Equilibrium of Groundwater with Carbonate Minerals of the Water-Bearing Rocks under Anthropogenic Impact (by the example of Kishinev, Moldova)

A N Timoshenkova¹, E Yu Pasechnik² and O G Tokarenko³

¹Institute of Geology & Seismology of ASM, MD-2028, Kishinev, Republic of Moldova
²,³Tomsk Polytechnic University, Tomsk, Russia

E-mail: ¹asia444@mail.ru, ²paseyu@yandex.ru, ³tog@tpu.ru

Abstract. The paper presents calculation results of equilibrium of groundwater in Kishenev with a variety of secondary carbonate minerals. It is shown that the groundwater-rock system is in equilibrium with some minerals, such as calcite, magnesite, dolomite, siderite, but at the same time is not in equilibrium with strontianite. It indicates that secondary mineral precipitation is possible. Specific nitrate chemical water type, which is rarely observed in nature and characterized by the presence of anthropogenic impact in this territory, in some cases is of higher saturation as compared to calcite, dolomite and magnesite due to the fact that nitrate ion content increases with the increase of calcium content.

1. Introduction

In recent years the interest of the world scientific community is directed to the study of geologic evolution of the water-rock interaction [1]. The water-rock-gas-organic matter system is studied by such scientists as R.M. Garrels, Ch.L. Christ, R.A. Berner, A.E. Blum, W.H. Casey, R. Hellmann, G.R. Holdren, G. Jordan, S.L. Shvartsev, V.A. Alekseev, B.N. Ryzhenko, I.K. Karpov. It can be explained by the fact that the water-rock system is universal on our planet and its geologic evolution leads to the formation of numerous geochemical types of natural water, various secondary minerals, including crust of weathering, hydrothermally altered rocks, various mineral deposits, etc. [2]. At present the theory of water-rock interaction is well-developed in geochemical terms, in terms of experimental modeling, physical and chemical modeling of the rock dissolution processes, etc. [3]. Moreover, the use of modern approaches is particularly relevant for the study of groundwater composition formation under anthropogenic impact. However, the solution to this problem is impossible without a detailed study of the thermodynamic equilibrium of groundwater with principal minerals of the enclosing rocks, carbonate in particular. The study of water-carbonate rock equilibrium is essential for understanding of evolutionary development of water and enables to determine indirectly relation between degree of water saturation to minerals and anthropogenic impact.

The main emphasis of this paper will be on groundwater as it is the least studied as compared to deep waters. In spite of the fact that nowadays groundwater aquifers are not currently used for the centralized water supply, some water bodies (pit wells and springs) are still of practical significance for individual water use in some areas of the city and in the periods when centralized water supply is impossible because of technical breakdowns [3]. Hence, the study of geochemical content of the groundwater of active water exchange zone is particularly relevant.
2. Geology and Hydrogeology of the Territory
Geologically the area under study is located in the south-west of the East European Precambrian platform in the center of the Moldavian platform. The crystalline basement is at a depth of 1600 ... 1800 m and is made up of the Archean and Lower Proterozoic dislocated igneous and metamorphic rocks. Sedimentary cover is in the sedimentation area of the Upper Proterozoic and Lower and Middle Paleozoic and Upper Cretaceous. When sedimentary cover comes to the end there are marine deposits of the Middle Paleogene (the Eocene), Neogene (Baden and Sarmatian stages), quaternary deposits of the Dnestr and Byk river terraces. Neogene deposits are characterized by the formation of three reef ridges, the second of which is Middle Sarmatian and go through Kishinev.

There are two types of groundwater depending on the hydrodynamic and genetic characteristics of the occurrence conditions. The first type is groundwater of the active water exchange zone which underlies mostly at a depth of 0 ... 15 m, it is rarely deeper. Water-bearing minerals are sands and sandy clays. Water horizon bottom is made up of the heavy blue-gray and greenish-gray Middle Sarmatian clays eroded in some areas. Groundwater is supplied by infiltration of atmospheric precipitation, groundwater inflow from terraces above flood-plain and by means of flood water under flooded conditions. Intermediate water is a complex of Sarmatian aquifers. Unconfined aquifers of the study area can be divided into four types: 1) aquifer in the modern alluvial deposits; 2) in the ancient alluvial deposits; 3) in the alluvial and deluvial deposits; 4) eolian and deluvial deposits [4].

