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THE ORIGIN OF MAGNESIUM IN THE GROUNDWATERS OF NORTHEASTERN BOSNIA

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ABSTRACT

The paper is based on 237 chemical analysis of groundwater, where the determination of magnesium origin in groundwaters of northeastern Bosnia were performed. The determination of magnesium origin in groundwaters were carried through on the basis of Mandel & Shiftan classification. Based on the results, a distribution map of Mg^{2+} ions in groundwaters in northeastern Bosnia were drafted.

Key words: *magnesium, chemical analysis, determination, map, northeastern Bosnia*

INTRODUCTION

Magnesium is a lithophile element which plays an important role in the composition of groundwater and the environment in general. It is usually a dominant Mg^{2+} cation in low-mineralized natural waters and it rarely exceeds 1 gram per liter. The origin of Mg^{2+} comes mostly from sedimentary rocks, such as magnesium carbonate and can also be of igneous rocks, where these ions are segregated in the process of decomposition of silicates (olivine, pyroxene, amphibole, etc.).

The investigated area is bounded by the rivers Sava on the north, Drina on the east, Bosna on the west and Drinjača and Krivaja on the south. The examined area is ca. 6350 km² and belongs to the part of the country with the highest population density (picture No.1).



Picture No.1. The geographic location of the examined area (complemented by Srkalović, D. 2015)

APPROACH AND METHOD

The data used in this research were derived from several sources and investigations conducted in 2015. The groundwaters were sampled at 237 locations across southeast Bosnia. The sampling points included wells, boreholes and springs. Sampling was conducted according to the Drinking Water Health Law Rulebook (Official Gazette of BiH 40/10). All groundwater samples were tested to determine the basic physiochemical parameters and the basic chemical composition. The analyses were conducted at the laboratory of the Public Healthcare Institute Tuzla and the Chemical Engineering Institute Tuzla. The Mg concentrations were determined by ICP-OES method (Inductively Coupled Plasma (ICP) based analytical techniques can provide quantitative bulk elemental composition of a wide variety of sample types, including powders, solids, liquids, and suspensions. Solid samples are generally dissolved or digested using a combination of acids in a closed microwave system, thus retaining potentially volatile analyte species.

The resulting sample solution is then nebulized into the core of an inductively coupled argon plasma, where temperatures of approximately 9000 K are attained. At such high temperatures, the nebulized solution is vaporized, and the analyte species are atomized, ionized and thermally excited. The analyte species can then be detected and quantitated with an optical emission spectrometer (OES), which measures the intensity of radiation emitted at the element-specific, characteristic wavelength from thermally excited analyte atoms or ions. Intensity measurements are converted to elemental concentration by comparison with calibration standards. This technique is especially powerful for quantitative chemical analysis when standards are not available). All data were statistically processed and hydrochemical map of Mg distribution in the area of northeastern Bosnia was generated. The map is generated by using Surfer 12 software. The Mg/Ca ratio is important because it is an indicator of lithological composition of the aquifer. The origin of magnesium in groundwater is given by the classification presented by Mandel & Shiftan, 1981. The origin of magnesium in groundwater is given by the Mg/Ca ratio. If the ratio of Mg/Ca is less than 0.7 - it is assumed that the ground water was formed in limestones.

If the Mg/Ca ratio is in the range 0.7-0.9, the origin of groundwater is from dolomite, and that the increased concentration of magnesium originates from the dissolution of dolomite. Values from 0.9 to 1.0 indicate that the origin of groundwater is from silicate rocks that are rich in magnesium.

