www.czasopisma.pan.pl PAN www.journals.pan.pl

JOURNAL OF WATER AND LAND DEVELOPMENT
e-ISSN 2083-4535

Polish Academy of Sciences (PAN) Institute of Technology and Life Sciences – National Research Institute (ITP – PIB)

JOURNAL OF WATER AND LAND DEVELOPMENT
DOI: 10.24425/jwld.2021.139941
2022, No. 52 (I–III): 34–43

Assessment of groundwater potability for the population: Geochemical evaluation of aquifers in the city of Krasnodar

Abdugani Azimov[1) ✉], Larisa Nekrasova[2)], Dmitry Gura[3), 4)]

[1)] M. Auezov South Kazakhstan University, Research Laboratory: Adsorption and Filtration Purification of Gases and Liquids, 5 Tauke khan Avenue, 160012 Shymkent, Kazakhstan

[2)] Federal State Budgetary Institution "Centre for Strategic Planning and Management of Biomedical Health Risks" of the Federal Medical and Biological Agency, Moscow, Russia

[3)] Kuban State Technological University, Department of Cadastre and Geoengineering, Kuban, Russia

[4)] Kuban State Agrarian University, Department of Geodesy, Kuban, Russia

RECEIVED 17.02.2021 REVIEWED 12.03.2021 ACCEPTED 15.03.2021

Abstract: This work aimed to evaluate groundwater potability for the population through geochemical assessment methods on the example of aquifers in Krasnodar city. In 2016 and 2019, on the territory of Krasnodar city (Krasnodar region, Russian Federation), a detailed geochemical analysis of groundwater quality was performed based on a total of 6000 samples, 3000 samples per each year. Samples were taken from 30 wells located at depths of up to 450 m in the layers of Anthropogen and Neogene stages. Quantitative analysis of wells according to the average water quality parameters showed that in 15 wells, the water condition met the *MAC* (maximum allowable concentration) standards in all layers. Water abundance between the layers of the Quaternary and Cimmerian stages is seven times as different ($p \leq 0.001$) towards the latter, the hardness between the same horizons is ten times as different ($p \leq 0.001$) towards the Quaternary stage and three times as different ($p \leq 0.05$) in terms of solid residue. Thus, the water hardness and water abundance index vary significantly between the vertical layers. A strong positive correlation between the solid residue and the hardness values (Pearson correlation 0.93, $p \leq 0.05$), and a negative correlation between water abundance and solid residue values (Pearson correlation –0.83, $p \leq 0.05$), as well as between the hardness and water abundance values (Pearson correlation –0.81, $p \leq 0.05$) was recorded. These findings can be used for regions with similar deposits of rocks and aquifers.

Keywords: aquifers, drinking water, geochemical analysis, heavy metals content, Krasnodar, morbidity stage, wells

INTRODUCTION

One of the most relevant problems of the 21st century is the lack of potable water [Rapant *et al.* 2015]. As the world's population grows, the use of surface water of lakes and rivers is increasing [Skevas 2020]. Intensification of agriculture involves the increasing use of various insecticides and herbicides that enter surface water and render it unsuitable for drinking and the irrigation of plant crops. In industrial areas, water pollution with heavy metals prevails, and in megacities, household wastes dominate among the factors affecting drinking water quality [Lekomtsev *et al.* 2020].

The human right to use quality potable water was recognized in 2010 at the United Nations General Assembly. Every second person in the world population uses tap water, which contain elevated and dangerous to human health concentrations of heavy metals, organic compounds, and pathogenic microorganisms [Silva, da Rocha 2020].

Relating to those mentioned above, special attention is paid to groundwater resources development, which are not as vulnerable to contamination as surface water if deposited deep enough [Rapant *et al.* 2017]. The health of the population depends largely on the quality of the water they drink since it is the main environment and a reagent of vital metabolic processes in the human body like digestion, respiration. Besides, water is the main component of the human body, counting for 55–60% of the body weight [KOCINA 1997]. The aquatic environment is perfectly suitable for electrolytic dissociation reactions and dispersion of colloidal solutions. The deviations in water quality from generally accepted standards lead to the development of endemic diseases among the population [NEGI *et al.* 2020]. Thus, fluorine deficiency promotes the incidence of caries in up to 70% of cases registered during visits to the dentist, whereas overabundance of fluorine incites fluorosis cases. Exceed in water hardness values over the standards can be the main factor inducing mass cases of kidney stone disease in the population. Hypothyroidism has been reported in cases of low iodine concentration. The presence of pathogens and parasites inciting various diseases is also important [BINDAL *et al.* 2020; BINDAL, SINGH 2019; RÉVÉSZ *et al.* 2010].

Recently, cases of technogenic disasters have become more frequent due to waste and industrial water emissions. Afterward, these waters penetrate aquifers underground [ELUMALAI *et al.* 2019; RENOCK *et al.* 2016]. Consumption of such waters has both short-term (poisoning) and long-term negative effects (increased digestive diseases, increased cancer-related mortality) [NGUYEN *et al.* 2011; OREM *et al.* 2017]. When wastewater is discharged into aquifers, hazardous carcinogens such as formaldehyde are released [BELITZ *et al.* 2016; MOLOFSKY *et al.* 2013]. Also, sulphates, oil products, nitrates, and nitrites are penetrating groundwaters as well. The result of such effluent is a qualitative change in groundwater properties for the worse, primarily in terms of hardness, mineralisation, and sulphate concentration.

For the Russian Federation, as in many other countries of the world, the shortage of groundwater resources is increasing. Thus, in 2012, 29.53 mln m^3 of groundwater was used, and in 2011 this volume decreased to 29 mln m^3 [TORKUNOV *et al.* 2013]. Therefore, against the background of groundwater deficit and deteriorating quality, performing a geochemical analysis for assessing the suitability for household and agricultural needs is of high relevance. Of particular significance are studies devoted to considering this problem within individual territories and model regions [BOGAS, GOMES 2015; KOZAR *et al.* 2017; ROSBORG 2015]. This is due to the difficulties in forecasting the prevailing trends in groundwater quality for a large territory as the situation may be precisely the opposite in different regions. Simultaneously, the results of data analysis on groundwater conditions in the model region can be used for areas with similar geological, climatic, and hydrological characteristics.

