Ground and Intermediate Water Equilibrium with Water-Bearing Rock Minerals (Moldova) under Anthropogenic Impact

A N Timoshenkova[1], C Ye Moraru[2], Ye Yu Pasechnik[3], O G Tokarenko[4] and V A Butoshina [5]

[1,2] Institute of Geology & Seismology of ASM, MD-2028, Kishinev, Republic of Moldova
[3, 4,5] Tomsk Polytechnic University, 30 Lenin Avenue, Tomsk, 634050, Russia

E-mail: [1]atimoshencova@gmail.com, [2]cmoraru@yahoo.com, [3]tog@tpu.ru, [3]paseyu@yandex.ru, [5]butoshina@list.ru

Abstract. The calculation results of ground water equilibrium with the major water-bearing rock minerals (Moldova) are presented under the condition of anthropogenic impact. As a calculation model the HydroGeo software is used. It is shown that both “ground water-rock” and “intermediate water-rock” systems are in equilibrium with a number of minerals.

1. Introduction

Ground water in Moldova is exposed to intensive anthropogenic impact. The representative examples of strong anthropogenic input are groundwaters of Kishinev, where an excess of nitrate pollution norms is observed, and the most examined Lower-Sarmatian aquifer, which is used for central water supply of residential areas and industrial sites.

The “water - rock” system is a global one on the Earth and its geological evolution leads to development of various geochemical types of ground and surface waters, different secondary mineral neogenesis including weathering crust, hydrothermally-transformed rocks, mineral deposits, etc. [1]. To understand the evolution mechanisms of underground hydrosphere composition is generally impossible without detailed research in thermodynamic equilibrium condition of groundwater with major water-bearing rock minerals. Therefore, the main goal of the article is to reveal the basic features of equilibrium in “water-rock” system and, hence, to determine the typical factors of water formation under the anthropogenic impact.

2. Materials and methods

2.1. Subject of research

The research subject is groundwater of Kishinev city and water of Lower-Sarmatian aquifer in the north-central part of Moldova (figure1).

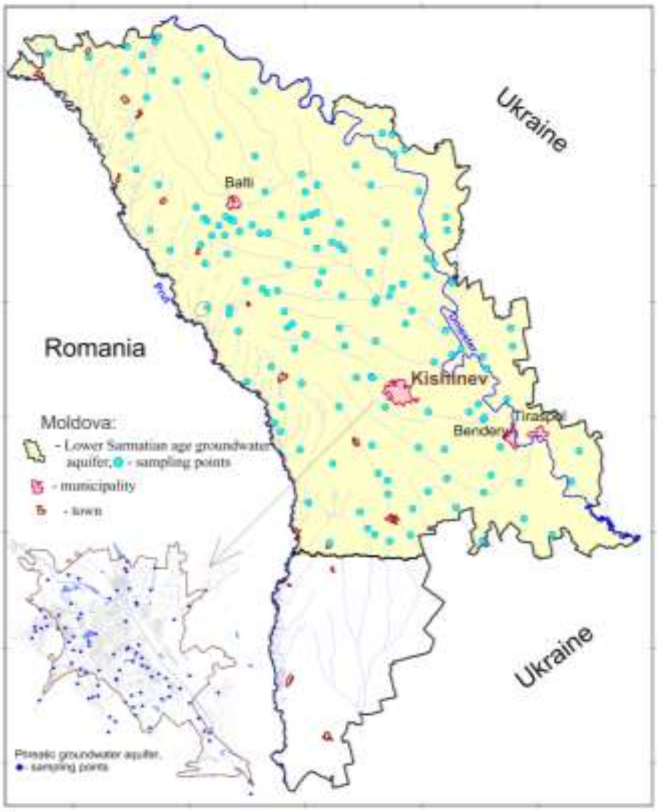


Figure 1. Sampling points.

2.2. Sampling and research methods

The research is based on the results of groundwater sampling (Kishinev city) that is performed in summer of 2012-2013 from 85 sources of temporary water supply [2]. To study Lower-Sarmatian aquifer 148 water samples are collected. The chemical analysis of water samples is performed in the accredited Laboratory of Hydrogeology and Engineering Geology, Geology and Seismology Institute (Academy of Science, Moldova) using the up-to-date analytical techniques such as titrimetry and ion chromatography.

