Hydrogeochemical characteristics of waters in connection with natural radioactivity of volcanoclastic sediments and metamorphic complex in the part of South Serbia – geoecological status

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Introduction

A regional hydrogeochemical prospecting and verifying of radioactive anomalies, based on aerogamma-spectrometry, morphostructural analysis and geological characteristics, were carried out in an area of the central Serbo-Macedonian Massif. The prevailing formations in the study area are crystalline schists with intrusions of granitoids, then a narrow belt of Upper Cretaceous sediments in the northern half of the region, and less extensive Tertiary volcanoclastic sediments in the south.

Well developed hydrography, presence of deep faults as paths of atmospheric and ground water circulation, developed oxidation zone particularly in Tertiary sediments, have conditioned the criteria for a hydrogeochemical prospecting.

The goal of the prospecting was to increase the depth of the regional geochemical prospecting, using dominantly the ground water data, and thus possibly register "concealed" indications of the uranium mineralization or ore bodies. It is important to remark that exploration area encompassed several inhabited places, thus the investigation results are of special interest for estimation of the risk factor for population existence of that area.

Geological and structural characteristics

Basic parts of the sedimentary complex in the northern part of investigated area are built of tuffaceous sandstones, limestones, dolomite and sandy shales overlain by conglomerates and sandstones. In the eastern part the volcanic-sedimentary formation consists of conglomerates, greywackes, coarse-grained sandstones, sandy shales, slates, sandy limestones and red tuffs. Clastic sediments are composed of volcanic rocks fragments, feldspars grains and rare fragments of crystalline schists. Tuffs are crystalloclastic and lithoclastic with grains of plagioclase, pyroxene, biotite and quartz.

The metamorphic complex represents a geosynclinal sequence that was under influence of magmatism and metamorphism up to amphibolite facies. This complex consists of fine-grained biotite gneisses, leptites, mica schists, quartzites, migmatites and locally intruded granites along regional structures (Slatinska Reka).

Several large tectonic units were singled out in crystalline schists: Vetetnica dislocation belt, the dome of Vlajna, zone of Vrvi Kobila and west limb of Juzna (South) Morava sinclinorium. Vertical movements of some blocks of Serbo-Macedonian Massif enabled restoration of longitudinal faults during Tertiary and transverse and diagonal faults and formation of grabens (Leskovac, Juzna Morava, Poljanica) at the beginning of Neogene. This phase is characterized by volcanic activities.

Materials and methods

The hydrogeohemical prospecting was carried out in two stages:

The first stage of regional geochemical prospecting (500 km^2) was carried out in a network relative to the hydrographic features, that included all surface streams, springs, shallow and deep aquifers (1909 samples) and 1754 alluvial samples. Water samples were analysed for uranium concentration and Eh, pH and Ep values.

The second stage of prospecting was the verification of radioactivity anomalies in both ground and surface waters. Besides radioactive uranium, radium, and radon elements as direct indications of uranium mineralization, also secondary indicators were examined, such as chemical type and character of aqueous media, general mineral rate in water, microelement and gas concentrations.

For hydrogeochemical analytical data processing, the model of mathematical statistics (table 1) was used. The data were processed and related to the corresponding rock complexes (table 2).

Several analytical methods were used. Determination of uranium in stream sediments and waters was performed by laser fluorimeter (LA UA-3) with fluran as characteristic reagent. Chemical analyses of metal were carried out by following methods: Atomic Absorption Spectrophotometry (AAS); Atomic Emission Spectrophotometry (AES); Inductive Coupled Plasma — Atomic Emission Spectrometry (ICP-AES).

Results and Discussion

Uranium concentrations and physical and chemical parameters of water were established (on 1909 samples) in the first stage of the regional hydrogeochemical prospecting in the area of sedimentary and metamorphic complex.

The average values of U content, pH, Eh, Ep in the water draining Paleogene (Pg), Neogene (Ng) and Quaternary (Q) sediments and the metamorphic rock complex are given in table 2.

Hydrogeochemical prospecting detected a number of radioactive anomalies in the study area as those in the sedimentary rocks of the Lepenca-Jovacka River area (fig. 1) and in the metamorphic rocks of the Slatinska River area. The U distribution and Ep values are represented by dispersion haloes on hydrogeochemical maps, which also show the percentage of samples with anomalous values in some classes.

Average Ep was 442.3 μS/cm in the sedimentary and 166.7 μS/cm in metamorphic complexes.

For areas of radioactive anomalies, water samples with increased U and newly collected samples were examined on: U, Ra, Rn, pH, Eh, Ep, anion-cation composition, gases and microelements, SiO_2 and general mineralization. The values of U, Ra and Rn concentrations in the radioactive anomaly area were: for sedimentary complex U 0.2 μq/l to 270 uq/l (X=17μg/l), Ra 0.053 to 0.355 Bq/l (X=0.142 Bq/l), and for Rn 7.1 to 88 Bq/l (X=28 Bq/l); for metamorphic complex U 0.2 to 28 μq/l (X=0.39 μq/l), Ra up to 0.355 Bq/l, and Rn 53.32 Bq/l, in the Slatinska River area.