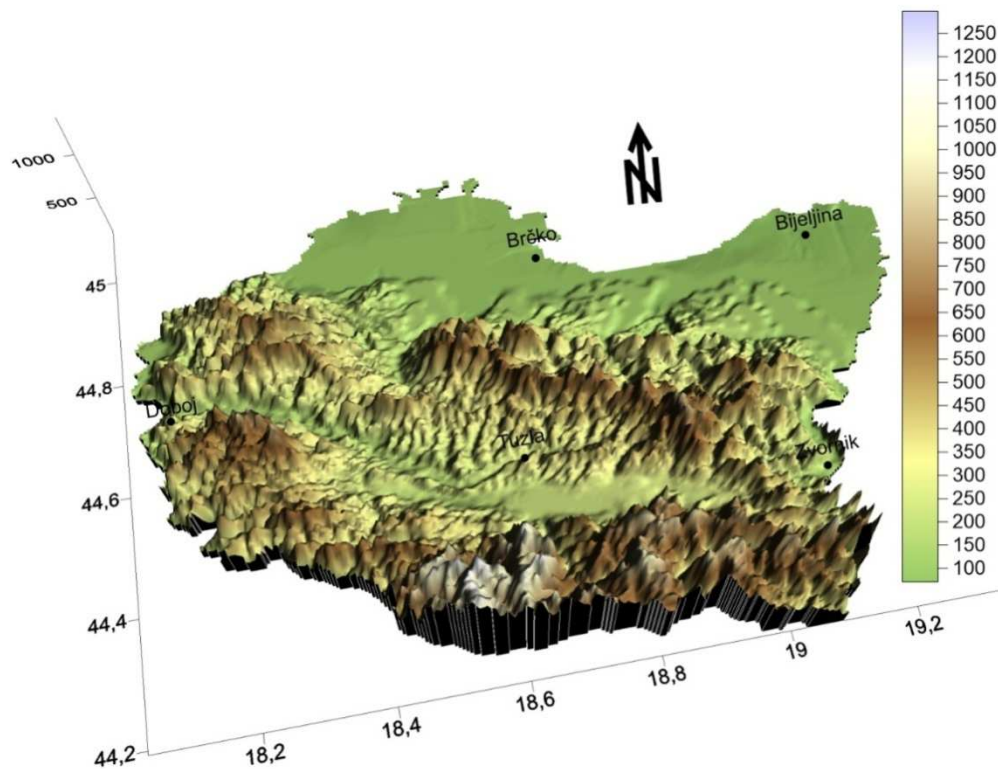
The values over 1.0 indicate that the origin of magnesium in the groundwater is from ophiolites and ultramafic rocks [1].

GEOMORPHOLOGICAL CHARACTERISTICS

The macro-regional area of northeast Bosnia is dominated by the block structure of horsts and grabens, formed by Plio-Quaternary radial tectonics.

The Sava runoff and the lower courses of the rivers Drina, Bosna, Spreča, Tinja and Tolisa are neotectonically directed by right horizontal tectonic shifts of the Sava graben, Spreča fault and the fault of the Drina [2]. The largest river meanders are shaped by lateral erosion of Sava river, the most water-rich stream in Bosnia and Hercegovina, whose average annual flow, downstream from the confluence of Bosnia river, exceeds 1,000 m³/sec [3]. The gradual elevation of the terrain to the south is morphologically expressed by a low foothill hillsides that are directly related to neotectonic older fault-block mountain morphostructures with foreland step: Konjuh 1328 m asl, Ozren 918 m asl, Majeвица 915 m asl and Trebovac 692 m asl [2].

Spatially, the minor depressions of Tuzla, Kotorsko, Doboј, Stanari, Ugljevik and others are orographically surrounded by mountain peaks and low hills. The low positions of basins and macro-regional depressions are expressed by meandering of river beds, floodplains and river terraces.