3. Materials and Methods
3.1. Study area
The study area clearly demonstrates anthropogenic impact which shows itself in the presence of nitrate pollution and its effect on the geochemical characteristics of groundwater in the Republic of Moldova as a whole. Fig. 1 shows the area under study of urban agglomeration, consisting of five residential districts, each of which is subjected to various degrees of anthropogenic impact.

3.2. Sampling and investigation methods
The given investigation conducted in summer in 2013 is based on the results of groundwater sampling from water sources used by residents for drinking purposes. Totally, 85 sources were sampled, among them there are 20 ascending and descending springs with the natural discharge within the city, and 65 wells with a depth not less than 10 m. Chemical analysis of water samples was carried out in an accredited laboratory of Hydrogeology and Engineering Geology of the Institute of Geology and Seismology of the Academy of Sciences of Moldova using state-of-the-art analytical equipment and methods of titrimetry and ion chromatography.

The equilibrium calculations were made using well-known methods developed on the basis of thermodynamics of hydrogeochemical processes [3] using HydroGeo software [5]. Free energies of formation of carbonate minerals and dissolved chemical elements are taken from [3]. To determine the degree of equilibrium of them to individual minerals, we used method of mineral stability fields developed by R.M. Carrels and Ch.L. Christ [6], and saturation index (si - saturation index) which is equal to

\[ si = \log Q/K, \]

where Q is a reaction quotient; K is a reaction constant. Saturation index increases to zero (state of equilibrium) with saturation of solution in relation to some minerals. With oversaturation its values become positive. Calculations were performed at 25°C.
4. Results and Discussion

4.1 Chemical composition

It was found that groundwater has a specific chemical composition. The first specific feature is salinity which varies in a wide range from 0.39 to 2.63 g/l in the samples studied. Water is mainly weakly alkaline, fresh, rarely weakly salted, with an average salinity equaled to 1.1 g/dm$^3$ (table 1).

Water under study is different by chemical type. In general, the following chemical types of water with predominant content of anions with different combinations of cationic component are abundant in Kishenev (according to S.A. Shechukarev) (in brackets – % of the total number of the samples under study in descending order):

- I type – $\text{HCO}_3$–$\text{Mg}$–$\text{Ca}$, $\text{Na}$–$\text{Mg}$–$\text{Ca}$, $\text{Na}$–$\text{Na}$–$\text{Mg}$, rarely $\text{Mg}$–$\text{Ca}$–$\text{Na}$ or $\text{Ca}$–$\text{Mg}$–$\text{Na}$ or – $\text{Ca}$, –$\text{Mg}$ and –$\text{Na}$ (40 %);
- II type – $\text{HCO}_3$–$\text{SO}_4$–$\text{Mg}$–$\text{Na}$, –$\text{Mg}$–$\text{Ca}$, rarely –$\text{Ca}$, –$\text{Na}$–$\text{Mg}$–$\text{Ca}$, –$\text{Na}$–$\text{Mg}$ and –$\text{Na}$–$\text{Ca}$ (37 %);
- III type – $\text{SO}_4$–$\text{HCO}_3$–$\text{Ca}$–$\text{Mg}$–$\text{Na}$, –$\text{Mg}$–$\text{Ca}$–$\text{Na}$, –$\text{Ca}$–$\text{Na}$–$\text{Mg}$, –$\text{Ca}$–$\text{Mg}$, –$\text{Mg}$–$\text{Ca}$, –$\text{Mg}$–$\text{Na}$, –$\text{Na}$–$\text{Mg}$ (12 %);
- IV type – $\text{SO}_4$–$\text{Ca}$–$\text{Mg}$–$\text{Na}$, –$\text{Ca}$–$\text{Mg}$–$\text{Na}$, –$\text{Ca}$–$\text{Na}$–$\text{Mg}$, –$\text{Na}$–$\text{Mg}$–$\text{Ca}$, –$\text{Mg}$–$\text{Na}$–$\text{Mg}$–$\text{Ca}$ (6 %);

