_{1a-s}) is overlain by the Turonian-Maastrichtian complex. Water-bearing rocks are fine-grained sands with clay interlayers 35 m thick. In the study area, the top of the aquifer complex is at a depth of 322 m from the surface. The horizon is recharged by infiltration of atmospheric precipitation outside the study area, as well as by flow from adjacent aquifers with hydraulic connection. The complex is characterized by high pressure. The waters are hydrocarbonate-sulfate calcium with mineralization of 0.5-0.6 g/l and total hardness of 5-7 mg-eq/l. Waters of this complex are used by individual wells to supply settlements located in watershed areas.

To assess the chemical composition of groundwater in Bykovsky RS, sampling was conducted in the ravine form of the left bank of the Vorskla River valley at 13 observation points (Figure 1). The results of the macrocomponent composition determination of groundwater are presented on Stiff diagrams, which reflect the equivalent water composition at characteristic sampling points (Figure 1).

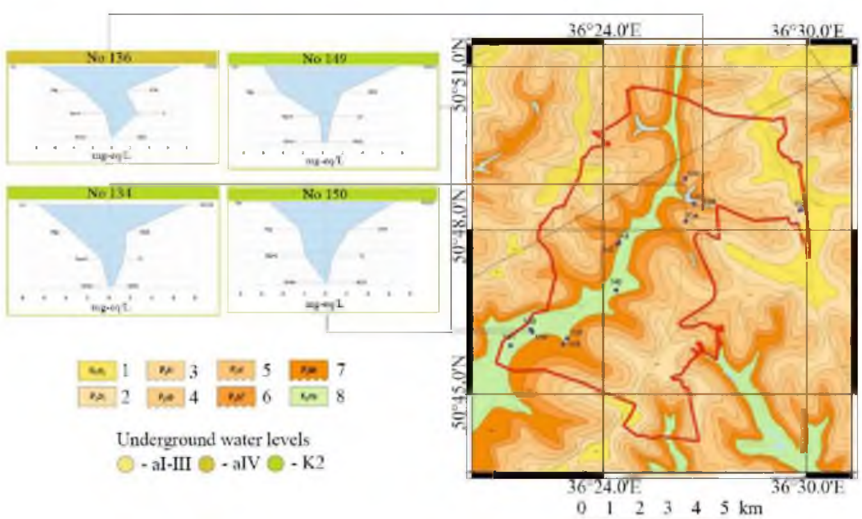

FIGURE 1. Macro-component composition of groundwater of Bykovsky rural settlement (Stiff diagrams).

The basis of Figure 1 is a fragment of the studied area pre–quaternary deposits a geological map. The legend of the geological map reflects the horizons:

1. Upper (Sivash) subformation. Sands with layers of clay (up to 12.5 m).
2. Lower (Zmievskaya) subformation. Clays, silts, sands (1-6 m).
3. Kantemirovskaya formation. Sands (1-7 m). Construction sands.
4. Obukhovskaya formation. Silts (3-20 m).
5. Vorobyovskaya formation. Clays, clayey flasks, silts (1-17 m). Kyiv suite (kv). Clays, clayey sands (up to 20 m). Steblyankino formation (st). Silts, sands (10-25 m).
6. Bottom pack. Sands with interlayers of siltstones and sandstones (up to 23 m). Construction sands.
7. Kanevskaya series. Siltstones and siltstones, sandstones (up to 20 m). Zeolite-containing rocks.
8. Maslovskaya formation. White chalk, writing chalk (up to 81 m). Chalk for construction paper, chemical industrial and lime production.

Groundwater sampling locations are shown by numbers on the map.

DISCUSSION

The results of the route survey of the Bykovsky RS territory showed that 20% of the surveyed wells are unsuitable for use. Unsatisfactory conditions of the first belt sanitary protection zones (SPZ) were noted for individual wells, which is more often due to the presence of livestock waste on the surface. Most indicators of the water's macrocomponent composition meet regulatory requirements, except for the magnesium content in sample No. 149 (with MPC = 50 mg/dm^3, the content was 53 mg/dm^3). A slight excess of magnesium and total hardness is apparently related to the geological structure of the area (the presence of carbonate rocks in the cross-section).