Equilibrium calculation is carried out by common methods developed on the basis of hydrogeochemical process thermodynamics [3] using HydroGeo software [4]. The data on free energy of carbonate, aluminosilicate mineralization and dissolved elements are taken from the work [3]. To establish the rate of water equilibrium with definite minerals, we used the mineral stability field mapping technique developed by R.M. Garrels and Ch.L. Christ [5], as well as saturation index (si), which is equal to: $si = lg\ Q/K$, where Q – reaction quatant; K – reaction constant. While saturating with some mineral, the solution saturation index increases to zero (equilibrium state). In case of oversaturation, its values become positive. The calculations are carried out at temperature 25°C.

3. Geological and Hydrogeological Structure of the Study Area

Geologically, the study area is located in the south-west of East-European Precambrian platform within the Moldovan plate. Crystalline basement is located at the depth of 0 – 100 m (north) and approximately 1600 – 1800 m and more (south) and consists of Archean and Lower-Proterozoic strongly dislocated rocks of magmatic and metamorphic origin. Sedimentary section is of sedimentary formation of Upper Proterozoic, Lower- and Middle Paleozoic, and Cainozoic eras. The upper part of sedimentary section is composed of marine deposits of Middle Paleogene (Eocene), Neogene (Baden and Sarmatian Stages), and Quaternary deposits. For Neogene deposits the formation of three reef ridges is typical, the second of which is Middle-Sarmatian one crossing Kishinev city [6].

Hydrogeologically, the study area is south-western part of the Black Sea artesian basin of the first order. N.F. Frolov [7] distinguishes the area between the Prut and Dniester Rivers as a separate artesian basin of the second order called “Moldovan artesian basin”.

Depending on hydrodynamic and genetic features of geological conditions, there are two types of groundwater. The first type is groundwater of active water exchange zone occurred mainly at the depth of 0-15 m, in rare cases deeper. Water-bearing rocks are inequigranular sand and sandy clay. The aquifer bottom consists of dense blue-gray and green-gray clays of different age, the surface of which is washed out in some areas. Groundwaters are fed by precipitation infiltration, water inflow from the terraces above flood-plain, in high water season – due to flood water. In the territory of Kishinev city four unconfined aquifers can be distinguished: 1) aquifer in the recent alluvial deposits; 2) that in ancient alluvial deposits; 3) that in alluvial-talus deposits; 4) that in eolian-talus deposits [8].

Intermediate water is a complex of Sarmatian aquifers.

Groundwater in Lower-Sarmatian deposits is distributed everywhere and well-studied over the territory of Moldova, with the exception of extreme south, where rocks of this age are absent. Groundwater reservoir is fractured limestone, which alternates with sand and clay loam in the Central Transdniester.

Lower-Sarmatian aquifer is separated from Upper-Cretaceous aquifer of Podolskian argillaceous sand formation that acts as an aquiclude between them.

Head waters: the pressure increases from north to south reaching 2 -40 m in the north and in the south more than 300 m, then decreasing towards south-west and south-east up to 7 - 10 m. Groundwater is discharged into the Black Sea; first it appears to flow into overlying Middle-Sarmatian deposits, from the latter it flows into the sea (S.T. Vznuzdayev, 1969). Besides, there is a discharge in the river valley, in the tectonic zones [6].

4. Results and discussion

As for their chemical composition, groundwaters of Kishinev city are mostly hydrocarbonate or hydrocarbonate-sulfate (in terms of prevailing anion and cation content) with different ratios of magnesium, calcium, sodium (Table 1). There are also sulfate-hydrocarbonate and sulfate waters. Waters are mostly weakly alkaline, fresh, seldom weakly brackish. Water mineralization varies in the wide range – from 0.39 to 2.63 g/L.

Table 1. Chemical composition of groundwater in Kishinev city (the number of samples – 85).

