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Hidrochemical data for the groundwaters in the Radovis valey on the area between the villages Topolnica and Gorno Zleovo, Republic of Macedonia

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Abstract

To determine the quality of ground water in the Radovis valley on the area between the villages of Gorno Zleovo and Topolnica, single samples were taken from 45 locations, 25 water wells, 6 springs, 2 boreholes and 12 hand pumps.

The measured values of pH indicate that water is weakly acidic to neutral (6.5 to 7.6), and the value of TDS, K^+ , Cl^- , SO_4^{2-} , PO_4^{3-} , NO_3^- , NH_4^+ and NO_2^- indicate possible for contamination of ground water from fertilization on agricultural land as well as communal wastewaters.

Knowing the quality of ground water on the investigated area is of particular importance because these springs and water wells are used by residents of this region as water for drinking and irrigation.

Keywords: cations, anions, pH, MPC, temperature, water hardness.

Introduction

Groundwater quality in recent decades has been steadily deteriorating, so it is necessary to make efforts to preserve it. In many parts of the country, the exploitation on ground water as drinking water is denied, because of their contamination by various human activities.

Investigated area is located in the eastern part of Macedonia and covers part of Radovis valley. (Fig. 1).



Fig. 1 Geographical location of investigated terrain.

In the geological structure on the wider environment on the investigated area can be found Precambrian rocks represented by different types of gneisses, micashist, marble; Ryphean-Cambria rocks are represented by schists and phylite, old paleozoic rocks are presented with shist carbonate series, marbles, cipollins, schists, phylite and metasandstone, coarse porfriric metarhyolites and aplitoide granites; cretaceous rocks are presented with limestone and tertiary rocks are represented by clays, sandstone, flysch, andesite and pyroklastite.

Methods and materials

To determine the quality of groundwater in the investigated area during March-April 2012, single samples were taken from 45 locations, 25 water wells, 6 springs, 2 boreholes and 12 hand pumps. pH values were determined with a field digital pH meter, and cations with AES-ICP, Libery 110, Varian. For determination of anions were used standard EPA methods (gravimetric - TDS, volumetric - Cl⁻, spectrophotometric - NO₃⁻, NH₄⁺ and NO₂⁻ and turbidimetric -SO₄²- with spectrophotometer 6715 UV/VIS, Jenway).

Results and discussion

The spatial position of the measured data is displayed in graphical form, based on measured Gauss - Krüger coordinates (x, y) from the locations where the samples were taken. The measured data are compared with Macedonian standards, which were made by pattern of European standards (**MPC-Official Gazette of R. Macedonia Nr. 57 of 27.08.2004 g.**).

pH is an important environmental factor which provides information about many types of geochemical balances (Shyamala et al., 2008). The measured pH values for groundwater are examined in the range of 6.5 (Kodzalija I-1) - 7.6 (from Raklish wells, Pokrajchevo and Zleovo) with median 7.3. In all tested samples the measured values (Fig. 2) are within MPC (maximum permissible concentrations) used by Macedonian standards for comparison.

TDS is used to estimate the total dissolved salts in water (Purandara et al., 2003), which might have an impact on the taste and suitability for applying water for various purposes. The measured values of TDS in the tested water are in range from minimum 97 mg/L in Kodzalija I-1 to maximum value from 2047 mg/L in Pokrajchevo B1 with median 537 mg/L. In all waters except Pokrajchevo B1, TDS values do not exceed the recommended MPC for drinking water, 2000 mg/L. (Fig. 3).

Increased concentrations for total dissolved ionic substances is a consequence from the geology of the ground but indicate possible about the contamination with communal wastewater.

According to WHO, water which contain more than 500 mg/L TDS are not recommended for drinking and can cause some diseases due to excess part of the dissolved salts. (EPA, 2002; Ballester and Sunyer, 2000).

Calcium (Ca²⁺) and magnesium (Mg²⁺). Contents of Ca²⁺ and Mg²⁺ determine the hardness of the water, which is an important parameter for reducing the toxic effects of some elements. In the three samples examined specific content of Ca²⁺ exceeding MPC for drinking water (Ca 200 mg/L), while in 6 tested samples content of magnesium is higher than 50 mg/L in drinking water.

On average, a larger number of samples where the measured concentrations for magnesium is higher than 50 mg/L, compared with calcium (Fig. 4 and 5). The high values for total hardness on the tested waters mainly due to the dissolution of the carbonate rocks.

Sodium Na⁺. Sodium concentration is with minimum value of 4 mg/L in Kalauzlija I-1 until a maximum 153,6 mg/L in the Pokrajchevo B2 with median 22 mg/L. In the all tested water (Fig. 6), the content of sodium is lower than MPC for drinking water (200 mg/L).

