HYDROCHEMICAL CHARACTERISTICS OF GROUND WATERS IN SARMATIAN AND MEDITERRANEAN-II LIMESTONES IN THE VICINITY OF BELGRADE

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SUMMARY

In this paper, the dependance of the hydrochemical characteristics of the ground waters on the geology of the particular area and on the other factors is discussed. The origin of the particular types of ground waters is also presented.

Using as the objects of investigation localities around Beograd: Obrenovačka Banja, Ovča and some others localities, the parallel in hydrothermal characteristics of the ground waters of these areas is presented together with the factors which may influence the observed difference between these waters. Starting with the facts that the above mentioned localities are situated within the same physical-geographic, lithological and some others environments, and are also situated within different structural-geological and hydrological environments, the authors are giving basic factors influencing the formation of the hydrochemical characteristics of ground waters in these area.

The work is illustrated with profiles and diagrams showing basic hydrochemical characteristics of these waters and the classification of ground waters is also presented.

INTRODUCTION

Because Sarmatian and Mediterranean-II limestones in the vicinity of Belgrade have special hydrogeological characteristics when compared with other Tertiary sediments, our purpose is to describe the essential chemical characteristics of their ground waters. In our study of some localities in which they occur (Obrenovačka Banja, Ovča, Rimski Bunar (Roman well at Kalemegdan fortress, Belgrade), Bele Vode, Kneževac limestone quarries, Rakovica) we shall try to explain briefly the relationship between the chemical composition of ground waters and specific conditions i.e. geological strata in which they occur, giving at the same time essential reasons for differences in the chemical composition of water in the localities cited.

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Mediterranean-II and Sarmatian sediments are widely distributed in the broad vicinity of Belgrade. Limestone of Mediterranean-II and Sarmatian age are a conspicuous lithological member and are invariably present in these sediments.

Fig. 1 — A geological sketch map: (1) Obrenovačka Banja spa; (4) Ovča; (5) Rimski Bunar; (7) Bele Vode; (8) Rakovica; (9) Sremčica.
I. Mesozoic; II. Tertiary; III. Quaternary.

Mediterranean-II limestones are developed in the Belgrade area (Tašmajdan, Kalemegdan, on Torlak, Višnjica, etc.). These are mainly reef (Tašmajdan, Torlak) and less frequently bedded limestones (Kalemegdan) which mostly crop out or are covered by younger sediments. These limestones are mainly built up of algae, corals, bryozoans, cerithiums (Višnjica), etc.

Their distribution is limited. Because of their reef character their thickness is small (about 50 m) so that this makes them readily noticeable and recognizable in the geological structure of these parts of the terrain.

Sarmatian limestones have by far the most extensive distribution. Their prevalently reef character makes them conspicuous and readily noticeable among other lithological members of the Tertiary in the vicinity of Belgrade.

These limestones occur in the form of elongated zones of an almost N-S strike. Several narrow zones which undoubtedly represented an integral whole are now exposed locally. They also crop out on the surface, viz. along the margin of Makiš through Žarkovo to Zeleznik and further southwest, and, from Rakovica to Kijevo along the left bank of the Topčiderska Reka, in the valley of the Reka (Sremčica), at several points between the Topčiderska Reka and Vrčinska Reka (south of Vrčin, etc.). Sarmatian limestones were established by boring in the southern parts of the Pannonian basin (Obrenovac, Ovča, etc.) They are mostly built up of clams and snails (cerithium limestone, ostrea banks, serpula limestones) less often of bryozoans and algae and are mostly of a reef character, often banked or bedded. The limestones are frequently marly, sandy,
or brecciated so that their present appearance definitely proves that they were formed in a shallow-water environment. They are of a gray to yellowish colour due to the presence of iron, and their thickness does not exceed 60 meters.

The limestones transgressively overlie Cretaceous or Mediterranean-II sediments and are mostly exposed or overlain by younger sediments generally of Pannonian age. These limestones belong to the Lower Sarmatian.