As a model region, this paper proposes the city of Krasnodar (Krasnodar Region, Russian Federation) with a population of about 1 mln people. The main river flowing through the city is the Kuban River, which is 870 km long. The hydrological regime of the River Kuban was characterised by a high amplitude of seasonal flood fluctuations up to 5 m before the construction of the Krasnodar reservoir, which regulated the flow of the river. At the same time, Krasnodar city demonstrates quite an increased level of pollution by road transport, oil refining enterprises, and other industrial facilities, even compared to other regions of Russia. By the number of cars per 1 people, Krasnodar city outnumbers other Russian cities, including Moscow. However, other data suggest that Krasnodar city is, on the contrary, one of the cities with a low level of pollution.

Thus, the proposed model region (Krasnodar city) involves a high number of wells and characterises by a high level of pollution at the same time, mainly due to vehicles and mineral oil refineries.

The authors assume that depending on the depth of the occurrence, aquifers will show different degrees of contamination by different cations and anions and different degrees of water hardness.

This work aimed to perform a comparative geochemical analysis of aquifers in terms of groundwater suitability for the use of the community.

The objectives of this work were:
– to perform geochemical characterisation of aquifers in terms of water hardness and mineralisation;
– to assess the dynamics of changes in water chemical composition over the period 2016, 2019 through the selected sampling points.

MATERIALS AND METHODS

RESEARCH REGION

Underground waters in the Krasnodar Region are extracted from 38 known deposits, from 200 to 500 m deep [DEMCHENKO *et al.* 2018]. Groundwater in the city is distributed unevenly, resulting in problems with potable water only in particular areas. The role of underground water for the population of Krasnodar city is undeniable as it accounts for 99% of all water supply. The total number of water intakes in Krasnodar is 12, and the number of artesian wells is 440 [NAGALEVSKY *et al.* 2010].

A full examination of the qualitative groundwater features requires the provision of the rock layers characteristics (depth) corresponding to different geological epochs. Within the city of Krasnodar, wells from which groundwater is extracted pass through five such rock layers covering the period from today (anthropogenic, up to 2.58 mln years) to Neogene (more than 2.58 mln years) – Table 1.

The degrees of anthropogenic load in aquifers of different stages vary depending on the depth of occurrence. Thus, the layer of the Anthropogen is most affected because here, surface water flows from the Kuban River, and groundwater flows from the underlying aquifers. Infiltration of waters of the second stage, the

Table 1. Aquifers and their depth on the territory of Krasnodar city

Name of the aquifer	Depth (m)
Quaternary stage sediments (Anthropogenic)	10–50
Apsheronian (Apsheron) stage[1)] (Calabrian)[2)]	50–60
Akchagylian (Akchagyl) stage[1)] (Gelasian and Piacenzian)[2)]	200–210
Kuyalnician stage[1)] (upper Pleistocene)[2)]	300–400
Cimmerian stage[1)] (Neogene)[2)]	400–420

[1)] Regional scale [SVITOCH 2016].
[2)] Names of stages in brackets are given according to the International Stratigraphic Classification [MURPHY, SALVADOR 1999].
Source: own elaboration.

Apsheron, occurs due to the inflow of surface water and precipitation in those places, where the corresponding rocks come to the surface. This stage is represented by clays and comes to the surface in the Caucasian Mountains foothills region. In terms of water supply, the Akchagyl stage layer is similar to the Apsheron. As to the Kuyalnician stage, water is supplied both from the surface, in the places where rocks come out in the foothills of the Caucasian Mountains, and from aquifers characterised by high water pressure. In the deepest stage, the Cimmerian, water also comes as from the surface so and from other horizons. Admixtures of hydrogen sulphide and ammonia mark the waters of this stage.

SAMPLING

The research was conducted in 2016, 2019 in Krasnodar city. Ten sampling locations were selected (Fig. 1), each with three wells. The total number of surveyed wells, thus, was 30.

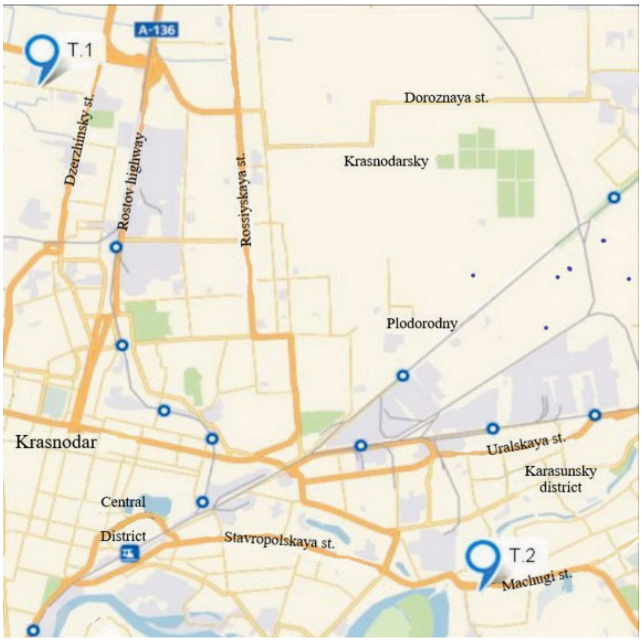

Fig. 1. Sampling points in Krasnodar city; source: own elaboration

Sampling was carried out in June–July 2016 (3 samples, ten samples per well) and June–July 2019 (also ten samples per well). Of each ten samples, two samples were taken in each of the five aquifers. Then they were combined into three groups according to the depth's parameters, namely, 10–50 m, 51–400 m, and 401–420 m. Thus, the spectrum of samples was obtained from depths of 10–420 m. The total number of samples was 6.

RESEARCH METHODS

Each sample was taken in the amount of 1 dm^3. The containers made of polymeric material intended for contact with foodstuffs are rinsed at least three times with water to be analysed and filled up to the top. The items shall be analysed not later than 5 h after the sampling, as a rule, the time did not exceed 1–2 h. Each sample was provided with a label that contained the following information: the name of the sample (well number, depth from which the sample was taken), place of sampling, date and time of sampling, additional information (if necessary). This method meets the requirements of the sampling standard developed by the Federal State Budgetary Institution "Hydrochemical Institute" [Minprirody Rossii 2012]. Samples were tested for compliance with drinking water standards. Drinking water intended for human consumption (drinking water) is defined as water whose composition according to organoleptic, physicochemical, microbiological, parasitic. Radiation indicators meet requirements of state standards and sanitary legislation designed to meet the physiological, sanitary, and hygienic, domestic, and economic needs of the population and the production of products that need to use drinking water.