Component	Concentration, mg/L		
	Min	Max	Average
TDS, g/L	0.4	2.6	1.1
pH	7.0	8.4	7.6
HCO_3^-	244.0	902.8	526.1
Cl^-	13.6	408.7	110.8
SO_4^{2-}	8.0	1488.0	270.4
NO_3^-	0.4	994.4	116.5
Ca^{2+}	14.2	383.2	121.6
Mg^{2+}	7.8	222.5	90.4
Na^+	28.0	305.0	124.9
K^+	0.1	125.2	6.4
Fe^{2+}	0.1	1.0	0.3
Sr^{2+}	0.5	6.8	1.8
SiO_2	1.9	35.0	9.7

The distinguishing feature of groundwater in Kishinev city is elevated concentration of nitrate (the maximum concentration is 994.4 mg/L), the source of which is agricultural activity [2, 8].

In terms of chemical composition water of Lower-Sarmatian aquifer is mostly hydrocarbonate sodium or sodium-magnesium (Table 2).

Table 2. Chemical composition of drinking intermediate groundwater of the north-central part of Moldova (the number of samples – 148).

Component	Concentration, mg/L		
	Min	Max	Average
TDS, g/L	0.48	4.64	1,38
pH	6.80	8.98	7.95
Na^+	27.00	1400.00	307.33
Mg^{2+}	0.50	215.00	33.28
Ca^{2+}	1.50	343.00	36.50
K^+	0.50	20.00	5.12

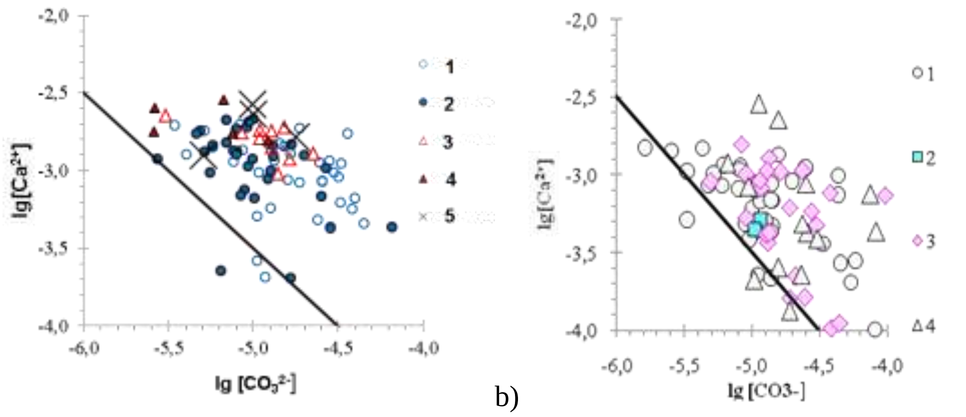
HCO_3^-	317.20	2656.00	691.06
Cl^-	7.00	574.00	68.16
SO_4^{2-}	2.00	1422.10	228.16
SiO_2	0.50	44.20	12.48

There is also hydrocarbonate-sulfate and sulfate-hydrocarbonate waters with different ratios of sodium, magnesium, calcium. In 5 % of cases there are hydrocarbonate-chloride sodium-magnesium waters. Water mineralization ranges from 0.48 to 4.64 g/L. Water is mostly alkaline (the average value of pH = 7.95), weakly brackish and fresh, seldom brackish, at the average salinity value 1.38 g/L.

Hence, water is mostly alkaline and the major salt-forming components of that water are hydrocarbon-ion and sodium. Taking this fact into account, one may state that it is typical alkaline sodium water sometimes distinguished by high mineralization.

4.1 Equilibrium with carbonate minerals.

Thermodynamic calculations have shown that, despite low mineralization values and calcium content, the major part of studied groundwaters of Kishinev achieves the equilibrium with such carbonate mineral as calcite (figure 2). The long distance between data points shows the state of water oversaturation with calcite. This is true for waters of all chemical types. Insignificant part of water still remains undersaturated with calcite. The average mineralization value of this water is 0.4 g/L, the content of hydrocarbonate ion – 329 mg/L, calcium – 16 mg/L at pH = 7.7.



a) b)

Figure 2. Diagram of equilibrium a) groundwater in Kishinev (chemical types of water: 1 – HCO_3; 2 – HCO_3–SO_4; 3 – SO_4–HCO_3; 4 – SO_4; 5 – NO_3–HCO_3) and b) Lower-Sarmatian ground water of the north-central part of Moldova (chemical types of water: 1 – HCO_3; 2 – HCO_3–Cl; 3 – HCO_3–SO_4; 4 – SO_4–HCO_3) with calcite at 25°C.