Potassium K⁺. Particular range from concentrations of the potassium is very wide (Fig. 7). The minimum value is from 1,08 mg/L in Oraovica Source 3, to the maximum 189,4 mg/L in Podares B4 with median 5,45 mg/L. The content of the potassium is higher than the MPC for drinking water (12 mg/L), in 16 samples.

HCO₃. Values for alkalinity of the the waters is expressed as hydrogen carbonate anions indicates the nature of the salts present in the water. The reasons for alkalinity of the water is dissolution of the minerals from the soil into the water. Different ions have a stake in alkalinity, such as hydrogen carbonate, hydroxide, phosphate, borate, and organic acids. These factors are typical for water resources and natural processes which occur (Sharma, 2004).

Particular range from concentrations of the hydrogen carbonate determined as alkalinity is with the minimum value from 38 mg/L in Podares B2 to the maximum 262 mg/L in Pokrajchevo B1, with median 174 mg / L (Fig. 8).

Chloride Cl^{\cdot} commonly encountered as NaCl, CaCl₂ and MgCl₂ in a large range of concentrations in natural waters. They can also be pollutants of the groundwater, whose source can be sewage water and waste (Shaikh and Mandre, 2009).

Chloride (Fig. 9) is determined in a concentration range from 24 mg/L in Kodzalija source to 512 mg/L in Pokrajchevo B2, with a median 104 mg/L.

Maximum permissible concentrations (MPC) for chlorides in drinking water, according to the rulebook safety of drinking water in Macedonia is 250 mg/L. According to the measured content of chlorides in 10 of the tested samples were measured content higher than 250 mg/L.

Sulphates $SO_4^{2^*}$. Sulphates can be an indicator of water pollution in mining wastewater. Concentration range for the tested sulphates in water (fig.10) is from minimal 1,65 mg/L in Raklish (hand pump 1) to maximum 697 mg/L at Topolnica (hand pump 1) and with median 29,2 mg/L. Only the concentration of sulphate anions in water Topolnica (hand pump 1) exceeding the MPC for drinking water. Probably because it is near to the copper mine "Bucim." PO_4^{3-} . The results from the measurements of the concentrations of dissolved phosphorus (expressed in form of phosphate) ranging from minimum 0,02 mg/L (Raklish B1 and Radovish P2) to the extremely high value of 4,75 mg/L (G. Zleovo B1), with a median 0,18 mg/L (Fig. 11). Only 9 of the tested samples exceed the content of phosphates from MPC for drinking water (0,91 mg / L).

The higher values from MPC, are unusual for the presence of phosphate in natural waters, and their increased concentration indicates possible contamination of water with fertilizers and pesticides.

Nitrates NO₃. Concentrations of nitrates in the water indicate biological contamination of water. The range of concentrations of certain nitrate anions (Fig. 12) is from the minimum value of 0,361 mg/L in Radovish P4 to maximum 461 mg/L in Podares B5 with median 31 mg/L. In 19 of the 45 tested samples measured values for nitrate anions exceed the limit value of 50 mg/L according to the MPC.

Obtained values in the tested samples indicate a greater saturation of groundwater with organic matter as a result of pollution with municipal wastewater, wastewater from farms or pollution by fertilizers which contain nitrate anions.

Nitrite NO₂. Nitrite ions (Fig. 13) were detected at concentrations higher than MPC in 28 of 45 examined samples of groundwater, with a maximum concentration from 0,069 mg/L in Raklish B3. $\mathbf{NH_4^+}$. Ammonium ions are indicators of the dynamics of self-purification of contaminated waters.

Ammonium ions are detected in the 25 tested samples (Fig. 14), with a maximum concentration from 0,202 mg/L in G. Zleovo B6. Only two trials (G. Zleovo B6 and Raklish B3) are determined content for ammonium ions higher than the MPC value in drinking water 0,1 mg/L. According to the classification of Alekin most of the tested waters by anion fall into hydrocarbons - chloride class, according cation in calcite - magnesium group.

Conclusion

Based on the obtained values for the content of TDS, K⁺, Cl⁻, SO₄²⁻, PO₄³⁻, NO₃⁻, NH₄⁺ and NO₂⁻ in samples from groundwater in the area between the villages Topolnica and Gorno Zleovo in Radovis valley can be concluded that in the most of the tested samples were observed higher concentrations from MPC for drinking water. Increased concentrations of these components indicate anthropogenic pollution of these waters from fertilization of agricultural land, livestock farms, copper mine "Bucim" as well as communal wastewater.

It is necessary to do additional research to determine the quality of groundwater in this area by expanding the analyzed parameters, and based on it, to take appropriate measures to prevent further contamination.

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Fig.10. Spatial distribution of SO4²⁻/mgL⁻¹ Fig.11. Spatial distribution of PO4³⁻/mgL⁻¹



Fig.12. Spatial distribution of NO₃^{-/mgL⁻¹}







Fig.14. Spatial distribution of NH₄⁺/mgL⁻¹