Drinking water should meet certain hygiene requirements, including the organoleptic quality of the water, its optimum hardness, and chemical composition. The analysis for pathogenic microorganisms is of high importance as well.

Hygienic assessment of safety and quality of drinking water is carried out based on the indicators of epidemic safety (microbiological, parasitic), sanitary and chemical (organoleptic), physicochemical, sanitary toxicological, and radiation indicators. Thus, if at least one of the parameters under consideration had deviations, the sample was considered unsuitable. The norms of water suitability for use and the values of maximum allowable concentrations (*MAC*) of cations, anions, and other water parameters (level of hardness, mineralisation) were taken from the mentioned standards [Postanovleniye ... 2021].

Standard methods for measuring potential salinity and determining sodium and magnesium adsorption coefficients, water permeability index, the content of trace elements, and cationic/anionic composition were used. Water quality (hardness parameter) was measured with the EC-308 Water Quality Monitor, and the presence of alkali metal cations and salts in water were measured with the TDS-meter. TDS-meter is designed to measure water salinity, i.e., a total amount of Total Dissolved Solids (TDS) impurities dissolved in water per one million water particles (parts per million). Salinity measurement range of TDS-meter: 0–199.9 ppt, accuracy: ±2% of full scale, automatic temperature compensation (ATC): from 0 to 60°C.

The content of arsenic, cadmium, anion nitrate, and other chemical elements was determined using atomic spectrometry. The method of atomic emission spectrometry with inductively coupled plasma allows determining the content of aluminum, barium, beryllium, boron, vanadium, bismuth, tungsten, iron, cadmium, potassium, calcium, cobalt, silicon, lithium, magnesium, manganese, copper, molybdenum, arsenic, sodium, nickel, tin, lead, selenium, silver, strontium, antimony, tellurium, titanium, chrome, and zinc. The method is based on measuring the radiation absorption of the resonant wavelength by the atomic steam of a defined element formed due to electrothermal atomisation of the analysed sample in the graphite furnace of the spectrometer.

Phenols were determined using the photometric method. The photometric method for determining the mass concentration of volatile phenols is based on phenols distillation from an acidic water sample, interaction of phenols in the distillation with 4-aminoantipirin in the presence of potassium hexacyanoferrate (III), and extraction of the formed coloured compound by chloroform. The optical density of the extract shall be measured on a spectrophotometer (λ = 470 nm) or photometer with a light filter having maximum transmittance in the range of λ = 460–490 nm. Range of measured concentrations: 2.0–30.0 μg·dm^{-3}. Method error at P = 0.95 (±δ, in %): 16–50%.

Potassium and magnesium adsorption was determined by the complexometric method. The method is based on the formation of complex trilon B compounds with ions of alkaline earth elements. The determination is performed by titration of the sample by trilon B solution at pH = 10 in the presence of the indicator. The lowest determinable water hardness was 0.1°J. Trilon B was dried at 80°C for 2 h, measured the amount of 9.31 g, placed in a measuring flask with a capacity of 1 dm^3, dissolved in a warm 40–60°C bidistilled water, and brought to the mark of bidistilled water after cooling the solution to room temperature. The correction factor to the trilon B solution concentration, prepared from the canopy, is set on a magnesium sulphate solution. The solution from GSO composition of trilon B or standard titer (fixation) of trilon B is prepared following the instructions for use, diluting it to the required concentration. The analysis of samples for full anionic and cationic composition was carried out in the Test Center for Potable Water and Wastewater "Rosvodokanal Krasnodar" (Krasnodar Vodokanal LLC).

Besides, the incidence rate of the digestive system diseases and oncology were compared with the sampling site. It assumes that residents of Krasnodar city districts that are adjacent to highly contaminated wells (with heavy metals) might have a higher incidence of the gastrointestinal tract diseases, such as gastritis or poisoning with heavy metals, and oncology compared to residents of those districts, where water quality meets sanitary standards. For this purpose, statistical data from three city primary health-care facilities (hospitals) were used. The prevalence of the digestive system diseases and oncology was expressed in % of the total number of residents compared to the level of contamination. The final correlation coefficient between these parameters was calculated.

The data obtained were recorded in the Microsoft Excel 2013 database. The statistical processing of the data was performed through the Statistica v. 7.0 program. For the analysis, the arithmetic mean number and the mean error were calculated for each of the parameters. The significance of differences between features was proved through the t-test for independent samples. The minimum acceptable level of significance was $p \leq 0.05$. To reveal the similarity between aquifers by parameters of solid residue, hardness, and water content, cluster analysis (Ward method) was performed. Pearson's correlations between these parameters were also calculated.

RESULTS AND DISCUSSION

Based on the results of determining the level of water hardness, solid residue, and water abundance indicator, a significant difference between aquifers was established (Fig. 2). Comparing the results by water parameters from samples from different aquifers is possible as the samples were taken at different depths and in different wells.

Thus, the water abundance between the layers of the Quaternary and Cimmerian stages is seven times as different ($p \leq 0.001$) towards the latter, the hardness between the same horizons is ten times as different ($p \leq 0.001$) towards the Quaternary stage and three times as different ($p \leq 0.05$) in terms of solid residue. Thus, the water hardness and water abundance index vary mostly between the vertical layers.

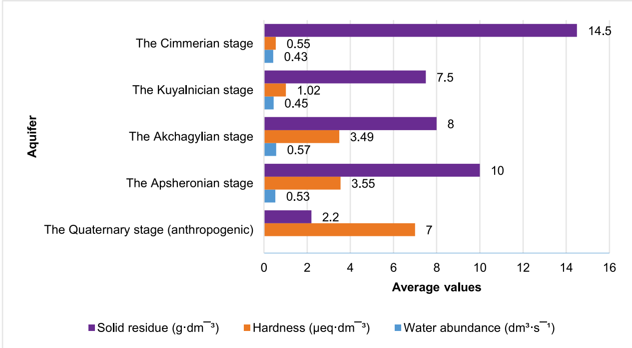

Fig. 2. Average values of water abundance, hardness, and a solid residue of water from wells depending on the depth; source: own study

A strong positive correlation between the solid residue and the hardness values (Pearson correlation 0.93, $p \leq 0.05$), and a negative correlation between water abundance and solid residue values (Pearson correlation –0.83, $p \leq 0.05$), as well as between the hardness and water abundance values (Pearson correlation –0.81, $p \leq 0.05$) was recorded. Thus, the deeper the aquifer is, the lower the hardness and solid residue parameters and the bigger the water abundance parameters. This pattern naturally extends to certain depths and can vary essentially from region to region. Due to the higher water abundance of lower horizons, vertical water migration to upper layers is possible.