In case of intermediate water, the group of calcite unsaturated water includes some waters of hydrocarbonate and sulfate-hydrocarbonate types with the average mineralization value – 1 g/L, hydrocarbonate-ion content – 512.2 mg/L, calcium – 39.38 mg/L at pH=7.37, whereas the average values of the above mentioned parameters of calcite saturated waters do not differ significantly.

4. 2 Equilibrium with aluminosilicate minerals.

The diagrams of saturation with aluminosilicate rock minerals are shown in figure 3. All groundwaters of Kishinev and intermediate waters of north-central part of Moldova (with the exception of several samples) are not in equilibrium with endogenous aluminosilicates (albite, anorthite) and are in equilibrium with secondary minerals (aluminum, kaolinite, montmorillonite oxides). Some samples are in equilibrium with gibbsite, potassium, and feldspar.

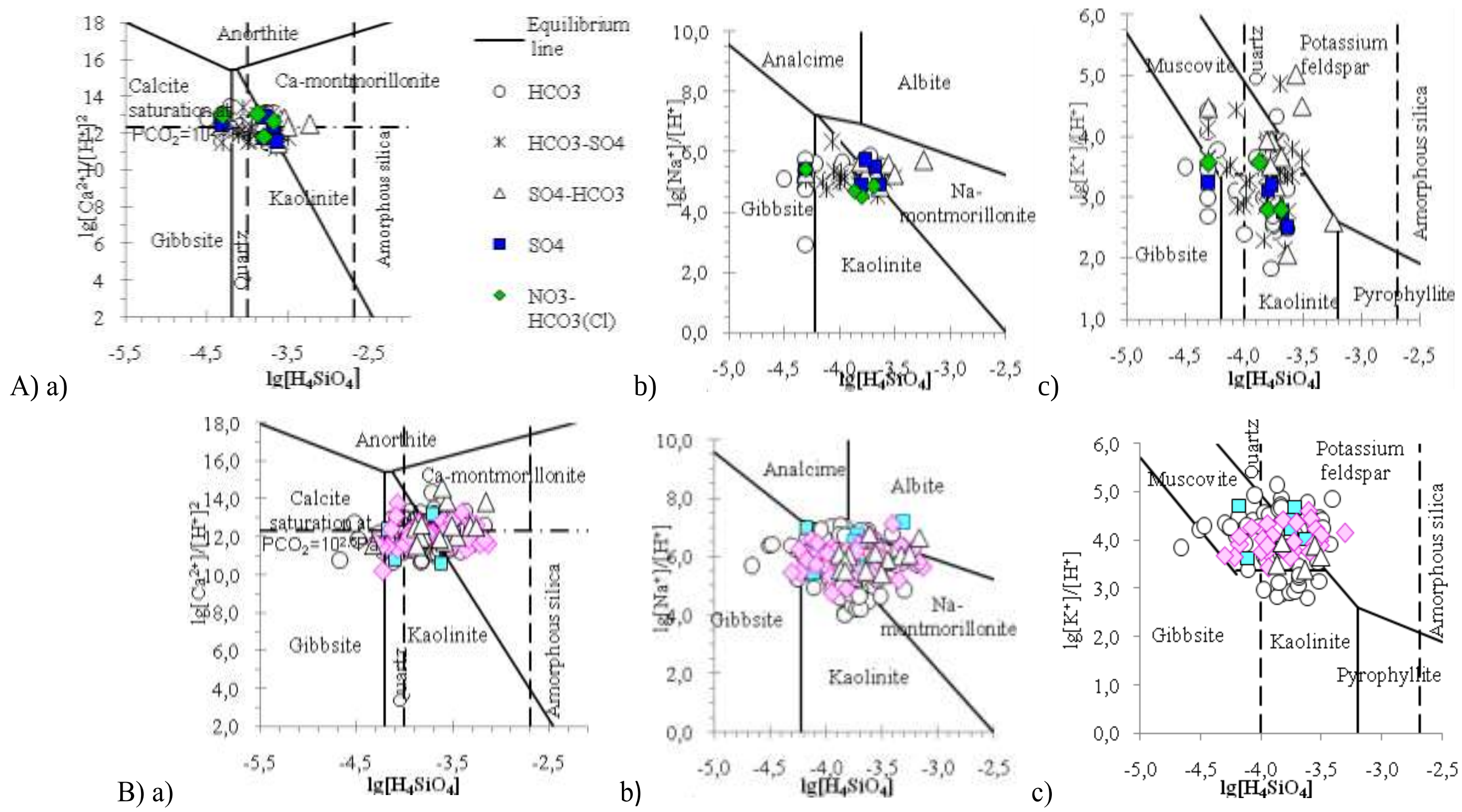


Figure 3. Equilibrium diagrams A) ground water of Kishinev city and B) Lower-Sarmatian ground water of north-central part of Moldova with aluminosilicate minerals at standard condition: a) HCl–H_2O–Al_2O_3–CO_2–CaO–SiO_2 system; b) HCl–H_2O–Al_2O_3–CO_2–Na_2O–SiO_2 system; c) HCl–H_2O–Al_2O_3–CO_2–K_2O–SiO_2 system.

5. Conclusions

All studied waters of Moldova territory are in equilibrium with carbonate minerals, even groundwaters of Kishinev, despite the rapid water exchange and short time of groundwater interaction with rock. The observed equilibrium of Kishinev groundwater with calcite proves the early stage of groundwater evolution which is accompanied with rather low mineralization values (less than 1 g/L) due to hydraulic connection with surface water and precipitations. It is just in those points where water equilibrium with carbonate shifts towards undersaturation. All groundwaters of Kishinev and intermediate waters of north-central part of Moldova (with the exception of several samples) are not in equilibrium with endogenous aluminosilicates (albite, anorthite) and are in equilibrium with secondary minerals (aluminum, kaolinite, montmorillonite oxides).

