We are IntechOpen, the world's leading publisher of Open Access books
Built by scientists, for scientists

5

Hydrogeological-Geochemical Characteristics of Groundwater in East Banat, Pannonian Basin, Serbia

Milka M. Vidovic and Vojin B. Gordanic
The University of Belgrade, The Institute of Chemistry, Technology and Metallurgy, Department for Ecology and Technoeconomics
Serbia

1. Introduction

Eastern Banat is the eastern part of Vojvodina Province, southern belt of the Pannonian Basin, a surface area of some 505 km^2 in NE Serbia (Fig. 1). It is rolling country at altitudes between 75 and 100 metres. The largest positive morphologic feature is Vrsac Mountains that extend eastward to the Romanian-Serbian border. The Mountains occupy an area of 170 km^2 surrounded by Mali Rit and Markovac stream in the north, Mesic and Guzijana ranges in the south, Vrsac suburbs in the west and Serbian-Romanian border in the east.

Major hydrographic features on the southern Vrsac Mountains are the streams Guzijana and Fizes by the Romanian border and the Mesic stream that drains most of the given area. The Mesic brook is 11.4 km long from the spring at el. 194 m and drains an area of 31.9 km^2. Highest peaks are Vrsacka Cuka (399 m), Botija Plate (469 m), Vrsacki Vrh (590 m) and Kudricki Vrh (641 m).

Major surface streams in the area are the Karas, across the area south of Vrsac Mountains, and the Nera, south of Bela Crkva. Both streams run from Romania and their discharges depend on the respective spring flows, or atmospheric precipitations over the year.

Southern Banat was prospected (Ivkovic, 1960) for the hydrogeological map of Vojvodina (Map scale 1:500,000, 1957). Background information on groundwater chemical composition in SE Banat, and Vojvodina, was reported in the sixties (Milojevic, 1963).

Most informative data on geology and production of groundwater from the aspect of data collecting and interpretation are those from Vrsac and Bela Crkva areas in eastern Banat, the SE Pannonian depression in Serbia. The Vrsac water supply source at Pavlis village was explored by drilling wells B-1 through B-17, preparing a Report with an estimate of the water supply demand by Vrsac municipality to 2005 and examining a source of low-mineral water at Mesic village (Lazic, 2010). The field works included tens drilled wells in which the water-bearing layers were deep between 27 and 110 metres, the maximum depth being about 220 metres (Vrsac). Deepest well in Bela Crkva area was 115 metres, with the water-bearing intervals from 43 to 111 metres.

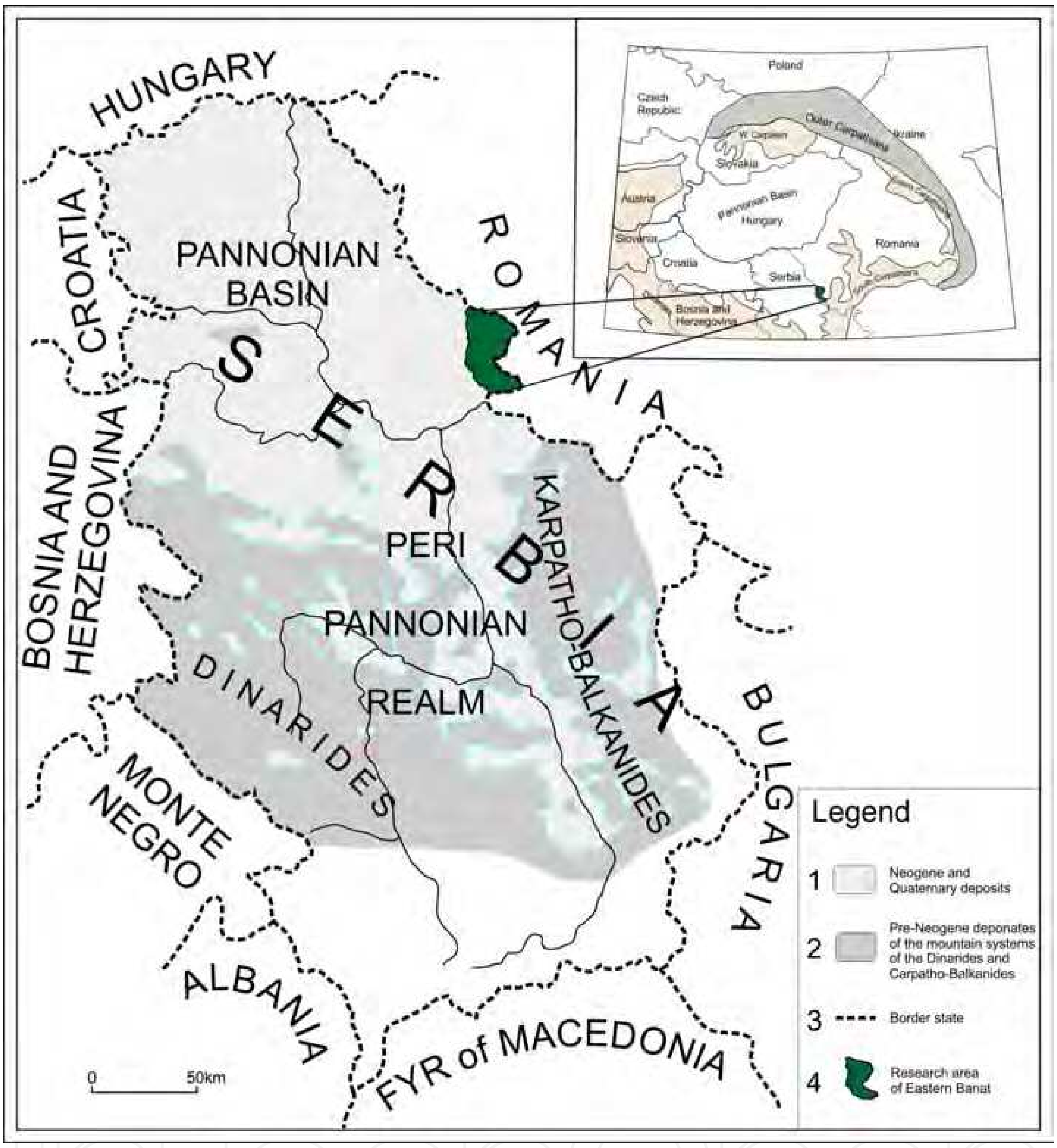


Fig. 1. Serbian part of the Pannonian Basin and the southern margin (Marovic, 2002; Dolton, 2006)

Regional investigations also yielded information about chemical composition of subsurface and surface waters (Puric & Gordanic, 1980; Cvetkovic & Gordanic, 1986; Gordanic & Jovanovic, 2007). Geochemical characteristics are particularly important for small municipal water supply systems, in view of the established elevated natural radionuclides of ^{238}U, ^{226}Ra and ^{222}Rn (on Vrsac Mountains) and other toxic elements exceeding maximum allowed concentrations (MAC) (at Bela Crkva) (Vidovic, 2007).

Extreme concentrations of U, Pb, Zn, Au and Ag, measured during the geochemical prospecting of metallic and non-metallic minerals, are correlative with the metallogenic nature of the region. There are Pb, Zn, Au and Ag mineral occurrences in eastern Vrsac Mountains in particular.

2. Methodology

Hydrogeological prospecting includes preparation of hydrogeological maps, chemical analyses of water from springs, wells and test-wells/boreholes, and continuous observation of water table fluctuation in wells, delineation of groundwater body and establishment of its type based on pumping tests.

Geochemical prospecting included sampling from different geochemical media mapped on the base geological map at scale 1:100,000 and other target maps of different scales (Fig. 2). More intensive investigation, made in Vrsac greater area for municipal water supply, was focused on lithology surveyed in boreholes (Figs. 3 and 4) and chemical analysis of groundwater (Tabs. 1 and 2).

Chemical analyses were used to classify water after Alekin (Fig. 5 a,b,c) for the Pavlis and Mesic sources (Fig. 6).

Geochemical prospecting used lithogeochemical, metallometric and hydrogeochemical techniques. For geochemical analyses samples were correlated of rocks (80 samples), stream sediments and humus (647 samples), springs (71 samples), wells (483 samples), surface streams (788 samples) and boreholes (14 samples). The results are presented on geochemical maps.

Similar results for Vrsac Mountains are given in Tab. 3.

Redeposition of natural radionuclides in the heterogeneous environment of Vrsac Mountains is expressed as $^{232}Th/^{238}U$ (Fig. 7).

The obtained concentrations of ^{238}U, ^{40}K and ^{232}Th were used to assess the effect of external equivalent of the ionizing radiation dose by Monte Carlo method (Tab. 4). Applying conversion factors for ingestion and inhalation, radionuclide intake (determined by radiometry) and the fatal cancer risk were assessed for 100,000 inhabitants for minimum and maximum activities (Tab. 5).