The cluster analysis results show that all five stages can be divided into three clusters (Fig. 3).

The first cluster includes one stage, the Quaternary, which differs significantly from all other indicators. The second cluster includes three stages – the Apsheronian, the Akchagylian, and

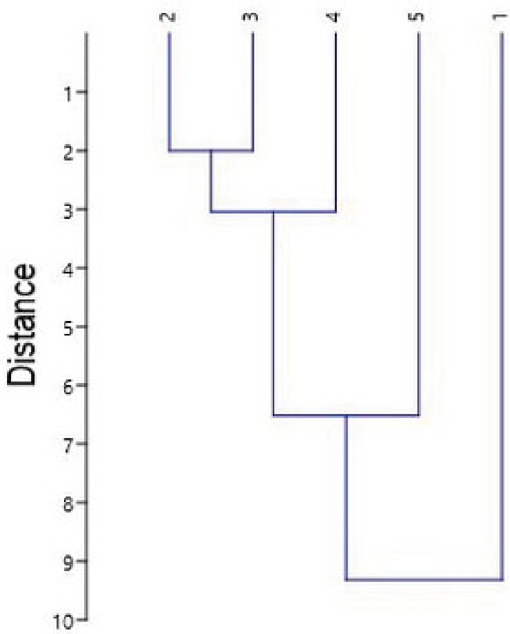

Fig. 3. Results of cluster analysis based on the principle of similarity between five aquifers: 1 = the Quaternary (anthropogenic) stage, 2 = the Apsheronian stage, 3 = the Akchagylian stage, 4 = Kuyalnician stage, 5 = the Cimmerian stage; source: own study

Kuyalnician, similar to hardness, solid residue, and water abundance parameters (Fig. 3). Finally, the third cluster includes one stage, the Cimmerian, which demonstrates the minimum values of hardness and solid residue and maximum water abundance. Such grouping into clusters coincides with the method adopted for sampling and their subsequent assemblage by three depth marks for each well.

When comparing the average values of the studied parameters of potable water quality in wells in Krasnodar city, the water quality was established to meet generally accepted sanitary standards (Tab. 2).

Groundwater in water depths starting from 50 m is fully compliant with sanitary and *MAC* standards set by SanPiN Regulations [Postanovleniye ... 2021]. Over three years, no

Table 2. Average values of surveyed water quality parameters in wells of Krasnodar city in 2016 and 2019

Parameter	*MAC* values according to SanPiN [Postanovleniye ... 2021]	2016[1)]	2019[1)]
Odour qualities, on a scale	≤2	0	0
Gustatory qualities, on a scale	≤2	0	0
Average temperature (°C)	–	14.6	16.1
Colour, gradient	≤20	0	< 5.0
Turbidity (mg·dm^{-3})	1.5≤2.0)	<0.53	<0.55
Value of pH	6–9	7.94	8.01
Solid residue (mg·dm^{-3})	≤1000	430	400
Total hardness (mmol·dm^{-3})	7–10	2.7	2.8
Alkalinity (mmol·dm^{-3})	–	4.7	5.2
Oxidation (mg·dm^{-3}) (hereinafter)	≤5.0	0.9	1.5
Contents of oil products	<0.1	<0.07	<0.07
Phenol content	<0.25	<0.01	<0.01
Ammonia concentration	≤2.0	0.37	0.56
Iron concentration	≤0.3	<0.17	<0.18
Cadmium concentration	≤1.0	<0.003	<0.002
Potassium concentration	–	<0.6	0.7
Calcium concentration	–	39.1	38.4
Magnesium concentration	–	9.9	8.5
Manganese concentration	0.1–0.3	0.06	0.07
Copper concentration	<1.0	<0.03	<0.02
Molybdenum concentration	<0.25	<0.0005	–
Arsenic concentration	≤0.05	0.009	0.008
Sodium concentration	≤200	87.9	89.9
Concentration of nitrate anions	<45	<15.0	<17.0
Concentration of nitrite anions	≤3.0	<0.07	<0.09
Concentration of phosphate anions	≤3.5	0.67	0.76
Lead concentration	<0.03	<0.002	<0.003
Silicon concentration	≤10.0	6.7	7.9
Strontium concentration	<7.0	0.90	0.87
Concentration of sulphate anion	<500	147	129
Fluorine concentration	≤1.2	0.39	0.33
Chlorine concentration	<350	29	31
Chromium concentration	≤0.05	<0.01	–
Zinc concentration	≤5.0	<0.1	<0.1
Hydrogen sulphide concentration	≤0.03	–	–

[1)] Average values for all 30 wells surveyed in 2016 and 2019 at a sampling depth of 50 m.
Explanation: *MAC* = maximum allowable concentration. Parameters from "Content of oil products" to "Hydrogen sulphide concentration" are expressed in mg·dm^{-3}.
Source: own study.

significant changes in cation and anion concentrations, hardness, pH values, and other parameters were recorded.

However, when comparing water quality parameters from samples taken at different depths and in different aquifers, the results significantly differed (Tab. 3). As an example, the data on three depths of aquifers corresponding to cluster analysis results, namely, of the Quaternary, the Apsheronian, and the Cimmerian stages, are given.