By their geological, lithological, and especially hydrogeological characteristics these limestones break the monotonous distribution of Tertiary sediments of the vicinity of Belgrade. Their geomorphological and hydrogeological features impart a special character to this part of the terrain.

**HYDROGEOLOGICAL PROPERTIES OF LIMESTONES**

These limestones are characterized by the process of karstification in which they were involved as a whole (merokarst, Cvijić, J., 1926). Because of their small thickness this process involved even their lowermost parts (Sremčica). Sinkholes, small uvalas, karstified dolines, small caves, karstic springs, etc occur frequently.

As can be seen from figure 3 they are distinguished by secondary porosity with a pronounced karstic porosity of the cavernous type. In addition to large and small cavities of highly irregular form, broadened fissures and cracks in the form of irregular channels often occur. Their upper parts are often filled with uncemented material.

In these limestones a karstic groundwater body has been formed.* It is of limited extent because of the reef character of limestones and their small distribution. This is a permanent and no doubt a true karstic groundwater body with all its characteristics. The amount of karstic waters can be judged from the occurrence of perennial springs. They are rather numerous although their discharge is not high (0.1-0.5, less often over

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* According to M.T. Luković (1946), this primarily refers to the groundwater body in Sarmatian limestones while Mediterranean-II limestones bear no water.
The groundwater table is found at a considerable depth in lower parts of the terrain, often at a depth of 20-30 m below the surface. The groundwater table is free in those parts where the limestones are exposed on the surface (above the base level of erosion), or is under pressure when they lie deep under the base level of erosion and under younger sediments (Obrenovačka Banja, Ovča, etc).

Fig. 3 — Karstified Sarmatian limestones, Rakovica.

The karstic groundwater body is recharged in a comparatively simple way. There is no doubt that the groundwater body is mostly recharged through precipitation (the mean annual rainfall is about 625 mm), to a smaller extent through waters of other groundwater bodies or through surface waters.

Ground waters issue in two ways: naturally through perennial springs of the gravity type, and artificially through wells in which water issues at a positive artesian pressure (Obrenovačka Banja, Ovča). Subsurface flow of these waters into alluvial drifts is not uncommon (the margin of Makilj).

**Physical and Chemical Properties of Ground Waters**

These are colourless waters free of odour except for the water of Obrenovačka Banja in which the presence of H₂S is noticeable. They mostly have no taste except the waters at Ovča which have a salty-bitter taste. It is quite understandable that these waters have different temperatures. The waters of Obrenovačka Banja have a temperature of 21-22°C which ranks them as thermal and mineral waters. The temperature of the water at Ovča approaches temperature of thermal waters (19.3°C) while the temperatures of waters in other localities are lower and range between 12 and 14°C, exceptionally
<table>
<thead>
<tr>
<th>Locality</th>
<th>Year</th>
<th>Cations</th>
<th>Anions</th>
<th>H₂S</th>
<th>CO₂</th>
<th>Dry Residue</th>
<th>Remarks</th>
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6-8 °C (Rimski Bunar). Temperatures are generally somewhat higher than the average annual air temperatures (11.5 °C). There are slight seasonal fluctuations in the course of the year.

These waters also differ in total hardness. The hardness of water at Obrenovačka Banja is 7.8° dH, at Ovča 29.54° dH and 42.75° dH, at Rakovica 6.7° dH, at Sremčica 11.2° dH, at Bele Vode 10.36° dH and 18.92° dH. It can be seen that these are mostly moderately hard waters, sometimes very hard, and rarely soft. The pH value of these waters is about 7.

Dry residue in the waters of Obrenovačka Banja amounts to 1.1 g/l, in those at Ovča 16.3 g/l while in other localities the total mineral content is 1 g/l, and mostly about 0.5 g/l.

The mineral composition is given in Table 1.