The parameters ^{238}U concentration, pH, Eh and Ep (Tab. 6) are determined for each water sample. Moreover, 165 samples were analysed for anion-cation composition, contents of microelements (Pb, Zn, Cu, Mo, Li, Sr, Ni and Co), of radioactive elements (U, ^{226}Ra and ^{222}Rn), of F, Br and I, dissolved oxides (SiO_2), mineral matter in water, hardness, gases CO_2, H_2S, O_2 and Rn, which were measured in the field. The excessive U, Ra and Rn concentrations in water and respective pH are given in Tab. 7 for Vrsac Mountains.

Concentrations of U, ^{226}Ra and ^{222}Rn in water (Fig. 8 a,c) are detected using two methods:

- Laser fluorometry (uranium analyzer Scintrex UA-3); the method (U-Fl-1 "Geoinstitut") measures uranium fluorescence provoked by added fluoran (inorganic phosphorous complex) that acts as a buffer for pH 7; and
- Emanometry (emanometer RDU 200 with ionization chamber) measures radium and radon in a scintillation chamber (vol. 160-170 ml) made of silver-activated ZnS. The instrument is calibrated to Bq/L unit using radium salt solution of a pre-selected concentration for three standard measures: 1, 10 and 1000 Bq/L. The obtained equivalent of 0.2489 Bq/L for 1 i/min is multiplied by the values read from the instrument.

Relative relationship of U and redox potential in water from excessive uranium areas is shown in Fig. 9, and excessive Zn, Sr, Li and Mo concentrations in relation to natural water are given in Tab. 8.

The analytical methods applied were the following:

- AAS (Atomic Absorption Spectrophotometry) for Ag, Au, Bi, Cd, Co, Cr, Cu, Mo, Na, Ni, K, Pb, Sb, V and Zn;
- AES (Atomic Emission Spectrophotometry) for Cs, Li and Rb;
- ICP-AES (ICP Atomic Emission Spectrophotometry) for B, Ba, Be, P and S.

Samples were prepared with open digestion and mineral acids or their mixtures were used for destruction. The agent used to destroy samples tested on Ag, Au, Bi, Cd, Co, Cu, K, Mo, Ni, Pb, Sb, Zn and V was aqua regia (HNO_3 : HCl). Modified aqua regia was used in destruction of the samples from which P and S were determined, and sample digestion with HF, HNO_3, $HClO_4$ to identify B, Ba, Be, Cr, Cs, Li, Rb and Sr.

Radiometric analysis for ^{238}U, ^{232}Th, ^{40}K concentrations in rocks (80 samples) used scintillation detector 4x4 Bicron with a NaJ crystal and a multiplier tube (MCA; 4096 channels) Ortec 7500 (Tab. 3, Fig. 8 b). The instrument measures flashes of a high-energy (0-3 MeV) agent. The calibration of spectra and the count of natural radionuclides, compared to the standards for uranium and thorium minerals, are NBL No. 103 0.005 % U and NBL No. 107 0.10 % Th and relative Th/U are shown in Fig. 7. The potassium standard used was potassium chloride (p.a., Merck).

3. Results and discussion

3.1 Geologic – Structure features

The geotectonic setting of Vrsac and Bela Crkva town areas is a depression formed in the early Miocene with intensive rising of the Carpathians, Dinarides and Alps (Fig. 2). The intermountain subsided and was invaded by the Mediterranean Sea. The communication with the Mediterranean Sea ceased in the late Miocene and the formed Pannonian Sea turned first into a brackish and later into a freshwater water body (Nikic & Vidovic, 2007). Neotectonic positive movements formed the horsts of Fruska Gora (a part of the Vardar Zone) and Vrsac Mountains (part of the Serbian-Macedonian Massif). The Pannonian basin has the floor pattern of minor troughs and horsts. The Vrsac Mountains and Bela Crkva sub-region is built largely of Miocene, Pliocene and Quaternary deposits with projecting Vrsac Mountains of crystalline schist and granite (Vukovic, 1965; Rakic, 1978).

Crystalline schist was found in the petroleum test wells on Vrsac Mountains at depths from 890 to 1100 metres under sedimentary rocks. The complex of crystalline rocks dated Precambrian or Lower Paleozoic underwent metamorphism during the Hercynian Orogeny. It is composed of gneiss, schist, phyllite, granite and granitic gneiss. Pegmatite, and aplite and leptynite associated with finegrained gneiss.

The Miocene (Upper Miocene, Pannonian), unconformable and transgressive over the Lower Paleozoic schist, consists of sands, clays and silts. Lower Congerian Beds or Pannonian (caspibrackish) deposits have the largest distribution east of Bela Crkva.

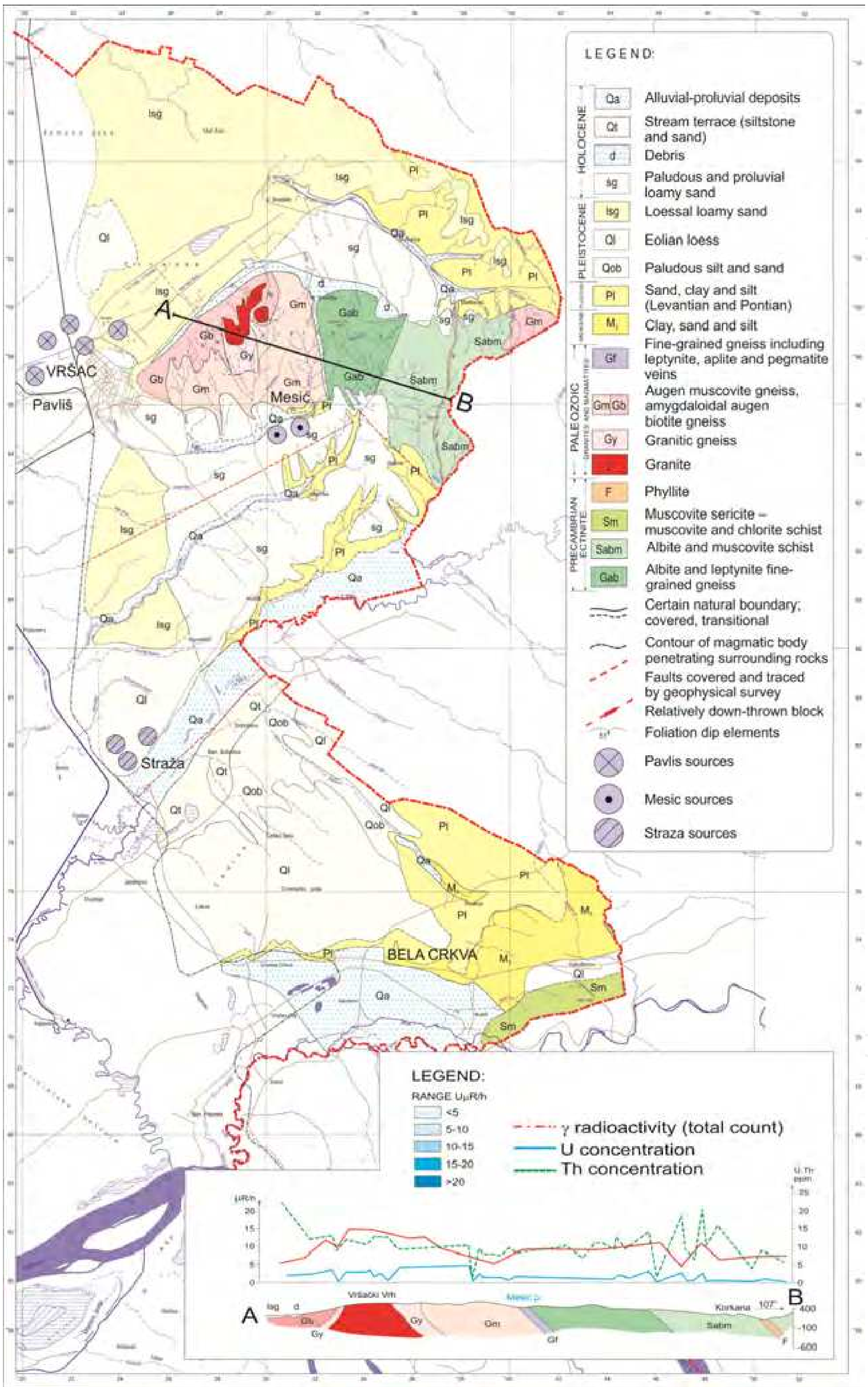


Fig. 2. Geological map of Vrsac and Bela Crkva areas (Scale 1:100,000) (Vukovic, 1965, Map compilation by Gordanic, 1980)

The Pliocene is represented by Pontian and Levantian deposits that form freshwater aquifers, which extend over the southern and central Banat and eastward into Carpathians of Romania (Vukovic, 1987). Levantian deposits with freshwater bodies are unconformable over the Pannonian, composed of gravel and sand tens of metres thick. Their lithofacial character indicates fluvial-lacustrine sediments. Lower Pliocene (Pontian) is exposed in the villages of Gudurica, Markovac, Socica, Kustilj and Jablanka near Bela Crkva, on the northern and southern Vrsac Mountains ridges and from Gudurica to Vojvodinci along the Romanian border. Minor outcrops are located at the Mesic village (IBD-1/01).