Significant differences between the layers of the Quaternary stage on the one hand and the Apsheronian and the Kuyalnician

Table 3. Average parameters of water quality and cationic-anionic composition depending on depth (stage)

Parameter	*MAC* values according to SanPiN [Postanovleniye ... 2021]	Quaternary stage (Anthropogenic)	Apsheronian stage (Apsheron)	Kuyalnician stage (upper Pleistocene)
Odour qualities, on a scale	≤2	2	1.0	1.0
Gustatory qualities, on a scale	≤2	2	1.0	1.0
Average temperature (°C)[1)]	–	14.6	12.4	34.7
Colour, gradient	≤20	15.0	3.0	2.0
Turbidity ($mg \cdot dm^{-3}$)[1)]	1.5 (≤2.0)	2.1	0.3	0.2
Value of pH	6–9	7.94	8.01	8.90
Solid residue ($mg \cdot dm^{-3}$)[1)]	≤1000	430	400	200
Total hardness ($mmol \cdot dm^{-3}$)[1)]	7–10	11.7	5.8	0.7
Alkalinity ($mmol \cdot dm^{-3}$)[1]	–	4.7	6.6	5.9
Oxidation ($mmol \cdot dm^{-3}$) (hereinafter)[1)]	≤5.0	6.9	0.9	0.6
Contents of oil products[2)]	<0.1	0.7	0.01	no
Phenol content[2)]	<0.25	0.23	0.05	0.01
Ammonia concentration[1)]	≤2.0	0.78	0.36	2.1
Iron concentration[1)]	≤0.3	0.45	0.20	0.25
Cadmium concentration[2)]	≤1.0	0.9	0.002	0.002
Potassium concentration	–	0.7	0.5	0.6
Calcium concentration	–	40.1	39.4	45.8
Magnesium concentration	–	9.7	9.5	9.6
Manganese concentration	0.1–0.3	0.09	0.07	0.08
Copper concentration[1)]	<1.0	0.4	0.07	0.08
Molybdenum concentration[2)]	<0.25	0.15	0.07	no
Arsenic concentration[2)]	≤0.05	0.07	0.009	no
Sodium concentration[1)]	≤200	209	79	75
Concentration of nitrate anions[2)]	<45	55.0	15.0	1.0
Concentration of nitrite anions[2)]	≤3.0	2.9	0.07	0.05
Concentration of phosphate anions[1)]	≤3.5	1.9	0.7	0.5
Lead concentration[2)]	<0.03	0.09	0.009	0.00004
Silicon concentration	≤10.0	6.7	7.9	5.5
Strontium concentration	<7.0	1.1	0.8	0.6
Concentration of sulphate anion[1)]	<500	447	429	113
Fluorine concentration	≤1.2	0.41	0.36	0.31
Chlorine concentration[2)]	<350	340	50	10
Chromium concentration[1)]	≤0.05	0.04	0.002	0.001
Zinc concentration[2)]	≤5	1.0	0.1	0.0001
Hydrogen sulphide concentration[1)]	≤0.03	0.03	0.001	0.02

[1)] The differences are reliable between the level of *MAC*, the value of the parameter in the Quaternary, the Apsheronian, and the Kuyalnician stages ($p \leq 0.05$).
[2)] The same, $p \leq 0.001$.
Explanation: *MAC* = maximum allowable concentration.
Source: own study.

stages, on the other hand, were noticed between almost all parameters. The exceptions were the concentrations of silicon, strontium, magnesium, calcium, potassium, and the pH value. The largest differences ($p \leq 0.001$) were recorded for chlorine, zinc, lead, nitrite and nitrate anion, arsenic, molybdenum, cadmium, phenols, and oil products. At the same time, oil products, phenols, molybdenum, cadmium, zinc, chlorine, arsenic, nitrates, and nitrites are supplied from the surface to the layer Quaternary stage. Later, they are infiltrated into the underlying aquifers. In the waters of the Cimmerian stage, ammonia and hydrogen sulphide are present in high concentrations. However, they do not exceed the *MAC* values, although their drinking attractiveness is lower than that in the waters of the Apsheronian stage.

Groundwater located at depths of up to 50 m does not meet the *MAC* standards set by SanPiN regulations and is not suitable not only for drinking but also for agricultural purposes [Postanovleniye … 2021]. Starting from the depths above 50 m (i.e., from the Apsheronian stage), the water is considered potable for the population and usable for agricultural needs.

Quantitative analysis of wells according to the average water quality parameters showed that in 15 wells, the water condition met the *MAC* standards in all layers. In 12 wells, calcium, sodium, and magnesium content outnumbered the *MAC* values by one-third. For three wells, an increased concentration of mercury (2.2 times above the *MAC*) and lead (3.5 times) was found.

The obtained results were compared with the register of the cardiovascular system diseases and oncology cases in the corresponding city districts, and a positive correlation (0.85) was established between the incidence rates and the level of phenols, lead, and other pollutants. Thus, the location of the well and the poor quality of water in it can determine an increased number of cardiovascular and oncological disorders. However, this area requires further detailed research efforts.

The results obtained demonstrate significant variability of water hardness indicators, concentration of mineral and other compounds (including pollutants) depending on the depth of the aquifer. It was established that pollutants cannot penetrate significant depths, which determines the greater value of groundwater compared to subsurface or surface waters. The results obtained in this research can be used for alike studies both in regions with similar bedrock and different geological structures. Geological horizons of different eras (Mesozoic, Paleozoic, etc.) might have different indicators of both water hardness and mineral content, whereas also indicators of water migration between horizons may vary. Accordingly, these horizons will be differently permeable for pollutants. It would be interesting to perform similar studies in other regions and compare them with the results of this work.

The supply of the population with quality freshwater is one of the most relevant tasks in modern society [Yan *et al.* 2017]. The situation with water resources, including groundwater resources, may vary significantly from country to country. Thus, European countries use 2–5 m^3 of water per inhabitant, Germany, and Sweden – 2.5, France – about 3.5, and in Great Britain, water consumption per capita amounts to 5 m^3. For Ukraine, this indicator is minimal and accounts for only 1 m^3 per inhabitant [Arendal 2002].

The Russian Federation is one of the countries with quite splendid reserves of freshwater, including groundwater. Water consumption per inhabitant is 5.9 m^3 (data for the European part). Such plentiful water resources imply the need for monitoring to ensure that it meets established quality standards [Postanovleniye ... 2021].

Water pollution is one of the most important factors affecting human health, and, at the same time, human activity is a major factor contributing to the deterioration of water. The pollution can be related to natural and anthropogenic factors. In the case of natural pollution, water is treated through cleansing mechanisms, and for the case of anthropogenic pollution, these processes cannot cope with the increasing pressure on water bodies. Increased contamination (>10 *MAC*s) and extremely high pollution (>100 *MAC*s) account for a growing share of groundwater pollution cases noted worldwide [EPA 2014; Heisig, Scott 2013].