To give a clearer idea of the relation between mineral constituents required for the study of conditions of their formation their composition will be first given in Kurlov's formula:

1. Obrenovačka Banja:

\[ M_{1.05}H_2SO_{0.006}CN_{0.06} \frac{HCO_3}{97.0} \frac{Na+K_{85.5}Mg_{8.8}Ca_{5.6}}{t_{22} °C} \]

4. Ovča:

\[ M_{16.2}Br_{0.03}I_{0.008} \frac{Cl_{95.6}}{Na+K_{93.2}Mg_{5.6}} t_{19.3} °C \]

5. Rimski bunar:

\[ M_{0.59} \frac{HCO_3}{51.6SO_4^{2-}} \frac{Cl_{10.8}}{Na+K_{75.4}Ca_{12.3}Mg_{12.3}} t_{8} °C \]

8. Rakovica:

\[ M_{0.59}CO_3^{2-} \frac{HCO_3}{75.3SO_4^{2-}} \frac{Cl_{19.6}}{Na+K_{77.4}Ca_{17.8}Mg_{4.8}} t_{13.8} °C \]

Classification of these waters according to the cation and anion contents can be seen from the diagram (fig. 4).

As can be seen from the diagram, according to the cation content they belong to the group of sodium waters, while in respect to the anion content some differences exist. In addition to pronouncedly hydrocarbonate waters there are also some chloride waters (Ovća).

After Sulin’s classification these waters can be classified into the following genetic types: the hydrocarbonate-sodium type (Obrenovacka Banja, Rimski Bunar, Sremčica, Rakovica, Bele Vode) and the chlorine-magnesium type (Ovća).

To make the relation between mineral constituents clearer the chemical composition of ground waters will be represented in Roger’s diagram. The diagram indicates the essential characteristics of these waters according to Palmer’s classification.

Fig. 5 — Roger’s diagram of the cation and anion contents of ground waters: (1) Obrenovacka Banja, (4) Ovća; (5) Rimski Bunar; (8) Rakovica.

Considerable differences in the chemical composition of ground waters evidently exist and they will be discussed later on.

**CONDITIONS AFFECTING THE CHEMICAL COMPOSITION OF GROUND WATERS**

The existing differences in the chemical composition are undoubtedly due to the differences in the conditions under which the waters occur. The main factors, or rather groups of factors affecting the chemical composition of ground waters will be dealt with first.

It should be pointed out that the localities studied occur under the same physico-geographical conditions and belong to the same stratigraphic units of given lithological composition. On the other hand it should be emphasized that there exists essential differences in structural-geological and hydrogeological conditions. and their analysis will lead us to reliable conclusions.

From the point of view of structural geology two strikingly different environments can be distinguished. In one of them the karstic groundwater body forms in an open
geological structure above the local base level of erosion with a free groundwater table and in this the degree of hydrogeological exposure* of the groundwater body is great. With other conditions more or less favourable, infiltration in this case is unlimited, i.e. direct infiltration is possible down to the groundwater table over the entire extent of the groundwater body of this type (Rakovica, Bele Vode, Sremčica, Rimski Bunar). Under these conditions the groundwater body is directly replenished through precipitation. The groundwater table is free and movement of ground water in the zone above the groundwater table is vertical, while in the zone of the groundwater body it is horizontal towards the lowermost draining channels. Springs are of the gravitational type (see fig. 2). Movement of ground waters is more intensive here than in other localities.

Under these conditions some mineral constituents, mostly carbonates, are leached from limestones under the action of water charged with carbonic acid, water and containing sodium hydrocarbonate is formed as a result. At the same time sulphates and sodium chloride occur in smaller or larger amounts. According to Sulin, this is one of the main genetic types formed in a continental environment. In addition to the characteristics cited waters of this type are distinguished by a comparatively low mineral content, generally below 1 g/l. It should be emphasized that under the conditions considered there are no essential differences between the chemical composition of Sarmatian and Mediterranean-II limestones. A somewhat higher mineral content of the water of Rimski Bunar is a result of the absence of free flow of ground waters. It follows that this type of water (sodium hydrocarbonate) results from intensive leaching of the medium through which the water flows.

