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Geological Environment Role in the Formation of Hydrogeoecological Conditions within Large Industrial Zones

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Abstract. Natural and man-made conditions of the Nizhnekamskaya industrial zone are discussed in the article. This zone includes large petrochemical and oil refineries, PJSC «Nizhnekamskneftekhim» is one of the largest companies in Europe. The article shows that significant changes in the composition of natural waters are manifested within the territory of a large operating surface landfill for industrial waste and in its vicinity. Here, the salinity of underground water can reach 12 g/l, and the concentration of petroleum products and phenols, which are characteristic pollutants, reaches 982 and 14 mg/l. Within the industrial site, underground water salinity reaches 1.25 g/l, their hardness is 18 mmol/l, and permanganate index is 17.3 mgO/l. The intensity of pollution of natural waters decreases with increasing distance from the boundaries of industrial zones. There are no signs of pollution of natural waters at a distance of 1.0-1.5 km from the landfill. The composition of natural waters has not changed over the past 40 years outside the industrial zone. Here, HCO₃/Ca and HCO₃/Mg-Ca are developed; waters with mineralization up to 0.5-0.6 g/l and total hardness up to 7 mmol/l are favorable for drinking. Natural water pollution is local, since the geological environment has high buffer properties. The nature of the geological section, consisting mainly of clay rocks, the favorable quality of precipitation at their rate of 550 mm / year determine these properties. The predominant type of pollutants, represented mainly by organic substances (petroleum products, phenols, etc.), which are subjected to chemical and biological degradation, also determine these properties. In addition, vertical hydrogeochemical zonality plays an important role. It changes with an increase in the depth of the HCO₃/Ca waters of the waters of HCO₃/Na composition. At the same time, the salinity of underground water is in the range of 430-600 mg/l, and the hardness decreases from 6.4-7.3 to 0.5-2.3 mmol/l. This determines the possibility of obtaining potable quality water in any part of the industrial zone, where the optimal depths of wells' filters are 140-160 m.

1. Introduction

One of the main problems of the modern world are the problems of environmental pollution and the deterioration of the quality of its main components. Pollution is maximum within large industrial zones and the surrounding area, as well as in areas of mineral deposits. First of all, the atmosphere, the pedosphere and the hydrosphere are exposed to negative effects. The nature and intensity of pollution of the hydrosphere are determined by the structural features of the geological environment [1, 2]. Protective (buffer) properties of the geological environment in some cases allow us to cope with the intensive anthropogenic impact. In this case, pollution of fresh underground water is distributed locally, does not change for a long time. Example - Nizhnekamskaya industrial zone is a geological



environment with significant buffer properties. Taking into account the protective properties of the geological environment is necessary for rational nature management, and the actual task is to identify them.

2. Object and methods of research

The object of the study is the Nizhnekamskaya industrial zone, the features of its geological structure and hydrogeological conditions, as well as the hydrogeochemical characteristics of the upper part of the section (upper 250 m), where fresh underground water is developed. This zone is located within the Tatarstan Republic in the European part of Russia (Figure 1).



Figure 1. Location of the Nizhnekamskaya industrial zone within the Tatarstan Republic.

Several major oil refining and petrochemical industries are located in the industrial area. PJSC «Nizhnekamskneftekhim» is the largest petrochemical company in Europe. The first industrial products here were obtained in 1967. The main products are synthetic rubbers. Currently, within the Nizhnekamskaya industrial zone, more than 15 million tons of oil are processed per year.

Nizhnekamskaya industrial zone is located on a forested watershed with an excess of up to 160 m above the base level of erosion. Its area is about 20 км². Small settlements are located outside the sanitary protection zone. There is active agricultural activity and development of oil fields. The geological section is represented by the platform carbonate-terrigenous stratum of the Permian age. It has a multiple alternation of interlayers of clay, sandstone, siltstone, less often marl and clay limestone. The thickness of individual layers rarely exceeds 6–8 m (Table 1). The quaternary complex covers the Permian sediments, it is represented by eluvial-diluvial loams. The loam thickness is 1–20 m [3].

Table 1. Features of the near-surface part of the geological section.

Stratigraphic age	Thickness, m	The composition of rocks, %		
		Clay	Sandstone	Limestone
P ₂ ur	less than 40-42	54	36	10
P ₂ kz ₂	77-79	67	28	5
P ₂ kz ₁	79-80	80	12	8

Note. Siltstones are not widespread, they are considered together with clays.