The study revealed that the upper layer of rocks corresponding to the Anthropogenic stage is the most affected by human activity. The chemical composition of water depends largely on the composition of rocks in which it is located [Brady *et al.* 1998]. Therefore, pollutants enter the water by accumulating in the upper layers [Harkness *et al.* 2017]. The migration of pollutants to aquifers below 50 m is difficult, so groundwater from this depth is suitable for human consumption and agricultural use. The hardness of water and solid residue also decreases with depth.

It is known from literature data that in most cases, groundwater that recharges springs at the surface in water depths up to 10 m [Haase *et al.* 2019]. Based on the unsuitability of groundwater from this depth in Krasnodar city for drinking and agricultural needs, water from springs is not suitable for use by the population as well.

Some pollutants, such as nitrates and nitrites, are characterised by seasonal variations in concentration. The minimum concentration of nitrates is observed in summer, and the maximum – in April and October [Domagalski, Johnson 2011]. Such changes in the content of nitrates and other pollutants are primarily due to industrial contamination and agricultural and household pollution. Among the indicators affecting human health are salinity, hardness, oxidation, the concentration of nitrates, sulphates, chlorides, strontium, cadmium, mercury, and lead [Cravotta *et al.* 2017].

In the case of low mineralisation of water, namely, up to 50 $mg \cdot dm^{-3}$, stomach function disorders and imbalance of water and salt metabolism might develop. The hardness is considered acceptable on the level of up to 7 $\mu eq \cdot dm^{-3}$, and its increased values might cause a general disruption of the digestive system and disorders of water and salt balance in the body. At an increase of the oxidation parameter, the spectrum of disorders in organisms enlarges to kidney nephrosis, irreversible liver changes, decreased reproductive function, and malfunctioning of nervous and immune systems. If permanganate oxidation indices are higher than 5 $mg \cdot dm^{-3}$, boiling is required. Phenols and their derivatives in groundwater may form chlorophenol compounds at the chlorination of water. Phenols are considered even in small concentrations in water (0.25 $mg \cdot dm^{-3}$). The values close to *MAC* standards were obtained when analysing the Quaternary ground waters adjacent to the surface [Cozzarelli *et al.* 2017].

The increased concentration of lead causes damage to the circulatory and cardiovascular systems, cadmium, and chromium incite nephrosis of the kidneys, copper affects the gastrointestinal tract, mercury promotes the deterioration of the nervous system blood vessels, and zinc harms the work of the muscles. All these substances were found in the underground waters of the anthropogenic layer adjacent to the surface. Moreover, the indicators of water quality from this layer do not meet Sanitary Regulations and the requirements of the World Health Organization [WHO 2007]. Therefore, in regions with a high level of pollution, the groundwater from depths up to 50 m is not recommended for drinking and agricultural needs.

CONCLUSIONS

The established patterns can be used as recommendations for extracting water from aquifers of different depths. First of all, it concerns regions with similar geological structure. It has been found that subsurface waters up to 50 m do not meet the maximum allowable concentration (*MAC*) standards for a number of indicators, and, thus, cannot be recommended as safe for drinking or appropriate even for agricultural purposes. Such waters are suitable only for technical use, requiring some treatment measures. Undoubtedly, it would be interesting for both engineers and geochemists to perform similar studies in other regions. It seems possible to conduct a series of studies in cities with different populations, different industrial structures, as well as the different occurrence of aquifers. The results obtained could be combined into a common database of patterns for a better understanding of how deep pollutants can penetrate and from what depth water can be extracted for the drinking needs of the population, as well as for agricultural activities.

The study performed allowed establishing the vertical distribution of toxic wastes (lead, nitrate, cadmium, zinc, and nitrite anions) depending on the depth of the aquifer. Thus, at depths up to 50 m, the concentration of most pollutants exceeds the *MAC* values by 5–10 times, which accounts for a high level of contamination. Such data were recorded for lead, phenols, chlorine, zinc, nitrite and anion nitrate, arsenic, molybdenum, and cadmium. All these compounds are highly hazardous to the health of the population. For water quality indicators, such as hardness and solid residue, a negative correlation (–0.84) between their values and depth of the layer was obtained.

Thus, the value of hardness and solid residue decreases with depth. In terms of a difference in hardness values, the layer of the Cimmerian stage outnumbers seven times ($p \leq 0.001$), and that of the Quaternary stage exceeds ten times ($p \leq 0.001$). For solid residue values, a difference of three times ($p \leq 0.05$) towards of the Quaternary stage aquifer is stated. Maximum variability between the vertical stages is noted for the hardness and water abundance.

A strong positive correlation between the solid residue and the hardness values (0.93, $p \leq 0.05$) was established. On the contrary, a negative correlation emerged between water abundance and the solid residue values (–0.83, $p \leq 0.05$) and between hardness and water abundance (–0.81, $p \leq 0.05$). It assumes that the deeper the aquifer is, the lower the hardness and solid residue values in groundwater samples and the greater the water abundance. This pattern extends to particular depths and may vary significantly from region to region. The higher water abundance of the lower horizons contributes to vertical water migration to the upper layers. Migration of water from the lower layers to the upper ones disables the pollutants from moving in the opposite direction and maintains water quality and quantity parameters.

ACKNOWLEDGEMENTS

The research was carried out using the equipment of the Research Center for Food and Chemical Technologies of KubSTU (CKP_3111) which development is supported by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2021-679).

REFERENCES

Arendal U.G. 2002. A world of salt: Total global saltwater and freshwater estimates [online]. Vital Water Graphics. [Access 25.11.2021]. Available at: https://www.grida.no/resources/5808

Belitz K., Jurgens B.C., Johnson T.D. 2016. Potential corrosivity of untreated groundwater in the United States (No. 2016-5092). Scientific Investigations Report 2016-5092. US Geological Survey pp. 16. DOI 10.3133/sir20165092.

Bindal S., Kumar A., Mallick J., Shashtri S., Kumar P., Singh C.K. 2020. Geochemical, topographical, and meteorological controls on groundwater arsenic contamination in Sharda River Basin of Uttar Pradesh, India. Journal of Climate Change. Vol. 6. Iss. 2 p. 71–87. DOI 10.3233/JCC200013.