The localities Obrenovačka Banja and Ovča differ fundamentally from these. Limestones lie deep below the local base level of erosion in closed or semi-open geological structures. The water-bearing horizon is mostly overlain by impervious clay. (fig. 6). In take areas are at a considerable distance from the point where the water issues on the surface. Groundwater is under pressure so that artesian springs occur.

It is evident that in these almost closed structures ground waters move slowly or very slowly from distant intake areas towards the point of discharge. In contradistinction to the case considered above, here the concentration of chemical constituents is higher. Under these conditions waters have a higher mineral content, a higher temperature and a higher content of specific constituents (H₂S, I and Br, CO₂, CH₄, etc. Structural-geological and hydrogeological conditions are reflected in the specific character of the chemistry of these waters.

It follows that the explanation of the chemical composition of the water of Obrenovačka Banja should be sought in the Sarmatian limestones. The pronounced sodium hydrocarbonate type of water forms exclusively from the sodium sulphate type (Sulin, 1948) through the transformation of sodium sulphate and its carbonate into bicarbonates during the calcium hydrocarbonate stage of leaching. The presence of hydrogen sulphate (H₂S) and ammonium ions (NH₄⁺) can be explained by the presence of organic matter in these waters (of the order of 0.030-0.050 g/l).

A low calcium content can also be explained by the cation exchange which greatly affects the composition of ground waters in sedimentary rocks.

Nevertheless, the chemical composition of the sodium hydrocarbonate type of waters depends on the original composition of waters subjected to desulphatization, the intensity of this process, and on the chemical composition of rocks leached. On the other hand this chemical composition can also be the result of intensive leaching of the rocks through which ground waters circulate and the influence of ground waters from other groundwater bodies in the recharge area which have a similar chemical composition. The organic matter present could also be transported from other recharge areas.

* V. A. Sulin, 1948, suggested the term "degree of hydrogeological exposure of the water-bearing horizon".
Ovča is another locality occurring under conditions of aggravated circulation of water. It differs from all others. Its water belongs to the chlorine-magnesium type, the sodium chlorine group (after Sulin) which indicates that it was formed in marine sediments. This is borne out by its higher I and Br contents and the fact that this locality occurs in the area of regional geological structures conditioning the formation of water of this type. It is striking that sulphates occur in traces as a result of the process of desulphatization. The content of magnesium is higher than that of calcium, while the content of hydrocarbonates is insignificant. Sodium chlorides predominate while magnesium chlorides take the second place with the ratio Na/Cl = 0.97.

Fig. 6 — (a) Geological section of the well B-3 at Obrenovačka Banja (after S. Radojičić and M. Janjić); (b) Geological section at Ovča: (1) Humus; (2) sandy clay; (3) clayey sand; (4) coarse- and fine-grained sand; (5) gravel and sand; (6) Sarmatian limestone; (7) clay.

Thus there are several factors influencing the composition of ground waters. First of all, the conditions discussed above. Next, the transformation of waters of the sodium sulphate type during their infiltration, movement, and leaching of rocks formed in a marine environment, which finally leads to the concentration of sodium chloride. The NaCl content is a result of the "struggle" between the continental and marine regimes.
Here the conditions of the marine environment are rather well preserved although there is a tendency towards the continental regime. The ratio $Na/Cl = 0.97$ approaches 1 i.e. the balance but is still within limits reflecting the marine environment (0.87-1).

In this case, too, a slowed-down movement of ground waters, more complex structural-geological relations, and a different lithological composition of rocks with a higher content of chlorides of sodium and magnesium played a decisive part.

In the survey of groundwater occurrences in Sarmatian and Mediterranean-II limestones we have pointed to essential factors which under given geological-lithological, structural-geological, hydrogeological, physico-geographical and other conditions affect the formation of various types of ground waters of a definite chemical composition. Besides this, they were classified after several authors and these classifications presented schematically in the triangular and Roger's diagrams showing relations between the basic mineral constituents of ground waters.

Special attention has been given to the factors influencing the formation and changes of the chemical composition of ground waters under existing conditions based on their study. The study of the regime of the chemical composition of these groundwater occurrences will be continued.