Upper Pliocene (Levantian), recognized mostly in boreholes, are gravel and sand, variable in thickness and extensive near Bela Crkva.

The Quaternary, both Pleistocene and Holocene deposits cover some 70% of the geochemically prospected Vrsac-Bela Crkva area.

Pleistocene deposits are paludous silt and sand (Qob), eolian loess (Ql) and loessal loamy sand (Lsg).

Holocene deposits form the northern and southern Vrsac foothills and extend along small and large streams (Mesic, Guzijana, Nera and Karas). Their heterogeneous composition includes paludous and proluvial loamy sand (Sg), detritus (d), stream terraces (silt and sand, Qt); alluvial-proluvial deposits (channel facies, gravel, sand and silt overbank deposits, Qa).

Two large structural units occupy the region: Rhodope, built of crystalline schist of low metamorphic grade (Rakic, 1978), and Banat or Banat-Morava unit a neoalpine structure, both extending from NE to SW, which is the main trend of the structural features (Askin, 1967) formed in result of the crystalline bedrock fracturing during the Savian and Pyrenean Orogenies.

Tectonic events of different intensities, from the Oligocene-Miocene to the present, formed horst and trough features in numerous faults. The Pavlis source area is in a deep trough that formed between the horst range Velika Greda-Jermenovci-Lokve-Nikolinci-Tilva and Vrsac Mountains, in which different chronostratigraphic units were brought to the same level. Further subsidence and diagenetic processes during the Quaternary developed a shallow surface depression, the Alibunar-Vrsac depression.

3.2 Hydrogeological characteristics

Different aquifers are related to the regional geological-structural and geolithological features of the rock masses and their porosity. Bodies of rocks that contain and conduct groundwater are either water-table or artesian aquifers.

3.2.1 Water-table aquifer

Phreatic water in the Vrsac municipality occurs in:

- alluvial deposits from the Karas (Filipovic, 2003), Guzijana, Boruga, Markovac, Moravica (minor intermittent streams), which are heterogeneous (sand, gravelly sand, clay soil, sandy clay and mud) and have transmissibility coefficient (T) up to $22x10^{-3}$ m^2/s;

- eolian sand of the Deliblato Sands (Filipovic, 2003) SW of the prospected area; its filtration coefficient (K) range is from $1x10^{-4}$ m/s to $2x10^{-4}$ m/s;
- loessal deposits of 35% to 45% porosity between Potporanj-Uljma and Deliblato Sands, SW of the area.

Unconfined groundwater has been used for water supply to households on the territory of Vrsac Municipality. The depth to groundwater is between five and ten metres. The water table contours are comparable with the topographic contours, only the slope of the water table is gentler than that of the land surface. Water table contours indicate directions of the groundwater drainage to the lower lands where are the local base levels of erosion (the streams Karas and Nera and the Danube-Tisa-Danube Canal). Diffuse aquifers are fractured Paleozoic schistose rocks of Vrsac Mountains and east of Bela Crkva. The complex of schistose rocks had been much deformed by multiple folding of a structure in NE and SW directions with minor local deflections. Rocks heavily fractured at the surface have fractures and cracks mostly filled with weathering waste. The density and size of cracks decrease with the depth nearly to the point of disappearance of water table. Groundwater is recharged almost entirely from precipitations and is discharged to small morasses or at intermittent springs. Most of precipitation runs off or evaporates, with only a very small amount percolating underground.

Very weak springs of less than 0.1 L/s occur some 50 to 100 metres down the hilltops or their occurrence is secondary. The spring-discharge fluctuation is small because the capacity of aquifers is small. A change in the water-yielding capacity of the aquifer involves other modifications such as water temperature, chemical composition (amount of minerals), etc. Classified by the water-yielding capacity of aquifers, this area is assigned to the low-yield group from 0.1 to 1.0 L/s per discharge point.

Surface streams that are draining the area run from NE to SW, same as the trends of the structural features. Groundwater flows through the weathering crust mainly in the same direction towards the local base level of erosion. Unconfined water does not occur below the base level, not even in fractures intersecting the area.

Groundwater is dominantly HCO_3-Ca-Mg, low mineralized (0.4 to 0.5 g/L), neutral (pH 7), contained in an unconfined hydrogeologic body of intensive water exchange, so that individual chemical constituents are susceptible to transformation with the time.

3.2.2 Artesian aquifer

A Neogene complex of Miocene lithological varieties more than a thousand metres thick forms an artesian water body between Miocene or Paleozoic crystalline schist and intrusive granite, where Miocene deposits are lacking, and 30-100 metres thick Quaternary.

Dense-rock aquifers are mostly Tertiary or Quaternary intergranular sand deposits, like in borehole IBD-1/0 at Mesic village (Fig. 3), either water-table (shallow, phreatic) or confined (deep, artesian or subartesian) aquifers.

A shallower artesian aquifer, less than 200 metres deep, is formed by Upper Pliocene water-bearing rocks that are not clearly differentiated from other rocks, because water-bearing layers occur at different depth intervals in boreholes within short distances.

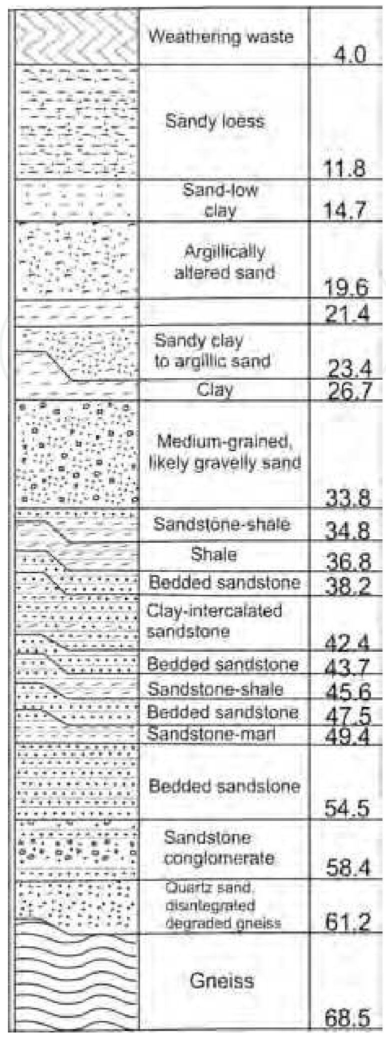


Fig. 3. Columnar section for borehole IBD-1/01 in the Mesic village (Lazic, 2002)

The groundwater body is difficult to outline, because it extends into Romania on one side and throughout the Pannonian basin on the other side. Its southern boundary is the Danube, and the eastern boundary is Vrsac Mountains (the SW offsets of the Carpathians) and a crystalline massif near Bela Crkva. Characteristic geological and hydrogeological sections beneath Quaternary deposits in Vrsac area near the artificial lake are reconstructed on the data from RB-1 and B-1 test-wells. Lithology of Paludine-Levantian sands under Quaternary deposits consists of the following intervals: 0-23 m Quaternary complex (clay, gravel, sand); 23-42 m grey-green sand; 42-44 m clayey sand; 44-67 m grey-green fine- to medium-grained sand on gravel; 67-73 m grey-green silty to fine sand; 73-96 m grey clay; 96-121 m grey medium-grained sand; 121-174 m grey clay; 174-188 m grey coarse quartz sand; and 188-220 m grey clay. The depth of good hydraulic properties is between 23 and 67 metres, particularly interval 44-67 m, confirmed by pumping test in well RB-1 (Milivojevic, 2004).

The hydrogeological setting is indicated by drilling data from B-1 (Gordanic, 1980) (Fig. 4).

On the profile of the borehole (Fig. 4), there was found four water-bearing horizons, which are mutually hydrogeological different. Deeper than these lithological members, there are water-bearing layers, which are not included from the point of these studies.