The increase of nitrate ion concentration in groundwater allows us to distinguish an additional chemical type which can be called ‘exotic’ and characterizes specific nature of the study area. i.e. V type – $\text{NO}_3$–$\text{HCO}_3$–$\text{Mg}$–$\text{Ca}$, sometimes with a high content of chloride ion (5%). It was found that nitrate chemical type of groundwater is abundant mostly in the northwestern part of the city. Nitrate ion concentration tends to increase with the increase of concentrations of calcium and magnesium, and sulfate ions as well. It was found [7] that elevated nitrate concentrations are caused by agriculture.
Table 1. Groundwater chemical composition, town Kishinev (number of samples – 85).

| Constituent | Concentration, mg/L | Min | Max | Average |
|-------------|---------------------|-----|-----|---------|
| TDS, g/L    |                     | 0.4 | 2.6 | 1.1     |
| pH          |                     | 7.0 | 8.4 | 7.6     |
| HCO₃⁻       |                     | 244.0 | 902.8 | 526.1 |
| Cl⁻         |                     | 13.6 | 408.7 | 110.8 |
| SO₄²⁻       |                     | 8.0 | 1488.0 | 270.4 |
| NO₃⁻        |                     | 0.4 | 994.4 | 116.5 |
| Ca²⁺        |                     | 14.2 | 383.2 | 121.6 |
| Mg²⁺        |                     | 7.8 | 222.5 | 90.4   |
| Na⁺         |                     | 28.0 | 305.0 | 124.9 |
| K⁺          |                     | 0.1 | 125.2 | 6.4    |
| Fe²⁺        |                     | 0.1 | 1.0   | 0.3    |
| Sr²⁺        |                     | 0.5 | 6.8   | 1.8    |
| SiO₂        |                     | 1.9 | 35.0 | 9.7    |

It was established that areal hydrogeochemical zoning of groundwater is characterized by the abundance of hydrocarbonate water with magnesium cations and calcium or sodium and magnesium base in the elevated areas of the city. Sulfate ion appears in the water composition in the areas of much lower absolute elevation. Water with the increased concentration of sulfate ion is abundant in the territory of the Russian Federation and other countries [8]. Their occurrence is associated with the areas of continental salinization development processes [9], or areas with sulphide deposits which are abundant, for example, in Trans-Baikal [10]. The content of sulphates in the water under investigation is comparable to the concentration observed in the water areas of the above mentioned areas and reaches about 1.5 g/l.

Correlation analysis of the main chemical components enabled to find out direct relation of sodium, magnesium and calcium content with sulfates. Positive correlation of sulphates with these elements might be explained by the fact that they accumulate due to the processes of evaporating concentration [9]. Positive correlation between nitrate and chlorine (r = 0.80) indicates a considerable impact of surface technogenic processes on the formation of chloride concentration in groundwater. Relatively high correlation coefficients are detectable for pairs of sodium, magnesium, calcium, sulphate, chloride and nitrate with salinity.

Table 2. Pair correlation coefficient of the chemical composition of groundwater.

| r   | TDS | pH  | Na⁺ | Mg²⁺ | Ca²⁺ | K⁺  | HCO₃⁻ | SO₄²⁻ | Cl⁻  | NO₃⁻ |
|-----|-----|-----|-----|------|------|-----|-------|-------|------|------|
| TDS | 1.00|     |     |      |      |     |       |       |      |      |
| pH  | -0.34| 1.00|     |      |      |     |       |       |      |      |
| Na⁺ | 0.61| -0.26| 1.00|      |      |     |       |       |      |      |
| Mg²⁺| 0.68| -0.08| 0.12| 1.00|      |     |       |       |      |      |
| Ca²⁺| 0.84| -0.42| 0.34| 0.38| 1.00|     |       |       |      |      |
| K⁺  | 0.16| -0.01| 0.07| -0.01| 0.12| 1.00|       |       |      |      |
| HCO₃⁻| 0.12| -0.17| 0.37| 0.21| -0.05| -0.02| 1.00|       |      |      |
| SO₄²⁻| 0.77| -0.28| 0.64| 0.62| 0.14| 0.01| 1.00|       |      |      |
| Cl⁻ | 0.77| -0.20| 0.19| 0.70| 0.69| 0.13| -0.01| 0.27| 1.00|      |
| NO₃⁻| 0.55| -0.10| -0.01| 0.52| 0.53| 0.03| -0.23| -0.03| 0.80| 1.00|

Thus, the carried out geostatistical analysis of the chemical composition of groundwater shows direct anthropogenic impact on the formation of the geochemical characteristics of groundwater in Kishenev which determines groundwater distinctive features associated with the given territory.
4.2 Equilibrium with carbonate minerals
Thermodynamic calculations showed that most groundwater under study, despite the low values of mineralization and calcium content, reaches equilibrium with carbonate minerals such as calcite (figure 2). Sufficiently remote location of imaging points indicates oversaturation of water with calcite and in water of all chemical types.