Exceedances of a number of macrocomponent composition indicators were identified by correlating their values with the average content in groundwater of leaching zones in temperate climates (GWLZ) [14]. The content in all samples is on average exceeded by calcium by 3 times, by hydrocarbonates and magnesium by 2 times. Sodium exceedances of almost 1.5 times were found in the Upper-Lower Cretaceous aquifer complex in three samples. The concentration coefficient of sulfates relative to GWLZ varies from 2.2 to 6.9, and chlorine on average by 3 times. Both aforementioned aquifer complexes are characterized by an excess of nitrate content over GWLZ (up to 14). For microcomponents, elevated lead content was detected in the modern alluvial aquifer complex in sample No. 139 (K_{MPC} = 1.8) (Table 1), which is due to the close location of the well to the road. The Upper-Lower Cretaceous aquifer complex was distinguished by high concentrations of cadmium (KMPC = 6.4 (sample No. 139)) and copper (K_{MPC} = 1.7 (sample No. 137)). The remaining microelement indicators did not exceed the MPC for drinking water.

TABLE 1. Coefficient of concentration of microcomponents relative to MPC.

Sample number (No)	Cd	As	Pb	Zn	Ni	Cu	Co	Mn	Se
	K_{MPC}								
Modern alluvial aquifer complex (aIV)									
136	LOD	LOD	LOD	LOD	LOD	LOD	LOD	0.17	LOD
138	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
Upper-Lower Cretaceous complex (K_{1-2})									
134	LOD	LOD	0.18	LOD	0.19	LOD	LOD	0.08	LOD
137	0.60	LOD	0.31	LOD	0.15	**1.74**	LOD	LOD	LOD
139	**6.40**	LOD	**1.81**	LOD	0.10	0.30	LOD	LOD	LOD
143	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
148	**4.60**	LOD	0.71	LOD	0.04	0.01	LOD	LOD	LOD
149	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
150	**4.50**	LOD	0.44	LOD	0.04	LOD	LOD	LOD	LOD
151	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD

Note. LOD is limit of detection.

The use of the PVZV (permissible value of harmful substances) normative indicator in addition to MPC (maximum permissible concentration) showed that, relative to its values, a significant excess in the Upper-Lower Cretaceous aquifer complex was observed for Cd (3 to 32), Pb (up to 6), Ni (up to 1.3), and Cu (up to 348 (sample No. 137)). Such indicators demonstrate significant anthropogenic transformation of the microcomponent composition of groundwater in the impact zone of mining and agrotechnical enterprises compared to background values. The assessment of groundwater pollution by elements of hazard classes 2 and 3 corresponds to the categories "Permissible" (18%) (due to the presence of MPC exceedance for total hardness and magnesium content), "Moderately hazardous" (45%), "Hazardous" (10%), and "Highly hazardous" (27%). The key groundwater pollutants belong to the second (Pb, Cd) and third (Cu) hazard classes.

The waters of the alluvial aquifer complex are characterized only by elevated lead concentrations and some exceedance in total hardness. Relative to PVZV, elevated concentrations were found for calcium, magnesium, bicarbonates, nitrates, sulfates, and chlorine. This indicates that as a result of active exploitation of the aquifer complex, its natural regime changes and leaching processes are activated.

The waters of the Upper-Lower Cretaceous complex in the Novoukolovskoye rural settlement have values of all microelement indicators that do not exceed the MPC for drinking water.

A comparative ecological and hydrogeochemical assessment of the situation in contrasting rural settlements was conducted at the final stage of the research to form a typical list of environmental protection measures that could guarantee the normative quality of drinking water for rural settlement residents.

For the Novoukolovskoye rural settlement, where there are potential sources of pollution that partially affect the state of aquifers, the priority task is to develop environmental protection measures aimed at regulating surface runoff in agricultural landscapes in the catchment area, but it is especially necessary to bring the state of sanitary protection zones to regulatory requirements. In the Bykovskoye rural settlement, where mining industry is developed, a complex hydrogeological situation has emerged, requiring attention and solutions at the municipal level. Purification of water from wells contaminated with heavy metals (cadmium and copper) can be carried out by various methods depending on the degree of contamination, water volume, and other factors. Among such methods are the use of coarse filters to remove large particles and impurities, the application of chemical reagents and special filters, as well as ozonation and ultraviolet irradiation.