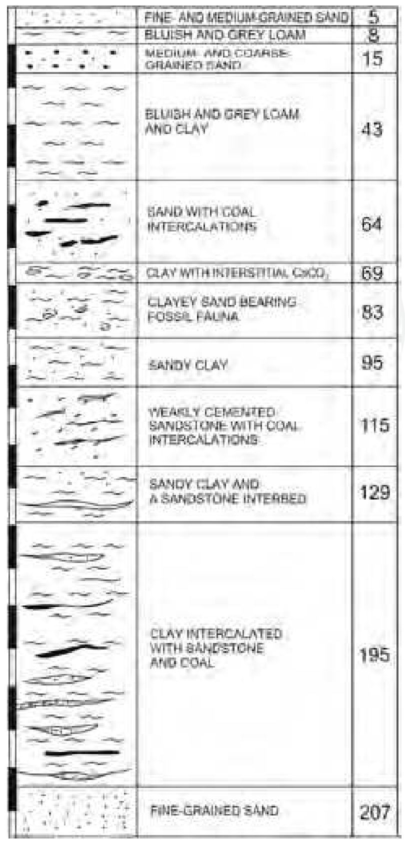


Fig. 4. Columnar section for borehole at the Vrsac artificial lake (Gordanic, 1980)

The Vrsac borehole (Fig. 2) penetrated four different water-bearing layers: Upper Pontian, Levantian and Pleistocene clay-sand deposits form several confined (artesian and subartesian) aquifers to a depth of 300-400 metres from the surface. Mineral salts and temperature of water are increasing with the depth, yet this is the main source of domestic and industrial water supply. Moreover, the prevailing hydraulic system is complex. Strata of deposits that include confined water bodies are interrelated because of the frequent vertical and lateral variations in facies. Horizontal and vertical communication of confined groundwater has also hydraulic connection with the shallow unconfined groundwater. Artesian water-bearing layers, established on the Vrsac Mountains margin, dip to the central basin along fault zones, which provides for overflow of mineral-high water from deep into the shallow layers. The test hole near the artificial lake at Vrsac produced water from the depth of 200 metres that had mineral content 6.91 g/L and temperature of 24ºC. Groundwater from the same depth in Banat, only unaffected by overflow from deeper aquifers commonly contains 1.1 to 1.6 g/L dissolved mineral material. Water from deep aquifers in Vrsac area moves along the contact of Tertiary deposits and crystalline schists and overflows into the shallower Pliocene aquifers of lower confining pressure.

The main groundwater reservoir (both artesian and subartesian) is replenished directly by percolating atmospheric precipitations on Vrsac Mountains margin and Bela Crkva area, and in Romanian side by infiltration from rivers. Indirect replenishment by precipitations occurs from water-table aquifer in the Deliblato Sands and on the loess plateau. Groundwater recharge during piestic low of the main reservoir in the Alibunar-Vrsac depression is small, indirect from the overlying semipermeable layer and from drainage canals.

Groundwater circulation is slow, decreasing from the Neogene basin borderland where water ^{14}C dated was 1100 years old (Gudurica). Further from the edge of the basin, the water age increases to 6950±160 years in Potporanj and 9900±100 years at Pavlis.

Groundwater in the main reservoir is chemically characterized by low TDS, with dry residue 280-420 mg/L, locally about 600 mg/L, pH 7.4-7.6 units. Total hardness varies from 12 to 16.5 °dH. The $KMnO_4$ rate is low, not exceeding 5 mg/L. Ammonia is always higher (0.6-1.2 mg/L) than MAC, and local concentrations of iron and manganese are 2.2 and up to 0.15 mg/L, respectively. Other mineral constituents are within the standards for drinking water.

3.3 Hydrochemical exploration of main groundwater reservoir

Results of the hydrochemical exploration are presented for the main reservoir in the Pavlis source and aquifers in the Mesic areas.

3.3.1 Pavlis source area

Groundwater in Pavlis area is used for municipal water supply to Vrsac and to small communities in the surroundings. Water production started in 1961 in an area bordered by the Keveris and Veliki Kanal and the village of Pavlis. A Feasibility Study was prepared in 1987, a water supply projection to 2005 needed by the growing town and its industry, from the main groundwater reservoir. On the basis of the Study, the source area has been extended to the present 17 wells (B-1 to B-17).

The production of 10 L/s at first increased to 180 L/s. When the Study was prepared, a drawdown of about 0.5 m/yr was recorded in the Pavlis area. The exploitation regime at Pavlis is considered to be “relaxed”, about 16 hours per day on average. Chemical composition of water was analysed previously in relation to the regime of production. Before 1977, only wells B-7 and B-8 in the main reservoir were analysed. After 1977, seven new wells were drilled from which natural water from the main aquifer has been analysed. The parameters analysed are: Na^+, K^+, CaO, Ca^{2+}, MgO, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, Fe, Mn, NO_3^-, NO_2^-, NH_3, F, SiO_2, pH, hardness, Ep, $KMnO_4$ consumption and M (mineralisation). Water quality deterioration has not been registered for any parameter in the given period.

Chemical composition of groundwater in Pavlis source area is expressed by Kurlov formula (1) (Slimak, 2005) as:

$$M_{0.284}\frac{HCO_{97}^{3}Cl_{3}}{Ca_{42}Mg_{31}Na+K_{27}}=t_{16.7} \quad (1)$$

and Table 1 gives the quality parameters resulting from chemical analyses for wells B-17, B-6 and B-7 in Pavlis source.

The amount of oxidizing organic substances is expressed by $KMnO_4$ consumption, the highest recorded being 3.1 mg/L for well B-7. The critical inorganic parameters are ammonia ion and Mn, which are excessive in each sample. Concentrations of heavy metals are at the detection level for the applied method.

PARAMETER	Test Results		
	B-17 1 July 2004	**B-6 1 Nov. 2004**	**B-7 31 Mar. 2005**
Colour, °Pt-Co	-	-	< 5
Odour and taste	-	-	+
Turbidity, NTU	< 0.6	< 0.6	0.55
pH	7.4	7.7	7.6
Oxidizability, mg $KMnO_4$/L	0.7	1.8	3.1
Temperature, °C	16.5	16.8	15.7
Dry residue, mg/L	312	417	430
Electrical conductivity, µS/cm	494	624	703
Hardness, °dH	12.2	17.5	18
Sulphates, mg/L	< 1	< 1	0.7
Ammonia (NH_4), mg/L	1.5	1.7	1.58
Arsenic (As), mg/L	< 0.005	< 0.005	< 0.004
Copper (Cu), mg L	< 0.002	< 0.002	< 0.01
Barium (Ba), mg/L	< 0.4	< 0.4	
Bromides (Br), mg/L	< 0.01	< 0.01	
Cyanides (CN), mg/L	< 0.002	< 0.002	< 0.01
Zinc (Zn), mg/L	< 0.005	< 0.005	< 0.01
Fluorides (F), mg/L	< 0.2	0.24	0.24
Phosphates (P), mg/L	< 0.03	< 0.03	0.01
Chromium total (Cr), mg/L	< 0.005	< 0.005	< 0.001
Chlorides (Cl), mg/L	9.7	14.2	20
Hydrocarbonates, mg/L	518	378	482
Cadmium (Cd), mg/L	< 0.002	< 0.002	< 0.001
Calcium (Ca), mg/L	85.4	54.5	72.5
Potassium (K), mg/L	9.3	5.6	2.1
Cobalt (Co), mg/L	< 0.005	< 0.005	
Lithium (Li), mg/L	< 0.01	< 0.01	
Magnesium (Mg), mg/L	40.1	29.7	34.3
Manganese (Mn), mg/L	0.15	0.21	0.11
Sodium (Na), mg/L	38.5	33.5	47.4
Nickel (Ni), mg/L	< 0.005	< 0.005	< 0.01
Nitrates (NO_3), mg/L	< 0.5	< 0.5	< 0.5
Nitrites (NO_2), mg/L	< 0.005	< 0.005	< 0.005
Lead (Pb), mg/L	< 0.005	< 0.005	< 0.01
Silicates (SiO_2), mg/L	35.0	34.1	28.18
Silver, mg/L	< 0.005	< 0.005	
Strontium, mg/L	< 0.05	< 0.05	
Mercury (Hg), mg/L			< 0.001
Aluminium, mg/L	< 0.01	< 0.01	< 0.05
Iron, mg/L	0.2	0.15	0.04

Table 1. Hydrochemical analysis of groundwater for Pavlis source

In Alekin classification, groundwater from the Pavlis main reservoir is hydrocarbonate-calcium-magnesium water, its chemistry in the reported period (Fig. 5 a, b and c).

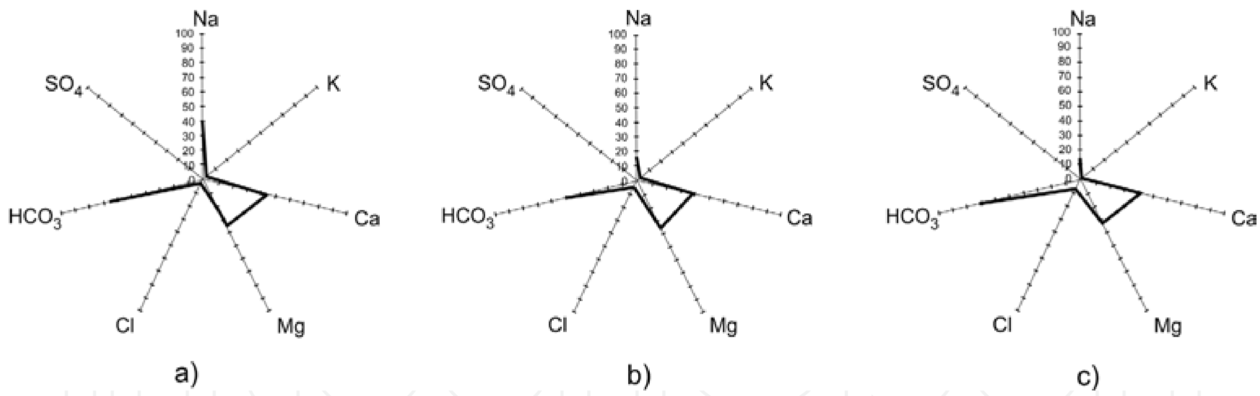


Fig. 5. Groundwater from Pavlis source in Alekin classification. a) Well B-17 on 1 July 2004; b) Well B-6 on 1 Nov. 2004; and c) well B-7 on 31 Mar. 2005

3.3.2 Mesic source area

Artesian aquifer (the village of Mesic) is located on the southern side of Vrsac Mountains. Water is pumped from three rock units: crystalline schist, gneiss, Neogene deposits and Quaternary alluvial deposits of the Mesic brook.