Underground waters form an interstratal water flow system. Their catchment areas are watersheds, and their discharge areas are river valleys. Aquifers located at different levels are connected by a downward flow. The high thickness of the zone of fresh underground water depends on the carbonate-terrigenous composition of water-bearing rocks, short flow path, as well as low mineralization of precipitation. The surface hydraulic network in the study area is represented by the upper reaches of numerous streams. In the low water season, they are formed only by the discharge of underground water.

Features of the composition of natural waters are considered with hydrochemical materials of different periods, including data of geological surveying and thematic works with different scales and different times [4-6], the results of research one of the working industrial waste landfill [7]; field and analytical researches within one of the industrial areas ($\sim 2 \text{ km}^2$, 2017) and the vicinity of the industrial zone ($\sim 220 \text{ km}^2$, 2018-2019) made by authors. The analytical researches include the determination of pH, permanganate oxidation, the contents of basic ions: HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- , NO_2^- , Br^- , F^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , Li^+ ; concentrations of a number of heavy metals: Fe, Mn, Cd, Pb, As, Cr, Cu, Ni, Zn, as well as petroleum products. The ionic composition was determined using Dionex ICS-1600 chromatograph, the metals were detected using ContrAA-700 atomic-absorption spectrometer, and petroleum products were determined using a Crystallux 4000-M gas chromatograph.

3. Results and discussion

Nizhnenskaya industrial zone has a maximum negative impact on the atmospheric air. In 2015, atmospheric emissions amounted to about 75 thousand tons. The main pollutants are sulfur dioxide (26%), nitrogen dioxide (17%), carbon monoxide (15%), mixtures of saturated hydrocarbons C1-C5, C6-C10 and C12-C19 (19%) [8].

In the hydrosphere of the area there is industrial, agricultural, municipal pollution and, probably, pollution associated with the development of oil fields. But this pollution has a local character, especially with regard to underground water. Utility pollution of underground water is usually within the settlements. In most cases, pollution is very high hardness and permanganate index (the article uses the maximum permissible concentration values for drinking water). Agricultural pollution is a local sharp increase in hardness, nitrogen and organic content. Industrial pollution is usually expressed in water salinity and hardness increasing, concentrations of oil products, phenols and many heavy metals in them (Cd, Pb, Cr, etc.). It exists at selected sites within production sites, in settlement lagoons and on surface waste disposal sites, as well as in their vicinity. At the same time, all types of pollution are usually manifested in the first underground water aquifer and extremely rarely occur at lower levels. All these features of the spatial distribution of various pollutants are in the surface waters.

On the main part of the Nizhnensky industrial region outside the industrial zone, there have been no changes in the composition of fresh underground water over the past 40 years (Table 2).

Table 2. Features of the composition of underground water in the upper part of the section around the industrial zone.

Time period	Number of samples	Mineralization, mg/l	Hardness, mmol/l	Permanganate index, mgO/l	pH	Predominant type of water
1979-1980	9	<u>382-509.5</u>	<u>3.8-6.0</u>	<u>1.1-5.7</u>	<u>7.4-8.4</u>	HCO_3/Ca ,
		448.9 $\pm$ 50.06	5.12 $\pm$ 0.68	3.3 $\pm$ 1.79	7.94 $\pm$ 0.37	$\text{HCO}_3/\text{Mg-Ca}$
1994-1999	27	<u>347.6-623.2</u>	<u>4.1-7.6</u>	<u>1.28-4.48</u>	<u>6.7-8.1</u>	$\text{HCO}_3/\text{Mg-Ca}$
		489.9 $\pm$ 60.82	5.44 $\pm$ 0.77	2.28 $\pm$ 0.99	7.35 $\pm$ 0.43	
2018	16	<u>417.3-587.0</u>	<u>3.02-6.33</u>	<u>0.48-4.08</u>	<u>7.18-8.06</u>	HCO_3/Ca ,
		482.8 $\pm$ 36.72	5.38 $\pm$ 0.76	1.60 $\pm$ 1.35	7.43 $\pm$ 0.22	$\text{HCO}_3/\text{Mg-Ca}$

Note. In the numerator - the limit values (minimum-maximum), in the denominator - the average and standard deviation; hardness is total water hardness (in this and subsequent tables).