The analysed microelements in water were: lead, zinc, copper, strontium, lithium, rubidium, manganese, iron^{2+}, chromium, aluminum, phosphorus, bromine and iodine. While most of these constituents were found in normal concentrations, those of zinc, lithium, strontium, and phosphorus were increased.

Microelement concentrations in water draining sedimentary rock complex are: zinc 0.01—0.4, X=0.34 mg/l, MPV=0.1; lithium 0.1—0.35, X=0.055 mg/l; strontium 0.05—6.5, X=1.15 mg/l; phosphorus 0.01—1.28, X=0.148 mg/l, MPV = 0.03 mg/l. In few samples, manganese content achieves up to 14 mg/l. Correlated with average microelement concentrations in natural waters of the Earth· crust, the obtained by us values allow to suggest that these microelements can be used as direct indicators for uranium mineralization in the study area.

The analyzed waters are predominantly of hydrocarbonate-sulphate and, rarely, sulphate-hydrocarbonate types. The prevailing cations are those of Ca and Na, which classify the water as sodium-calcium type. The calcium-magnesium and magnesium-calcium types are subordinate. Other cations contained in small amounts are those of potassium, trivalent iron, and ammonium (NH_4).

Waters with increased uranium content, which drain particularly the volcanoclastic sediments, were analyzed for carbon dioxide, CO_2, oxygen, O_2, and hydrogen sulphide, H_2S. The increased uranium in water is associated with the increased carbon dioxide, which may be as high as 205.92 mg/l, O_2 from 0.48 to 8.69 mg/l, and H_2S from 0.07 to 0.44 mg/l. Gases in metamorphic rocks (the Slatinska River

Table 1. Hydrogeochemical characteristics of water

Source	Number	Eh(mV)	pH	Ec(μS/cm)	U(μg/1)	MPV U(μg/1)
Springs	550	+150 to +200	6.2 to 8.5	33-1600	0.1-164	50
Wells						
(<6m)	31	+165 to +190	6.7 to 8.1	140-860	0.2-270	50
(6-20)	126	+160 to +200	6.4 to 8.3	200-4200	0.1-90	50
(>20m)	21	+160 to +195	6.5 to 7.7	110-1800	0.2-70	50
Surface streams	1181	+160 to +200	6.3 to 8.8	36-130	0.1-170	50

Table 2. Hydrogeochemical characteristics (Eh, pH, Ep, U) of water in sedimentary and metamorphic rock complexes

Complex	Eh(mV)	pH	Ec(μS/cm)	U(μq/l)
Sedimentary	+150 to +200	6.3 to 9.0	58 to 4200	1.74
Metamorphic	+160 to +195	6.1 to 8.6	33 to 1100	0.39