A structural feature in the area is a fault with the northern block of some 20 metres relative downthrow. The Mesic Brook runs from the source in southward direction from the fault, then deviates 90º to SW. In context of local geology and hydrogeology, groundwater reservoirs must have formed in an open structure, and in semi-open Pleistocene quartz sand. Based on the geological setting, porosity of lithostratigraphic units and hydrodynamic conditions, the types of groundwater bodies (Lazic, 2010) are the following:

- Compact water-table aquifer of considerable water-yielding capacity in alluvial deposits of gravel and sand;
- Compact subartesian aquifer of smaller water-yielding capacity in Pontian and Pleistocene sand deposits (IBD-1/01 Mesic); and
- Fractured-rock aquifer of low water-yielding capacity in muscovite gneiss.

Table 2 gives chemical data of groundwater from test/production well IBD-1/01 in a low-capacity aquifer, for period 2008-2009. The water-bearing formation is largely quartz sand in two layers (lower/basal and higher/upper) at different depths, whose total thickness in test/production well IBD-1/01 is some 10 metres.

The main water-bearing formation consists of two (lower and upper) layers of about 10 m total thickness in test well IBD-1/01 area of influence. The formation is overlain by Quaternary clay and sand 10-15 m thick (26.7 m in the well-influence area) and underlain by crystalline schist. Loam is a kind of confining bed for the surface Mesic brook surface water. Groundwater in this formation is under mild subartesian pressure from the mentioned upper layer.

Pressure in the lower layer of quartz sand is somewhat higher, to 1.5 m below the surface, although IBD-1/01 is 2-3 m higher than BD-1/02. This water-bearing layer, where sands under a thin cover lie near the surface, is replenished by atmospheric precipitations that infiltrate from the crushed and fractured contact zone with crystalline schist.

PARAMETER	Well IBD-1/01 test results			
	25 Mar. 08	26 June 08	13 Apr. 09	12 Oct. 09
Temperature, °C	-	15.2	15	15.3
Colour	clear	< 5	< 5	< 5
Turbidity, NTU	< 0.6	0.1	0.2	0.2
pH	6.3	6.4	6.3	6.2
$KMnO_4$ consumption, mg $KMnO_4$/L	1.3	0.3	0.4	1.2
Dry residue at 180°C, g/L	0.185	0.177	0.17	0.191
Electrical conductivity, µS/cm	247	250	250	250
Free hydrogen sulphide (H_2S), mg/L	< 0.02	< 0.02	-	< 0.02
Free carbon dioxide (CO_2), mg/L	-	69	82.8	99.7
Total hardness, °dH	6.70	6.30	6.10	6.10
Hydrocarbonates (HCO_3), mg/L	134	130.5	122	129.3
Nitrites (NO_2), mg/L	< 0.004	< 0.006	< 0.006	< 0.006
Nitrates (NO_3), mg/L	15.7	16.2	17.5	18.1
Chlorides (Cl^-), mg/L	9.3	10.4	9.2	10.4
Sulphates (SO_4^{2-}), mg/L	14.4	11.9	12.3	15.2
Ortho-phosphates(P), mg/L	< 0.06	< 0.02	0.03	< 0.02
Fluorides (F), mg/L	< 0.1	0.022	< 0.05	0.09
Phenols, mg/L	< 0.002	< 0.001	< 0.001	< 0.001
Arsenic (As), mg/L	< 0.005	< 0.001	< 0.001	< 0.001
Copper (Cu), mg/L	< 0.05	0.002	< 0.002	0.003
Zinc (Zn), mg/L	< 0.005	0.0014	0.004	0.009
Iron (Fe^{++}), mg/L	0.05	0.027	0.001	< 0.004
Total chromium (Cr), mg/L	< 0.002	< 0.001	< 0.002	< 0.002
Cadmium (Cd), mg/L	< 0.001	< 0.0005	< 0.0008	< 0.0008
Calcium (Ca^{2+}), mg/L	28	31.7	30.8	30.7
Potassium (K^+), mg/L	1.1	1.08	1.14	1.19
Magnesium (Mg^{2+}), mg/L	6.8	8	7.6	7.89
Manganese (Mn), mg/L	< 0.01	0.0006	< 0.0002	< 0.0002
Sodium (Na^+), mg/L	5.6	11.3	10.7	11
Nickel (Ni), mg/L	< 0.001	< 0.004	< 0.006	< 0.006
Lead (Pb), mg/L	< 0.005	< 0.007	< 0.005	< 0.005
Mercury (Hg), mg/L	-	< 0.0005	< 0.0005	< 0.0005

Table 2. Hydrochemical analysis for well IBD-1/01 in the Mesic source area

Groundwater is assigned on the basis of chemical results (Tab. 2) to the group of hydrocarbonate-calcium-magnesium water of the Alekin classification. In cationic composition, calcium ions (28-31.7 mg/L) are dominant, followed by 6.8-8 mg/L Mg, then 5.6-11.3 mg Na^+/L and 1.08-1.19 mg K^+/L. In anionic composition, hydrocarbonate ions are dominant in concentrations from 122 to 134 mg/L. Sulphate ions are 11.9 to 15.2 mg SO_4^{2-}/L, and chloride ions are 9.2-10.4 mg Cl^-/L.

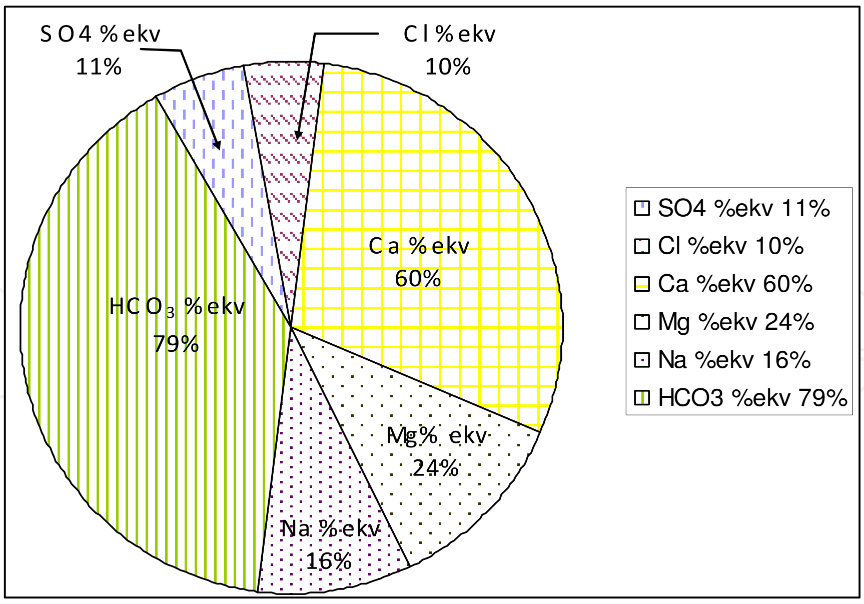


Fig. 6. Circle graph of the principal anion and cation mean concentrations in water from IBD-1/01 at Mesic village in the observation period (from March 2008 to October 2009)

Stability of chemical macro-composition or of individual constituents is based on the proportion of minimum and maximum concentrations of some elements expressed by the stability coefficient (K) for the period from March 2008 to October 2009.

The coefficient of stability is determined only for cations and anions and may be expressed by Kurlov formula. Its value does not exceed 5%, viz.: 6.1056% $K_{Ca^{2+}}$, 7.9234% $K_{Mg^{2+}}$, 29.534% K_{Na^+}, 4.653% K_{HCO3^-}, 12.268% $K_{SO4^{2-}}$ and 6.1069% K_{Cl^-}. These coefficients indicate stable chemical composition of water in the 'compact low-capacity aquifer' drained by well IBD-1/01. This refers to the dominant anions and cations (HCO_3^-, Ca^{2+} and Mg^{2+}) which qualify the type of water. The type of water from IBD-1/01 is hydrocarbonate-calcium-magnesium, written as (Kurlov formula):

$$M_{0.18}\frac{HCO_{79}^{3}SO_{11}^{4}Cl_{10}}{Ca_{60}Mg_{24}Na_{16}} = t_{15.15}Q_{0.9} \quad (2)$$

In relation to the pumping coefficient ($Q_{0.9}$), the water resource is classified as "economic" or "B reserve" (Lazic, 2010).