The table shows the data on springs, their composition of water does not have a significant change due to any locally manifested pollution. The counted springs drain watered sedimentary strata, its lithological composition are in table 1. Their chemical composition is similar to the composition of underground water, which is determined by the rather short-term interaction of precipitation with the rocks of the section. In this regard, the spring waters in table 2 are not assigned to any specific hydrostratigraphic levels, but are considered together for each time period. Removal of tested springs from the restrictions of the industrial zone is 0.4-6.0 km.

The compositions of surface and underground water are very similar (Table 3, 2018). At the same time, the permanganate index and concentrations of SO_4^{2-} , Cl^- , Br^- are slightly higher in surface waters, which is probably due to aerogenic pollution of the surface.

Table 3. Comparison of underground water and surface water compositions in the Nizhnekamskaya industrial zone.

Type of natural waters	Number of samples	Mineralization, mg/l	Hardness, mmol/l	Permanganate index, mgO/l	Petrochemicals, mg/l	Predominant type of water
Underground water	16	<u>417.3-587.0</u> 482.8±36.72	<u>3.02-6.33</u> 5.38±0.76	<u>0.48-4.08</u> 1.60±1.35	<u>0.020-0.065</u> 0.032±0.017	HCO_3/Ca . $\text{HCO}_3/\text{Mg-Ca}$
Surface water	25	<u>240-614.9</u> 492.6±72.4	<u>2.24-7.09</u> 5.63±1.18	<u>0.48-6.08</u> 2.82±1.56	<u>0.004-0.19</u> 0.041±0.05	HCO_3/Ca , $\text{HCO}_3/\text{Na-Ca}$

The situation is different in industrial areas. In one industrial area underground water from the first aquifer is confined to Permian clay-sandy rocks, and also to Quaternary surface loam. The depth of its occurrence is 1.5-2 – 5-8 m. The aquifer which is second from the surface is in Permian sandstones, its top is occurs at the depth 10–20 m (Table 4).

Table 4. Features of underground water composition at one of the industrial sites (data 2017).

Aquifer	Number of samples	Mineralization, mg/l	Hardness, mmol/l	Permanganate index, mgO/l	Petrochemicals, mg/l	Predominant type of water
First	31	<u>264-1249</u> 772±232	<u>3.56-17.74</u> 10.02±3.63	<u>1.28-17.28</u> 5.39±3.59	<u>0.008-0.13</u> 0.045±0.033	HCO_3/Ca , $\text{Cl-HCO}_3/\text{Ca}$, $\text{HCO}_3/\text{Mg-Ca}$
Second	6	<u>390-681</u> 560.7±119.1	<u>5.08-9.76</u> 7.51±2.01	<u>1.92-4.12</u> 3.48±0.82	not determined	HCO_3/Ca , $\text{HCO}_3/\text{Mg-Ca}$

Mineralization value increases because of the concentration of almost all macro- and meso-components, as well as Fe and Mn. The contents of some components can reach (mg / l): HCO_3^- – 879; Cl^- – 267; SO_4^{2-} – 126; NO_3^- – 141; Br^- – 0.81; Fe – 4.16; Mn – 3.0. This is due to locally manifested leaks from numerous conduits, aerogenic pollution, as well as more intensive leaching of minerals by underground water, which gets high carbon dioxide aggressiveness. Only an increase in the partial pressure of carbon dioxide causes the carbon-dioxide aggressiveness increasing. This is possible due to chemical and biological degradation of organic matter. The high content of organic matter in the near-surface section depends on information in Table 3 and other data. The composition of underground water varies greatly within and in the immediate vicinity of sludge reservoir and landfills for industrial waste. Characteristic of one of the landfills is given in [4]. Here, underground water salinity can reach 7–12 g / l; hardness – 70–135 mmol/l; concentrations of the most characteristic pollutants (mg/l): petrochemicals - up to 500–982; phenols - up to 13.9; total iron - up to 153 (the predominant hydrogeochemical type of water is sodium chloride-hydrocarbonate-hydrocarbonate). But it is possible to reduce the concentrations of many pollutant components by 1-2 orders of

magnitude already at a short distance from the landfill (150-200 m). at a distance of 1.0-1.5 km from the landfill there are no signs of pollution of underground water caused by landfill work. Thus, within the large industrial zone of the Republic of Tatarstan, there are large changes in the chemical composition of underground water only within the various landfills of the petrochemical industry and their surroundings (100-300 m). Further away, signs of contamination gradually disappear. This is due to the high buffer properties of the geological environment of the Nizhnekamskaya industrial zone.