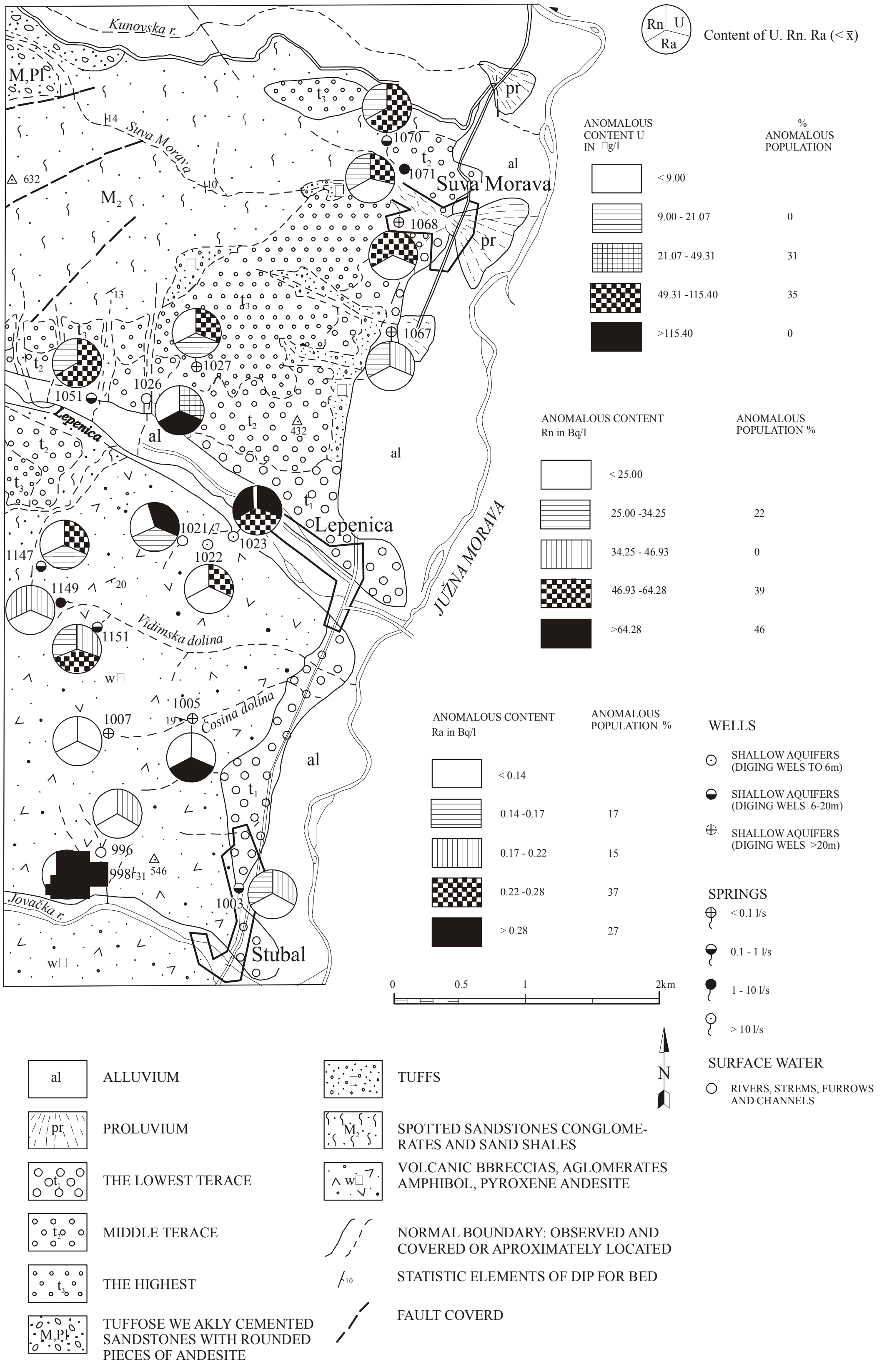

Fig. 1. Hydrogeochemical map of U, Ra, Rn contents

anomaly) vary: 5.72 to 15.84 mg/l CO_2, 4.37 to 8.11 mg/l and 0.08 to 0.20 mg/l O_2.

Mineralized waters (500-1000 mg/l) contain also increased U concentrations, associated with the increased SiO_2 ranged from 15.3 to 69 mg/l.

Although the average U contents in the waters of sedimentary and metamorphic complexes are low (table 2), anomalous U concentrations, higher than MPV which is 50 μg/l, were detected in ground and surface waters of certain locations. Obtained results represent one of the risk factors for local inhabitants and it is important element in defining the ecological status of the area.

The hydrogeochemical prospecting took place along with sampling from the alluvion for assay of U concentration which is: from 0.4 to 8.09 g/t (X=1.17 g/t) for sedimentary rocks, and from 0.4 to 7.5 g/t (X=1.08 g/t) for metamorphic rocks.

The map of electrochemical conductivity (Ep) of waters shows the areas of increased mineralization, which are in direct contact with the areas of preferential ground water flows, i.e. the areas of highest permeability. The increased Ep in subsurface and surface waters is consistent with the anomalous U concentrations in them (fig. 1).

Waters with increased uranium are predominantly of hydrocarbonate type, because at pH 8 it is a very active dissolver of all uranium minerals. The alkaline rock/water interaction provides for dissolution of the uranium silicate minerals. The increased presence of cations, particularly of Na, Ca and Mg, can be associated with weathering processes in volcanoclastic rocks which enhance the water aggressiveness to the media flown through or over.

The increased carbon dioxide in water is partly associated with the late phase of the volcanic activity, and partly resulted from a chemical process of sulphide oxidation which produced sulphuric acid, H_2SO_4 and this product reacted with carbonates releasing carbon dioxide. The increased carbon dioxide and the presence of carbonates contribute to the solubility of all uranium minerals and their leaching from adjacent rocks, particularly volcanoclastic sediments, into underground and less into surface waters.

The obtained data (table 1) show variable U concentrations, depending on water drainage. The water drainage fluctuation amplitudes depend on the precipitations over the year, which cause and intensive water-exchange. Thus, the concentration of individual chemical components is relative to the time.

Mixing of ground and surface waters increases oxygen which characterizes the system in relation to oxidation conditions. Lowering of the oxidation zone deeper under the surface is associated with the active ground/surface water exchange and consequent uranium leaching from adjacent rocks and re-deposition deeper underground. The analysis of secondary haloes of uranium dispersion is related to geostructural, geochemical, geophysical, and hydrogeological characteristic of the ground where minor deep-infiltration uranium deposits can be expected (the Lepenica-Jovacka River).

Conclusion

1. The hydrogeochemical prospecting for radioactive elements revealed several radioactive anomalies in 8 Pg, Ng and Q sediments and metamorphic rocks.
2. Hydrogeochemical anomalies in metamorphic rocks are weaker then those in sedimentary rocks, but not less important.
3. The verification of radioactive anomalies included identification of the mechanism of the secondary haloes of U dispersion formation and the U migration and precipitation in geochemically suitable media.
4. The knowledge of the process that leads to the formation of hydrogeochemical haloes of U dispersion facilitated the selection of radioactive anomalies for detailed investigation.
5. U, Ra and Rn content anomalies that were singled out in waters in accordance with MPV values represent one of parameters for defining ecological status of smaller inhabited places of investigated area.

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