3.4 Geochemical exploration

Geological-radiometric profiling and different geochemical prospecting techniques, adjusted to the given geological-structural setting, indicated areas of extreme metallic mineral and natural radionuclide concentrations in Vrsac Mountains. Two zones of elevated U, Mo, Pb (1-360) ppm), Zn (1-1800 ppm), Ag (1-48 ppm), Au (0.02-0.24 ppm) were detected in gneiss in the eastern part of the area (Gordanic, 1980).

Occurrences of deposits and veins of hydrothermal quartz with pyrite, magnetite and chalcopyrite in salbands at the contact with schist were located south of Gudurica in Vrsac

Mountains. Geochemical anomalies for W (3000-5000 ppm) and Mo (up to 250 ppm) were detected in granitic gneiss near a granite intrusion, south of Vrsac peak (Botija Plate). Concentrations of ^{238}U, ^{232}Th, ^{40}K, total uranium (Ut) and dissolved uranium (Ud) are determined (Tab. 1) in samples collected during the radiometric profiling (Gordanic, 1980; Spasic-Jokic & Gordanic, 2010a).

	GRANITE AUGEN BIOTITE GNEISS (Gb) GRANITE - GNEISS (Gy) i AUGEN MUSCOVITE GNEISS (Gm)			**ECTINITE** ALBITE LEPTYNOLITE GNEISS (Gab) ALBITE MUSCOVITE SCHIST (Sabm)		
	min	**max**	**mean**	**min**	**max**	**mean**
^{238}U, ppm	0.58	5.57	1.81	0.25	4.41	1.78
^{232}Th, ppm	0.22	22.2	7.66	0.84	22.08	9.75
^{40}K, %	1.82	5.39	3.75	0.27	9.92	1.75
Ut, ppm	0.2	22.0	1.31	0.1	7.6	0.55
Ud, ppm	0.1	21.0	0.71	0.1	2.1	0.40

Table 3. Radiometric results for granite-migmatite and ectinite-gneiss (Gordanic, 1980)

Natural radionuclides have a log-normal distribution in the heterogeneous environment of the Vrsac Mountains. Concentrations of uranium in granite-migmatite indicate its redistribution in the older metamorphic rocks during a long geological period, or it resulted from subsequent hydrothermal and metasomatic processes. Dominant character of Th is represented in relation to U on a Th/U diagram in Fig. 7.

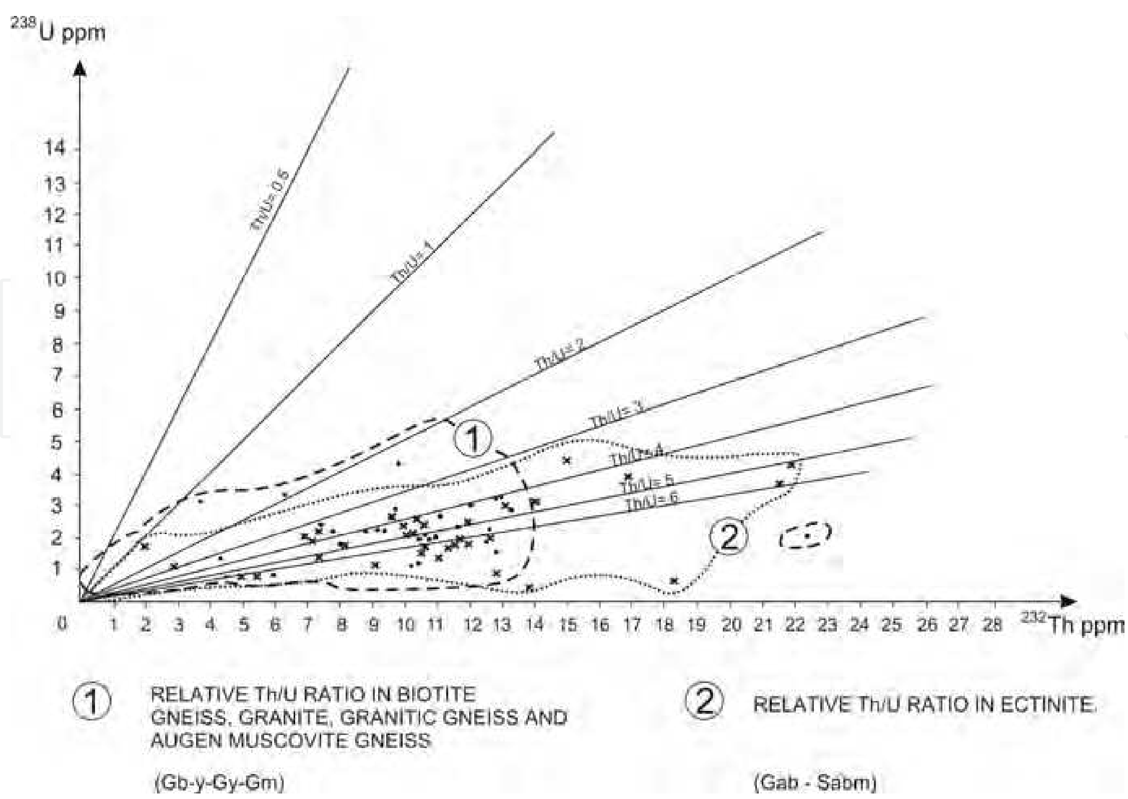


Fig. 7. Diagram of relative Th/U (Gordanic, 1980)

Potassium is twice higher in gneiss than in ectinite, a likely consequence of metamorphism with the supply of magmatic melts and fluids during the Hercynian Orogeny.

The effect of natural nuclides on rural environment was assessed on the Vrsac Mountains using the Monte Carlo method (Spasic-Jokic & Gordanic, 2010a) to establish external equivalent of the ionizing radiation dose 1 m above the ground, which depicts the natural environmental radiation; this in view of the natural uranium concentrations of 99.284% ^{238}U + 0.711% ^{235}U + 0.0058% ^{234}U and negligible other isotopes. Annual effective doses from ingestion (UNSCEAR, 2000) are given in Tab. 4.

INGESTION	Average (UNSCEAR, 2000)	Bela Crkva and Vrsac (present study)
^{40}K, μSv	0.17	0.004
U and Th series, μSv	0.12	0.017
Total ingestion exposure, μSv	0.29	0.021

Table 4. Annual effective dose from ingestion of terrestrial radionuclides

The effective doses for ingestion in Table 4 are lower than those of UNSCEAR.

Applying conversion factors for ingestion and inhalation, radionuclide intake (determined by radiometry) and the fatal cancer risk were assessed per 100,000 inhabitants for minimum and maximum activities (Zupunski et al., 2010; Spasic-Jokic & Gordanic, 2010b) (Tab. 5).

SOURCE	ACTIVITY (Bq)		RISK INHALATION		RISK INGESTION		Normalized on 100,000 Inhabitants	
	mean	range	mean	range	mean	range	mean	range
^{238}U	13.5	1.60-36.0	$0.9x10^{-5}$	$(0.1-2.3) x10^{-5}$	$47.1x10^{-8}$	$(5.7-126) x10^{-8}$	0.9	0.1-2.4
^{232}Th	21.1	1.70-45.2	$2.3x10^{-5}$	$(0.2-5) x10^{-5}$	$6.10x10^{-8}$	$(0.40-11) x10^{-8}$	2.3	0.2-5
^{226}Ra	12.8	1.60-34.8	$0.8x10^{-5}$	$(0.1-2.3) x10^{-5}$	$44.9x10^{-8}$	$(5.5-122) x10^{-8}$	0.9	0.1-2.4
^{40}K	490	42.4-1560	$0.3 x10^{-5}$	$(0.02-0.8) x10^{-5}$	$28.3x10^{-8}$	$(2.5-93) x10^{-8}$	0.3	0.02-0.9

Table 5. Absolute fatal cancer risk assessments after exposure to radionuclides ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K

The triple higher Ut concentration in granite and gneiss than in ectinite suggests a primary source of uranium. Favourable pH, Eh, Ep (Table 6) must have provided for uranium leaching from adjacent rocks, migration and precipitation in suitable geochemical environments.

Parameter	Min	Max
U, ppb	0.1	166
pH vrednost	5.5	7.9
Eh, mV	- 65	+ 190
Ep, mSv	160	4545

Table 6. Water analysis during the regional hydrogeochemical prospecting

The presence of augen biotite gneiss (Gb) around the granite intrusion on Vrsac Mountains, then the presence of granite varieties, largely altered by sericitization, muscovitization and feldspathization a younger phase of which is expressed through albitization, are the reasons for elevated U, ^{226}Ra and ^{222}Rn concentrations in water of the following anomaly zones:

- Socica-Korkana-Markovac,
- Mesic-Malo Srediste and
- Vrsacka Kula-Mali Rit.