Bindal S., Singh C.K. 2019. Predicting groundwater arsenic contamination: Regions at risk in highest populated state of India. Water Research. Vol. 159 p. 65–76. DOI 10.1016/j.watres.2019.04.054.

Bogas J.A., Gomes A. 2015. Non-steady-state accelerated chloride penetration resistance of structural lightweight aggregate concrete. Cement and Concrete Composites. Vol. 60 p. 111–122. DOI 10.1016/j.cemconcomp.2015.04.001.

Brady K.B.C., Kania T., Smith M.W., Hornberger R.J. 1998. Coal mine drainage prediction and pollution prevention in Pennsylvania. Pennsylvania Department of Environmental Protection. [Access 25.11.2021]. Available at: https://wvmdtaskforce.files.wordpress.com/2016/01/00-pbrady.pdf

Cozzarelli I.M., Skalak K.J., Kent D.B., Engle M.A., Benthem A., Mumford A.C., ..., Jolly G.D. 2017. Environmental signatures and effects of an oil and gas wastewater spill in the Williston Basin, North Dakota. Science of the Total Environment. Vol. 579 p. 1781–1793. DOI 10.1016/j.scitotenv.2016.11.157.

Cravotta C.A., Sherrod L., Galeone D.G., Lehman W.G., Ackman T.E., Kramer A. 2017. Hydrological and geophysical investigation of streamflow losses and restoration strategies in an abandoned mine lands setting. Environmental and Engineering Geoscience. Vol. 23. Iss. 4 p. 243–273. DOI 10.2113/gseegeosci.23.4.243.

Demchenko O.P., Larionova L.V., Sklyarenko O.B. 2018. Sanitarno-gigiyenicheskiye problemy vodnykh resursov krasnodarskogo kraya i g. Krasnodara. V: Ekologiya Rechnykh Landshaftov [Sanitary and hygienic issues of water resources in Krasnodar Krai and the city of Krasnodar. In: Ecology of river landscapes]. Ed. N.N. Mamas. Krasnodar. KubGAU p. 52–60.

Domagalski J.L., Johnson H.M. 2011. Subsurface transport of orthophosphate in five agricultural watersheds, USA. Journal of Hydrology. Vol. 409. Iss. 1–2 p. 157–171. DOI 10.1016/j.jhydrol.2011.08.014.

Elumalai V, Nwabisa D.P., Rajmohan N. 2019. Evaluation of high fluoride contaminated fractured rock aquifer in South Africa – Geochemical and chemometric approaches. Chemosphere. Vol. 235 p. 1–11. DOI 10.1016/j.chemosphere.2019.06.065.

EPA 2014. Framework for human health risk assessment to inform decision making framework for human health risk assessment to inform decision making [online]. U.S. Environmental Protection Agency pp. 63. [Access 10.12.2020]. Available at: https://www.epa.gov/sites/production/files/2014-12/documents/hhra-framework-final-2014.pdf

Haase K.B., Kozar M.D., Mcadoo M.A., Casile G.C., Steffy L., Risser D.W. 2019. Dataset of trace dissolved hydrocarbons in surface water and groundwater in North Dakota, Pennsylvania, Virginia, and West Virginia between 2014 and 2017. Reston. U.S. Geological Survey. DOI 10.5066/P9RDPWXO.

Harkness J.S., Darrah T.H., Warner N.R., Whyte C.J., Moore M.T., Millot R., Kloppmann W., Jackson R.B., Vengosh A. 2017. The geochemistry of naturally occurring methane and saline groundwater in an area of unconventional shale gas development. Geochimica et Cosmochimica Acta. Vol. 208 p. 302–334. DOI 10.1016/j.gca.2017.03.039.

Heisig P.M., Scott T.M. 2013. Occurrence of methane in groundwater of south-central New York State, 2012-systematic evaluation of a glaciated region by hydrogeologic setting. Denver, Colorado. US Department of the Interior, US Geological Survey. ISSN 2328-0328 pp. 32.

Kocina P. 1997. Body composition of spinal cord injured adults. Sports Medicine. Vol. 23 p. 48–60. DOI 10.2165/00007256-199723010-00005.

Kozar M.D., McCoy K.J., Britton J.Q., Blake Jr. B.M. 2017. Hydrogeology, groundwater flow, and groundwater quality of an abandoned underground coal-mine aquifer, Elkhorn Area, West Virginia. Cheat Lake. West Virginia Geological and Economic Survey. ISSN 0363-1052 pp. 103.

Lekomtsev A.V., Iliushin P.Y., Korobov G.Y. 2020. Modeling and proving of design solutions for the reconstruction of treatment facility of oil and water [online]. Periódico Tchê Química. Vol. 17. Iss. 35 p. 269–282. [Access 25.11.2021]. Available at: http://www.deboni.he.com.br/arquivos_jornal/2020/35/24_LEKOMTSEV_pgs_269_281.pdf

Minprirody Rossii 2012. Rekomendatsii R 52.24.353-2012. Otbor prob poverkhnostnykh vod sushi i ochishchennykh stochnykh vod [Document R 52.24.353-2012. Sampling of surface water and purified waste water] [online]. Ministerstvo prirodnykh resursov i ekologii Rossiyskoy Federatsii. [Access 15.11.2021]. Available at: https://files.stroyinf.ru/Data2/1/4293792/4293792809.htm

Molofsky L.J., Connor J.A., Wylie A.S., Wagner T., Farhat S.K. 2013. Evaluation of methane sources in groundwater in northeastern Pennsylvania. Groundwater. Vol. 51. Iss. 3 p. 333–349. DOI 10.1111/gwat.12056.

Murphy M.A., Salvador A. 1999. International stratigraphic guide—an abridged version. Episodes. Vol. 22. Iss. 4 p. 255–272. [Access 10.12.2020]. Available at: https://www.idigbio.org/wiki/images/7/7f/255-271_Murphy_pdf

Nagalevsky Y.Y., Nagalevsky E.Y., Chuprina S.T. 2010. Meliorativno-vodokhozyaystvennyy kompleks basseyna reki Kubani [Reclamation and water management complex of the Kuban river basin]. Zashchita okruzhayushchey sredy v neftegazovom komplekse. Vol. 9 p. 78–84. [Access 25.11.2021]. Available at: https://www.elibrary.ru/item.asp?id=15236595

Negi P., Mor S., Ravindra K. 2020. Impact of landfill leachate on the groundwater quality in three cities of North India and health risk assessment. Environment, Development and Sustainability. Vol. 22 p. 1455–1474. DOI 10.1007/s10668-018-0257-1.