The zone of fresh underground water in the watershed areas of the Nizhnekamsky industrial region is characterized by vertical hydrogeochemical zonality. Samples were taken from four observation wells in the territory of one of the enterprises, where the wells are located at a small distance from each other and have almost the same altitudes. It was concluded that, in the downward direction, HCO_3/Ca and $\text{HCO}_3/\text{Mg-Ca}$ water type changes to HCO_3/Na and $\text{SO}_4\text{-HCO}_3/\text{Na}$ (Table 5).

Table 5. Vertical hydrogeochemical zoning within the Nizhnekamskaya industrial zone.

Hydrostratigraphic level	Filter depth, m	Water-bearing rocks	Mineralization, mg/l	Hardness, mmol/l	pH	HCO_3^- , mg/l	Na^+ , mg/l
P_{2ur}	20.7-24.5	Limestones, marls	595-595	6.4-7.3	7.8-7.5	421-400	29.0-6.5
P_{2kz_2}	49.2-53.0	Sandstones, limestones	425-397	3.1-3.6	7.7-8.0	287-261	53.4-27
P_{2kz_1}	59.4-62.5	Sandstones, limestones	448-446	2.7-1.4	8.8-8.2	262-224	72.5-88
P_{1ss}	160-174	Sandstones	433-517	2.3-0.5	9.9-8.8	287-221	67.9-143

Note. In analytical data: the first - data for May 2016, the second - October 2016

This zonality is due to ion exchange processes and the precipitation of calcium and magnesium carbonates by increasing the alkalinity of underground water. The lack of carbon dioxide to bond the hydroxyl ion causes an increase in pH to 8.8-9.9. Hydroxyl-ion is released during the hydrolysis of silicates and aluminosilicates, which is accompanied by the entry into the underground water Na^+ , as well as a decrease in the redox potential. This vertical zonality is also associated with large thickness (up to 250 m) of fresh water zones, when deep underground water is soft and, in most cases, has a favorable drinking quality.

4. Conclusion

The Nizhnekamskaya industrial zone is characterized by the composition of natural waters almost unchanged over the past 40 years. These are mainly hydrocarbonate magnesium-calcium waters with a salinity of not more than 0.5-0.6 g/l and hardness up to 7-8 mmol/l. Pollution of surface water and underground water is noted directly within industrial sites, as well as within and around various settlement lagoons and landfills for industrial waste. This pollution is locally prevalent. It is usually at the very top of the section (at the underground water level) and is not noted at a distance of more than 1.0-1.5 km, even from such major pollution sources as working landfills for industrial waste. Local pollution is caused by high buffer properties of the geological environment. These properties are determined primarily by the nature of the geological section, the rather favorable quality of precipitation at a standard of 550 mm / year, and the predominant type of pollutants. These substances are mainly organic substances (petroleum products, phenols, etc.), which are subjected to chemical and biological degradation. The carbonate-terrigenous character of the section with the predominance of clays determines the formation of numerous interstratal water horizons that prevent deep penetration of surface pollution. When water pollution from the first aquifer is manifested, polluted water is filtered and discharged into nearby valleys of rivers and streams. In the low streamflow period, underground water is discharged into all surface watercourses. They cannot affect the quality of underground water. Pollution is local within the watercourses themselves, because the surface waters of the region can also self-clean (dilution with clean waters (atmospheric, surface, underground

water), sorption on suspended particles and precipitation, etc.). Vertical hydrogeochemical zonality determines the possibility of obtaining drinking water in almost any part of the Nizhnekamskaya industrial zone. In watershed areas, it is optimal to install well filters at the level of aquifers in the Lower Kazakhstan substage (depths are 130-180 m). This is confirmed by the constancy in time (several decades) of the composition and favorable quality of drinking underground water from production wells in most of the settlements around the Nizhnekamskaya industrial zone, as well as the high quality of underground water within zone.

5. References

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