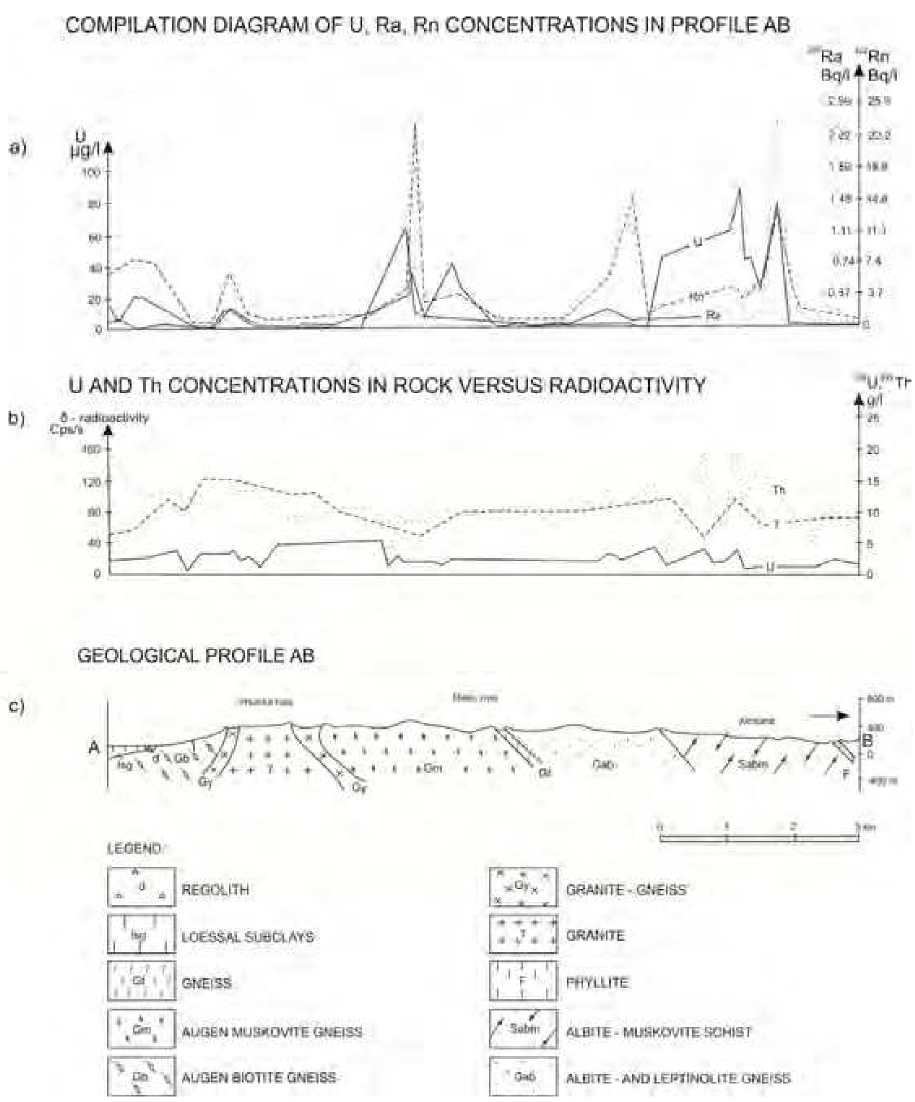


Fig. 8. a) Compilation diagram of extreme concentrations of uranium in water and b) U and Th in rocks related to the c) geologic-structure setting (Gordanic & Zunic, 1994)

The exploration data were used to delineate anomaly zones, for which geological section A-B is drawn Fig. 2 that shows the proportions of radionuclides in water and rocks. Proportions of U, Ra and Rn concentrations in water of the anomaly zones, radioactivity and U and Th concentrations in rocks are diagrammatically represented in geologic section AB, Fig. 8 a, b, c (Gordanic & Zunic, 1994).

Concentrations of U, Ra and Rn in well and spring waters of Vrsac and Bela Crkva areas are given in Tab. 7.

Classified by anionic and cationic composition (Kurlov formula), depending on the quality, waters in the exploration area range:

$$\text{from } \frac{HCO_3 - SO_4 - Cl - NO_3}{Ca - Mg - Na + K} \text{ to } \frac{SO_4 - HCO_3 - Cl - NO_3}{Na + K - Mg - Ca}.$$

Parameter	Range	Mean
U, ppb	0.1 - 166	4.2
^{226}Ra, Bq/L	0.02 - 5.92	0.11
^{222}Rn, Bq/L	0.74 – 3.33	2.74
pH	5.9 - 7.9	7.2

Table 7. Concentrations of U, Ra and Rn in waters and pH for Vrsac and Bela Crkva areas

Waters with excessive concentration of uranium have pH from 6.5 to 7.6. The range of dissolved minerals in water is from 138 mg/L to 4557 mg/L. Uranium-high waters are mainly low in dissolved mineral materials (< 1 g/L), only few are > 1 g/L to 5 g/L, suitable for uranium migration in an aquatic environment. The amount of SiO_2 in water of the anomaly zones is about 30 mg/L, which is related to the weathering zone, and somewhat higher (up to 99 mg/L) in water in contact with structural features.

The oxidation-reduction potential (Eh), determined in each water sample, varies within the range from -65 mV to +190 mV. The diagram of relative Eh and uranium relationship (Fig. 9) shows that waters in extreme zones are dominantly oxidizing, with Eh from 130 mV to 170 mV. Such an environment enhances uranium solution from adjacent rocks, which is manifested in the extreme concentration zones. In view of the metallogenic character of the explored area, waters were analyzed on concentrations of the microelements Zn, Pb, Cu, Sr, Li, Mo, Ni, Co, F, Br, I, Fe^{2+}, Fe^{3+} and SiO_2. Elevated concentrations of Zn, Sr, Li and Mo can be used as direct indication of concealed ore bodies and of uranium mineral (Tab. 8). Other analyzed elements were found in ore or less standard amounts for natural waters.

Elevated Li, Sr, U, Ra and Rn are related to the nearness of a granite intrusion, a zone of fine-grained gneiss with leptynite, aplite and pegmatite veins. The presence of Li in subsurface and surface waters may be an indication of pegmatite deposits in respect of extreme U, Mo, Pb, Zn and Ag contents in gneisses (Hawkes & Webb, 1960), which are potential sources of elevated concentrations of radioactive elements in waters.

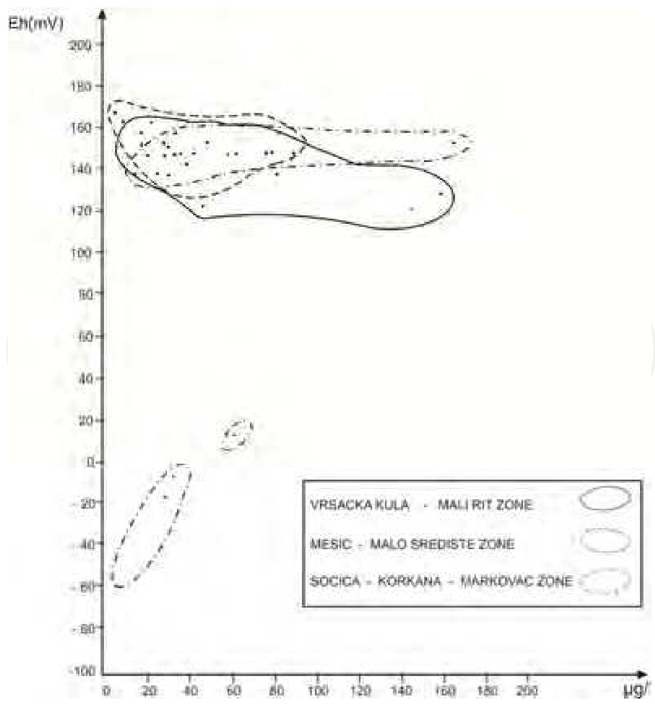


Fig. 9. Relative relationship of redox potentials in waters of extreme uranium concentration zones (Gordanic, 1980)

	min	**max**	**Mean**	**NATURAL WATER, (Hawkes & Webb, 1960)**
Zn, ppb	3	3800	13	1 – 200
Sr, ppb	30	3250	300	-
Li, ppb	3	60	5	0.3 – 3
Mo, ppb	1	14	2	0.05 – 3

Table 8. Amounts of Zn, Sr, Li and Mo in water

Unconfined groundwater in Upper Pliocene (Levantian) deposits of Bela Crkva is pumped for domestic water supply in small communities. Water in most wells (3-34 m deep) is below the MAC standard for drinking water (Drinking Water Regulations, Official Gazette SRY No. 42/98 and 44/99) being highly mineralized, with elevated amounts of nitrogen compounds, high conductivity and concentrations of heavy metals: Pb, Cd, Ni, Br, Al (Vidovic, 2007). Anionic and cationic compositions of waters are dominantly HCO_3-SO_4-Cl to HCO_3-Cl-SO_4, and Ca-Mg to Ca-Na, respectively. Particularly elevated are the amounts of NH_4, NO_3, NO_2, SO_4, K, Ca and F (in Kustilj and other minor communities). Water in all wells is oxygen-high between 3 and 13.1 mg/L. The effect of human activities is manifested at the water-table level. Large communities, such as Bela Crkva, supply water from drilled wells in which the depth to water table varies from 43 to 111 metres.