CONCLUSION

Analysis of the macrocomponent composition of groundwater for the background territory (outside mining areas) showed that all indicators comply with the MPC. However, due to active exploitation of aquifers, their natural regime changes and leaching processes are activated, which is reflected in high concentrations of nitrates, sulfates, and hydrocarbonates compared to the parameters of average content in groundwater of the leaching zone in temperate climate. For rural settlements with strong anthropogenic pressure, the quality of groundwater from the modern alluvial aquifer complex meets environmental standards, while groundwater from the Upper-Lower Cretaceous complex is characterized by exceeding the maximum permissible concentration for pollutants from the second (Cd, Pb) and third hazard class (Cu). The results of assessing the degree of groundwater contamination by elements of the 2nd and 3rd hazard classes for the background territory showed that 85% and 15% of the samples collected are distributed between the "Permissible" and "Moderately dangerous" categories of pollution, respectively. The state of groundwater in the rural settlement with strong anthropogenic pressure is significantly differentiated between pollution categories: "Highly dangerous" accounts for 27% of samples, "Dangerous" 10%, "Moderately dangerous" 45%, and "Permissible" 18%. Comparative ecological-hydrogeochemical assessment of groundwater in the territory of two rural settlements, which differ in economic activity profiles (mining and agro-industrial complex), allows for the development of differentiated sets of measures to maintain groundwater quality. Maintaining groundwater quality in the territory of the rural settlement with an agricultural profile will be facilitated by implementing a number of measures to bring sanitary protection zones to regulatory requirements to prevent possible future problems. Due to the fact that 37% of the samples collected in the territory of rural settlements with strong anthropogenic pressure showed dangerous and highly dangerous degrees of water pollution, it is recommended to use coarse filters to remove large particles and impurities, apply chemical reagents to precipitate heavy metals and their subsequent removal, as well as the use of special filters (ion exchange or membrane).

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REFERENCES

1. N. Kazakis, M. Mastrocicco and K. Chalikakis, Water **16**, 2385 (2024).
2. E. V. Mezentseva, S. A. Nemykin and L. A. Loginova, Gornyi Zhurnal **6**, 9–13 (2022).
3. T. N. Gzogyan, S. R. Gzogyan and E. V. Grishkina, Eurasian Mining **1**, 3–7 (2019).
4. A. N. Petin, O. N. Polukhin, I. A. Kireeva-Genenko, M. A. Khovanskaya, I. I. Kosinova and V. P. Zakusilov, Int. J. Pharm. Technol. **8 (2)**, 14165–14173 (2016).
5. E. A. Kornilova, F. N. Lisetskii and M. E. Rodionova, Region. Geosyst. **4**, 550–568 (2023). (in Russian)
6. A. I. Pogoreltsev, V. I. Petina, L. I. Belousova, N. I. Gaivoronskaya and E. A. Bugaeva, Nauch Ved Belgoro EN. **11 (232)**, 172–182 (2016).
7. Y. Guo, G. Li, L. Wang and Z. Zhang, Water **15 (6)**, 1038 (2023).
8. S. Sloan, P. G. Cook and I. Wallis, Groundwater **61 (3)**, 305–317 (2023).
9. L. Fedor and C. Oleg, Adv. Environ. Biol. **8 (4)**, 996–1000 (2014).
10. F. N. Lisetskii, Z. A. Buryak, O. A. Marinina, P. A. Ukrainskiy and P. V. Goleusov, Geosciences **13 (9)**, 278 (2023).
11. F. Lisetskii, M. Kitov, A. Spesivtseva and O. Marinina, E3S Web Conf. **548**, 01018 (2024).
12. V. A. Budarina, F. N. Lisetsky and I. I. Kosinova, Gornyi Zhurnal **11**, 57–62 (2022).
13. A. I. Stifeeva, O. V. Nikitina, V. I. Lazarev and R. A. Zinovieva, Agrohimia **7**, 62 (2021).
14. S. L. Shvartsev, Geochem. Int. **38 (2)**: 260–276 (2000).
15. H. A. Stiff Jr, JPT. **3 (10),** 15–17 (1951).