In the territory of Moldova agriculture is widely developed that has a great impact on water composition. For example, elevated concentration of nitrite is a typical feature for Kishinev that allows distinguishing so-called “exotic” type of water – NO_3–HCO_3–Mg–Ca, sometimes with increased chloride ion.

All these factors point to equilibrium-non-equilibrium nature resulted from interactions in the “water-rock” system and a definite evolution stage.

Acknowledgements

Authors thank Prof. Dr. S L Shvartsev for his helpful advice and suggestions. The investigations were supported by The Russian Foundation for Basic Research (Project No 14-35-50510).

References

[1] Shvartsev S L 2008 Geochemistry of fresh groundwater in the main landscape zones of the Earth *Geochem. Int.* **46** 3 128–1398

[2] Timoshenkova A N, Pasechnik E Y and Tokarenko O G 2014 Equilibrium of Groundwater with Carbonate Minerals of the Water-Bearing Rocks under Anthropogenic Impact (by the example of Kishinev, Moldova) *IOP Conf. Ser.: Earth Environ. Sci.* **21** 1 12-24

[3] Alekseev V A, Ryzhenko B N, Shvartsev S L, Zverev V P, Bukaty M B, Mironenko M V, Charykova M V and Chudaev O V 2005 *Geological evolution and water-rock self-organization* V.1. Water-Rock System on the Earth Crust: interaction, kinetics, equilibrium, simulation. (Novosibirsk: Punlishing House SB RAS) p 244 [in Russian]

[4] Bukaty M B 2002 *Bulletin of Tomsk Polytechnic University* **305** 6 348–65 [in Russian].

[5] Garrels R M and Christ Ch L 1965 *Solutions, Minerals and Equilibria* (New York: Harper & Row) p 450

[6] *USSR Geology. Moldavian SSR. Moldavskaya SSR* 1969 Vol. 45 (Moscow: Nedra) p 456 [in Russian]

[7] Frolov N M 1961 Groundwaters of the western part of the Black Sea artesian basin (Moscow: Academy of Science of the USSR) p 230

[8] Moraru C Ye 2012 Hydrogeochemistry of active water exchange zone in the southwest of the Black Sea artesian basin (geoecological aspects): abstract of dissertation … Doctor of Geol.-Mineral. Sciences: / C Ye Moraru (Moscow: Institute of Environmental Geoscience of Russian Academy of Science) p 52