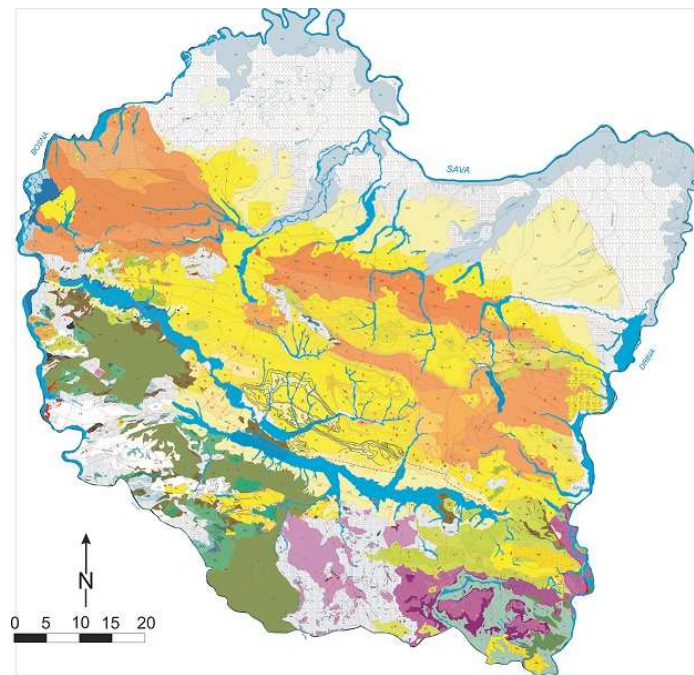
Picture No. 2. The relief of southeastern Bosnia (Srkalović, D. 2015)

GEOLOGICAL CHARACTERISTICS

The study area of northeastern Bosnia is located in Central and Inner Dinarides. Starting from the south in the Central Dinarides, a zone of Paleozoic schist and Mesozoic limestones are separated, followed by Jurassic-Cretaceous and Upper Cretaceous flysch (picture No.3). Northern of these flysches, the Inner Dinarides are spreading, which can be divided into two zones [4].

The first one is the Central ophiolite zone, which the Bosna river intersects at the profile that starts about 5 kilometers northern of Vranduk and ends in the region of Doboј. The second one is northern from Doboј to the Sava river, where the river Bosna is intersected by the formations of horst and graben zone [5]. The formations of the Central ophiolite zone are presented by Triassic, Jurassic and Cretaceous sediments. The ophiolite zone is presented by ultramafic rocks (peridotite, dunite and serpentinite, which is a hydrothermal alteration process of peridotite and dunite) and subordinated gabbros, diabase, basalt and spilite. It is divided into Upper Jurassic ophiolite mélangé, ophiolite complex and the rocks that were deposited over the massif. The mélangé consists of schist - muddy matrix with fragments of greywacke, ultramafites, gabbro, diabase, basalt, tuff, amphibolite, cherts and limestone blocks of various ages and creation environment [6]. The youngest limestone fragments are Tithonian age (J_3^3). In the area of the Bosna river, northern of Žepče, most of the mélangé consists of massive greywacke, whereas in other regions are dominated by limestones. The ultramafic rocks occur in the form of cm to decimeter-sized fragments or as a formation of kilometeric scale and of course as a large masses (100-500 km²), as Krivaja - Konjuh massive, which is divided into several blocks. The thickness of ultramafic deposits varies from a few hundred meters to 2 kilometers. Some smaller ultramafic massifs, such as the Ozren massive shows often more complex structure than the larger massifs [7,8,9].

The entire area of Semberija is located in the alluvial plain of the Drina river, with the altitude of the terrain of 85-90 m, and a uniform geological composition. It consists of sedimentary Quaternary age rocks [10].