4. Conclusion

Controlled by the geological-structural setting of the region, groundwater bodies have formed on Pontian-Levantian deposits that extend over the southern, central and eastern

Banat and further to Carpathian offsets in Romania. Zones of groundwater recharge are the following:

- Deliblato Sands, percolation of precipitation;
- Vrsac Mountains offsets (in water-bearing layer exposures), and
- Carpathians offsets in Romania (in aquifer exposures).

Groundwater drainage in the Vrsac-Bela Crkva area operates through groundwater bodies in:

- overbank deposits from the Nera and Karas streams, or
- rises through the overlying less permeable layer to the shallower aquifer in a large confined area of groundwater (piezometric surface above the land surface),
- through many flowing wells and
- water-intake facilities.

The zones of extreme natural U, Ra and Rn radionuclides are related to the geological-structural and metallogenic features of Vrsac Mountains and have no effect on the Pavlis groundwater source for supply to Vrsac and its suburbs.

The identified extreme concentrations of Pb, Zn, Mo, Ag, Au and W in Vrsac Mountains have no effect on groundwater in Pavlis area.

Total concentrations of ΣU, ^{232}Th and ^{40}K are used to assess the fatal cancer risk per 100,000 inhabitants exposed to ingestion and inhalation of natural radionuclides in soil. Measured concentrations UNSCEAR, 2000) in the region of Vrsac Mountains are within the allowed range. This information is important for the geomedical status of the region and for other environmental-geochemical research.

Extreme concentrations (above MAC) of Pb, Li, Sr, Mo in groundwater of Vrsac Mountains are noteworthy because this water is used in rural households (Drinking Water Regulations, Official Gazette SRY No. 42/98 and 44/99). Water from tested wells used in the communities near Bela Crkva does not meet the standard for drinking water. The above-mentioned elements are below the MAC in the source of the Bela Crkva water supply. No impact of human activities in the nearby communities has been established on the source of Bela Crkva water supply.

5. Acknowledgment

This work was supported by the Ministry of Education and Science (Project OI 176018).

6. References

Askin, V. (1967). *Theoretical Classification Problems of Petroleum and Gas Deposits and Its Importance for Exploration with Particular Reference to Banat* (in Serbian). Special Edition, Vol.15, Institute for Geological and geophysical exploration, Belgrade.

Cvetkovic, D. & Gordanic, V. (1986). 1986 Report on Basic Uranium Prospecting in Socica-Markovac, Vrsac Mountains (in Serbian). Documentation fund, Geoinstitut, Belgrade.

Dolton, G.L. (2006). Panonian Basin Province, Central Europe (Province 4808) – Petroleum Geology, Total Petroleum Systems, and Petroleum Resource Assessment: U.S. Geological Survey Bulletin 2204-B, 47 p.

Filipovic, B. (2003). *Mineral, Thermal and Thermomineral Waters of Serbia. Monograph* (in Serbian). Udruzenje banjskih i klimatskih mesta Srbije, Vrnjacka Banja. Faculty of Mining and Geology, Institute of hydrogeology, Belgrade.

Gordanic, V. (1980). Special Geochemical Part, In: *Report on Regional Exploration of Nuclear Mineral Resources in Vrsac Hills and Bela Crkva Area* (in Serbian), Puric, D. & Gordanic, V., 1980, Geoinstitut, Belgrade.

Gordanic, V. & Zunic, Z. (1994). Geochemical Prospecting, in: *1st Mediterranean Congress on Radiation Prospecting, Proceedings*, pp. 291-294. Athens 1994, Greece.

Hawkes, H.E. & J.S. Webb (1960). Geochemistry in Exploration of Mineral Resources (in Serbian), Belgrade.

Ivkovic, A. (1960). Hydrogeology of South Banat (in Serbian). Documentation fund, Geological Institute, Belgrade.

Lazic, M. (2002). Report on the Low-Mineral Water Reserve in Mesic- Vrsac Municipality (in Serbian). Documentation fund, Municipality of Vrsac.

Lazic, M. (2010). Revised Report of Groundwater Reserve at Mesic for the Moja Voda Bottling Plant.(in Serbian). Documentation fund, Faculty of Mining and Geology, Hydrogeology Department.

Marovic, M., Đokovic, I., Pesic, L., Radovanovic, S., Toljic, M. & Gerzina, N. (2002). Neotectonics and Seismicity of the Southern Margin of the Pannonian Basin in Serbia. *EGU Stephen Mueller Special Publications*, Series 3, pp. 277-295.

Milivojevic, M. (2004). A Study: Quality of Water and Sediment in the Vrsac Lake and Assessment of the Groundwater Resource in the Surrounding Area (in Serbian). Documentation fund, Faculty of Mining and Geology, Institute of hydrogeology, Belgrade.

Milojevic, N. (1963). Hydrochemical Character and Regime of Groundwaters in Vojvodina (in Serbian). *Radovi – Geoinstitut*, Belgrade.

Nikic, Z. & Vidovic, M. (2007). Hydrogeological Conditions and Quality of Ground Waters in Northern Banat, Pannonian Basin. *Environmental Geology*, Vol.52, No.6, pp. 1075-1084, DOI: 10.1007/s00254-006-0547-z.

Pravilnik o Higijenskoj ispravnosti vode za pice (Regulations in Drinking Water – in Serbian). Official Gazette SRY No.42/98 and 44/99.

Rakic, M. (1978). Textual Explanation of the Map Sheet Bela Crkva at Scale 1:100,000 (in Serbian), Geological Institute, Belgrade.

Slimak, T. (2005). Report on the Pavlis Water Resource (in Serbian). Documentation Fund, Institute Institute for Water Management „Jaroslav Cerni".

Spasic-Jokic, V. & Gordanic, V. (2010a). Geochemical Radiation Load in the Vrsac Hills, *Proceedings of the 15th Congress of Geologists of Serbia*, pp. 651-655, Belgrade, Serbia.

Spasic-Jokic, V. & Gordanic, V. (2010b). Monte Carlo Calculation of Ambient Dose Equivalent and Effective Dose from Natural Radionuclides in the Soil of Vojvodina Province of Serbia. *Third European IRPA Congress*, Helsinki.

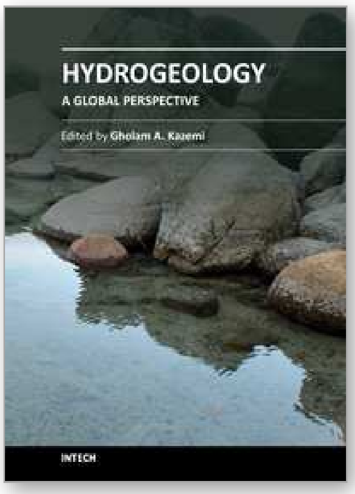
UNSCEAR Report of the United Nationas Scientific Committee on the Effects of Atomic Radiation to the General Assembly 2000: United Nations, New York.

Vidovic, M. (2007). Water Quality, In: *Report, Geochemical-Geoecological Atlas at Scale 1:50,000 of Radioactive and Other Elements in Vrsac-Bela Crkva Area* (in Serbian), Gordanic, V. & Jovanovic, D. , 2007, Geological Institute of Serbia, Belgrade.

Vukovic, A. (1965). Textual Explanation of the Map Sheet Vrsac L34-103 (in Serbian), Institute for Geological and Geophysical Explorations, Belgrade.

Vukovic, M. (1987). Study and Prediction of Safe Water Supply to Vrsac and Nearby Communities to 2005 (in Serbian). Technical Documentation Fund, Institute Institute for Water Management „Jaroslav Cerni".

Zupunski, Lj., Spasic-Jokic, V., Trobok, M. & Gordanic, V. (2010). Cancer Risk Assessment After Exposure from Natural Radionuclides in Soil Using Monte Carlo Techniques. *Environmental Science and Pollution Research*, Vol.17, No.9, pp. 1574-1580. DOI: 10.1007/s11356-010-0344-9.



Hydrogeology - A Global Perspective
Edited by Dr. Gholam A. Kazemi

ISBN 978-953-51-0048-5
Hard cover, 222 pages
Publisher InTech
Published online 10, February, 2012
Published in print edition February, 2012

The field of groundwater hydrology and the discipline of hydrogeology have attracted a lot of attention during the past few decades. This is mainly because of the increasing need for high quality water, especially groundwater. This book, written by 15 scientists from 6 countries, clearly demonstrates the extensive range of issues that are dealt with in the field of hydrogeology. Karst hydrogeology and deposition processes, hydrogeochemistry, soil hydraulic properties as a factor affecting groundwater recharge processes, relevant conceptual models, and geophysical exploration for groundwater are all discussed in this book, giving the reader a global perspective on what hydrogeologists and co-scientists are currently working on to better manage groundwater resources. Graduate students, as well as practitioners, will find this book a useful resource and valuable guide.