Groundwater as well as typical water of a leach cap falls under a general idea about its equilibrium with calcite. According to this fact water with salinity of more than 0.6 g/l and pH higher than 7.4 at the same time reaches equilibrium with the calcium carbonate [2, 8] which under certain geochemical conditions can not only dissolve but also precipitate from the solution to form a secondary mineral.

Minor part of water still remains undersaturated with calcite. This group includes hydrocarbonate and hydrocarbonate-sulphate types of water. The average value of salinity in this water is 0.4 g/l, content of sodium ion is 329 mg/l, calcium content is 16 mg/l at pH equaled to 7.7, whereas average values of these parameters in calcite-saturated water is much higher. In this water calcium can be accumulated in solution as a result of its leaching from water-bearing rocks under conditions of active water exchange.

Oversaturation is observed in groundwater in relation to dolomite and siderite (figures 3 a and b). However, despite lower free energy of dolomite formation, secondary calcite will be the first to form because of a smaller number of components in the mineral composition. Siderite characterized by fairly high energy of formation will be the last to form.

Figure 2. Diagram of equilibrium of groundwater in Kishinev with calcite at 25°C. Chemical types of water: 1 – HCO$_3$; 2 – HCO$_3$–SO$_4$; 3 – SO$_4$–HCO$_3$; 4 – SO$_4$; 5 – NO$_3$–HCO$_3$

5. Conclusion
Despite high water retention time and short time of interaction of groundwater in Kishinev with rocks there is equilibrium with many carbonate minerals. As a result of this water-rock interaction most of the elements which get into solution bind to the newly formed secondary minerals: Ca – calcite and dolomite, Mg – magnesite, Fe – siderite. Thus, groundwater under study can be attributed to carbonate forming geochemical type according to the classification of S.L. Shvartsev [1]. Observed equilibrium with calcite substantiates the early stage in the groundwater evolution which is characterized by relatively low salinity (less than 1 g/dm$^3$) as a result of hydraulic connectivity with surface water and atmospheric precipitation. Equilibrium to water carbonates shifts towards undersaturation at these very points. Since water continues to interact with aluminosilicates which are abundant in this area, the carbonate formation processes characterize groundwater composition in Kishinev at this stage.
Figure 3. Diagram of equilibrium of groundwater in Kishinev with dolomite (a), siderite (b), magnesite (c) and strontianite (d) at 25°C (nomenclature see in figure 2)

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6. References
[1] Shvartsev S L 2013 Procedia Earth and Planetary Science 7 810
[2] Shvartsev S L 2008 Geoch. International 46 (13) 1285
[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: Publishing House SB RAS) p 244 [in Russian]
[4] USSR Geology. Moldavian SSR. Moldavskaya SSR 1969 45 (Moscow: Nedra) p 456 [in Russian]
[5] Bukaty M B 2002 Bulletin of Tomsk Polytechnic University 305 (6) 348–65 [in Russian]
[6] Garrels R M and Christ Ch L 1965 Solutions, Minerals and Equilibria (New York: Harper & Row) p 450
[7] Moraru C E 1995 Buletinul Academiei de Stiinte a Rep. Moldova.ser. Fizica si Tehnica 1 93–99
[8] Shvartsev S L 1998 Hydrogeochemistry of hypergenesis zone (Moscow: Nedra) p 366 [in Russian]
[9] Perelman A I and Kasimov N S 1999 Landscape geochemistry (Moscow: Astreya-2000)
[10] Plyusnin A M, Zamana L V, Shvartsev S L, Tokarenko O G and Chernyavskii M K 2013 Russian Geol. and Geoph. 54 (5) 495–508