Picture No. 3. Geological map of southeastern Bosnia (scale 1:25000) (Srkalović, D. 2015)

HYDROGEOLOGICAL CHARACTERISTICS

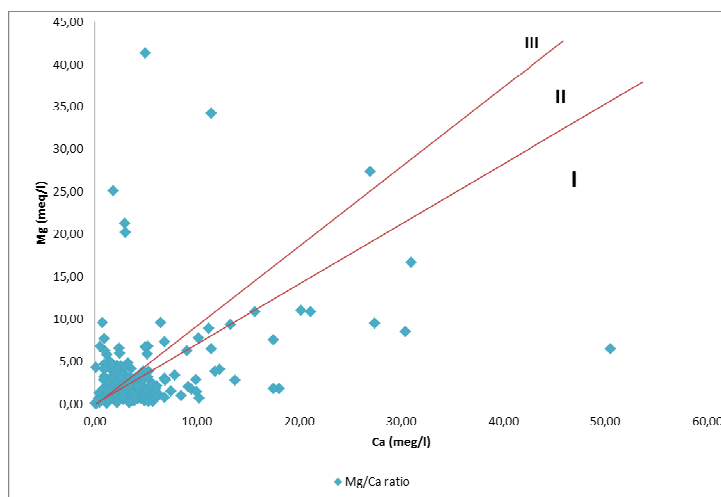
The more extensive accumulations of groundwaters exist in separated deposits of Triassic karstified limestones of the mountains Zvijezda, Javor, Romanija, Ozren, Konjuh and the Gostelja basin, southern of Spreča field. Near Doboј, on the left and right sides of the Bosna river, the fracture-karst porosity of hydrogeological collectors were discovered [5]. In the Spreča river basin, in the source of the left Gostelja tributary, a separate accumulation of groundwater in the middle and upper Triassic limestones were formed. Serpentinites and peridotites represent aquicludes, impermeable rocks, intersected with fissures. Middle Triassic limestones are developed in separate areas at Brateljevići, Turalići and Draguša [11]. In the lower parts of the terrain, on contact with impermeable layers of these limestones, the occasional or permanent sources (Brateljevići, Kladanj and Bjelašnica) are occurring. In the basin of the Drina river, three types of watershed were developed: surface (orographic), underground (hydro) and zonally (hydro) [12]. The surface one passes through parts of the terrain where lithological composition and position of the rocks do not allow the penetration of water into deeper lithosphere. These terrains are made of impermeable Paleozoic, volcanogenic-sedimentary formations and ultramafic rocks. The carbonate complexes of upper Drinjača flow contains separated accumulations of groundwater. The groundwater is drained through springs in settlements Brateljevići, Podpauč, Plahovići, Plazače, Stanići and Lovnica. In the wider area of Kladanj, the most important sources are Podpauč, Pećina and Plahovići. The highest accumulation overflows from the Veliki Bratnik ($Q_{\max} = 20$ l/s). From the mountain Javornik, the water is drained into the river Drinjača by the springs Kulješ ($Q_{\max} = 25$ l/s), Bjelašnica ($Q_{\max} = 40$ l/s) and Lovnica ($Q_{\max} = 10$ l/s). The balance reserves of underground water basin of the Drina river in the territory of Bosnia and Herzegovina, due to the size of the basin in fracture-karst rock mass, is calculated at 4414 l/s. From these balance reserves, about 80% are of the C₁ category, while A and B reserves are accounted at about 20%.

RESULTS AND DISCUSSION MAGNESIUM DETERMINATION

In the study area, the largest concentration of Mg^{2+} are related to ophiolite zone (along the Spreča fault zone), where the origin of Mg^{2+} is from the decaying ultrabasic rocks with forsterite Mg_2SiO_4 and enstatite $MgSiO_3$.