Nguyen C.K., Clark B.N., Stone K.R., Edwards M.A. 2011. Role of chloride, sulfate, and alkalinity on galvanic lead corrosion. Corrosion. Vol. 67. Iss. 6 p. 065005-1–065005-9. DOI 10.5006/1.3600449.

Orem W., Varonka M., Crosby L., Haase K., Loftin K., Hladik M., ..., Cozzarelli I. 2017. Organic geochemistry and toxicology of a stream impacted by unconventional oil and gas wastewater disposal operations. Applied Geochemistry. Vol. 80 p. 155–167. DOI 10.1016/j.apgeochem.2017.02.016.

Postanovleniye ot 28 yanvarya 2021 goda No. 2 Ob utverzhdenii sanitarnykh pravil i norm SanPiN 1.2.3685-21 "Gigiyenicheskiye normativy i trebovaniya k obespecheniyu bezopasnosti i (ili) bezvrednosti dlya cheloveka faktorov sredy obitaniya" [Regulation dated January 28, 2021 No. 2 On the approval of sanitary rules and norms SanPiN 1.2.3685-21 "Hygienic standards and requirements for ensuring the safety and (or) harmlessness of environmental factors for humans"]. Glavnyy gosudarstvennyy sanitarnyy vrach Rossiyskoy Federatsii. [Access 10.12.2020]. Available at: https://docs.cntd.ru/document/573500115?marker=6540IN

Rapant S., Cvečková V., Fajčíková K., Dietzová Z., Stehlíková B. 2017. Chemical composition of groundwater/drinking water and oncological disease mortality in Slovak Republic. Environmental Geochemistry and Health. Vol. 39. Iss. 1 p. 191–208. DOI 10.1007/s10653-016-9820-6.

Rapant S., Fajčíková K., Cvečková V., Ďurža A., Stehlíková B., Sedláková D., Ženišová Z. 2015. Chemical composition of groundwater and relative mortality for cardiovascular diseases in the Slovak Republic. Environmental Geochemistry and Health. Vol. 37. Iss. 4 p. 745–756. DOI 10.1007/s10653-015-9700-5.

Renock D., Landis J.D., Sharma M. 2016. Reductive weathering of black shale and release of barium during hydraulic fracturing. Applied Geochemistry. Vol. 65 p. 73–86. DOI 10.1016/j.apgeochem.2015.11.001.

Révész K.M., Breen K.J., Baldassare A.J., Burruss R.C. 2010. Carbon and hydrogen isotopic evidence for the origin of combustible gases in water-supply wells in north-central Pennsylvania. Applied Geochemistry. Vol. 25. Iss. 12 p. 1845–1859. DOI 10.1016/j.apgeochem.2010.09.011.

Rosborg I. 2015. Drinking water minerals and mineral balance importance, health significance, safety precautions. Switzerland. Springer. ISBN 978-3-030-18034-8 pp. 175.

Silva E.B., da Rocha J.R.C. 2020. Avaliação antrópica no litoral Paranaense através da determinação da concentração do íon fosfato em recursos hídricos [Anthropic evaluation in the Paraná coast through the ion phosphate concentration determination in water resources]. Periódico Tchê Química. Vol. 17. Iss. 35 p. 293–303. [Access 25.11.2021]. Available at: http://www.deboni.he.com.br/ccount/click.php?id=929

Skevas T. 2020. Evaluating alternative policies to reduce pesticide groundwater pollution in Dutch arable farming. Journal of Environmental Planning and Management. Vol. 63. Iss. 4 p. 733–750. DOI 10.1080/09640568.2019.1606618.

Svitoch A.A. 2016. Polozheniye v razrezakh Bol'shogo Kaspiya nizhnikh granits yarusov verkhnego pliotsena i kvartera Mezhdunarodnoy stratigraficheskoy shkaly i paleogeograficheskiye sobytiya [The position in the Greater Caspian Sea sections of the lower layers of the Upper Pliocene and the Quarternary of the International Stratigraphic Scale and Paleogeographical events] [online]. Byulleten' Moskovskogo obshchestva ispytateley prirody. Otdel geologicheskiy. Vol. 91 Iss. 2–3 p. 63–73. [Access 25.11.2021]. Available at: https://cyberleninka.ru/article/n/polozhenie-v-razrezah-bolshogo-kaspiya-nizhnih-granits-yarusov-verhnego-pliotsena-i-kvartera-mezhdunarodnoy-stratigraficheskoy-shkaly-i

TORKUNOV A.V., ORLOV A.A., CHECHEVISHNIKOV A.L., ALEKSEENKOVA A.S., BORISHPOLETS K.P., KRYLOV A. V., ..., CHERNIAVSKY S.I. 2013. Problema presnoy vody. Global'nyy kontekst politiki Rossii [The problem of fresh water. The global context of Russia's policy] [online]. Yezhegodnik Instituta mezhdunarodnykh issledovaniy Moskovskogo gosudarstvennogo instituta mezhdunarodnykh otnosheniy (Universiteta) Ministerstva inostrannykh del Rossiyskoy Federatsii. Vol. 1. Iss. 3 p. 8–65. [Access 10.12.2020]. Available at: https://www.elibrary.ru/item.asp?id=21134567

WHO 2007. Guidelines for drinking-water quality. Fourth edition incorporating the first addendum. Geneva. World Health Organization. ISBN 978-92-4-154995-0 pp. 631.

YAN B., STUTE M., PANETTIERI JR. R.A., ROSS J., MAILLOUX B., NEIDELL M.J., SOARES L., HOWARTH M., LIU X., SABERI P., CHILLRUD S.N. 2017. Association of groundwater constituents with topography and distance to unconventional gas wells in NE Pennsylvania. Science of the Total Environment. Vol. 577 p. 195–201. DOI 10.1016/j.scitotenv.2016.10.160.