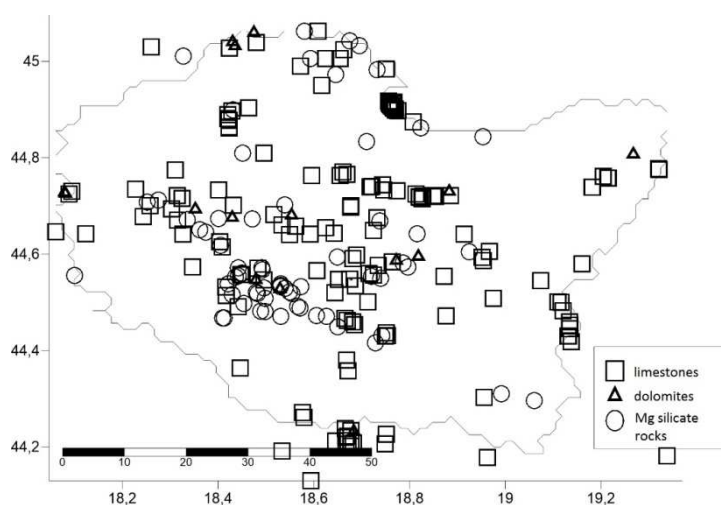
The increased concentrations of Mg ions are in Lendići near Gračanica, well BK-1 near Tuzla, Priboj and Domaljevac. In Lendići, the sediments K₂ are discordant on diabase chert melange, which contains peridotite, diabase, spilite and serpentinite in its composition, which are mainly of the Mg ion sources. Borehole BK-1 is related to the Ophiolite zone. The increased concentration of Mg²⁺ in Priboj has the same origin as the water at Lendići (underlying Cretaceous sediments are the diabase chert melange). In the area of Domaljevac, the magnesium originates from the dissolution of dolomite and limestone deposition (picture No.4 and picture No. 5). The maximal concentration of magnesium is registered on the BK-1 well (Tuzla mineral water) (495,72 mg/l), while the lowest concentration is registered on Gornji Moranjci (0,366 mg/l).

The diagram (picture No.4), indicates that the magnesium in groundwater is formed mainly in limestones and ophiolites, while the dolomite originated magnesium is the least represented. Picture No.5 shows the spatial distribution of magnesium origin in groundwaters. The stake of groundwater formed in limestones 65,4% (cube), the groundwater that is formed in dolomite stakes 6,3% (triangle) and the water from silicate rocks rich in magnesium stakes 28,2% (circle) which originates from ophiolite Krivaja-Konjuh and Ozren complex.



Picture No.4 Mg/Ca ratio. I – Groundwater formed in limestones, II – Groundwater formed in dolomites, III – Groundwater formed in silicate Mg rocks (Ophiolite complex) (Srkalović, D. 2016)

This method can also be used to give the first insight to the geology and hydrogeology in some areas. Also, based on the borehole-log profile, the depth of the groundwater can be determined.



Picture No. 5. Spatial distribution of magnesium in groundwaters (Srkalović, D. 2016)

Analyses of the Mg/Ca ratio of groundwater in the examined area and the identification of the types of rocks in which groundwater occurs, reveals, based on specified theoretical values, that these ratios largely match the geological makeup. It is, therefore, safe to conclude that the Mg/Ca ratio may be used as a parameter for identification of rock types that had a dominant influence on the formation of the chemical composition of the groundwater.

The groundwater with magnesium originating from ultramafic rocks are presented mainly in the area between Tuzla, Banovići, Srebrenik and Gračanica, near Maglaj and partly on the territory of Domaljevac. It may be noted that these rocks are accompanied by silicate rocks rich in magnesium. Magnesium originating from dolomite and those that are formed in limestones, are present in the central, eastern and southern part of the exploration area, and are related to, Triassic, Cretaceous and Miocene carbonates.

CONCLUSION

In order to define the origin of magnesium in the groundwaters of southeastern Bosnia, groundwater samples were taken and processed according to the Mandel & Shifftan (Papić & Petrović) classification. The origin of magnesium is calculated based on the Mg/Ca ratio, which shows that the dominant source of Mg^{2+} ion is from limestones (65,4%), followed by ophiolite complex rocks (28,2%) and dolomites (6,3%). Based on groundwater samples and the Mg/Ca ratio the geology of the examined area is complemented. The maximal concentration of magnesium is registered on the BK-1 well (Tuzla mineral water) (495,72 mg/l), while the lowest concentration is registered on Gornji Moranjci (0,366 mg/l).

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