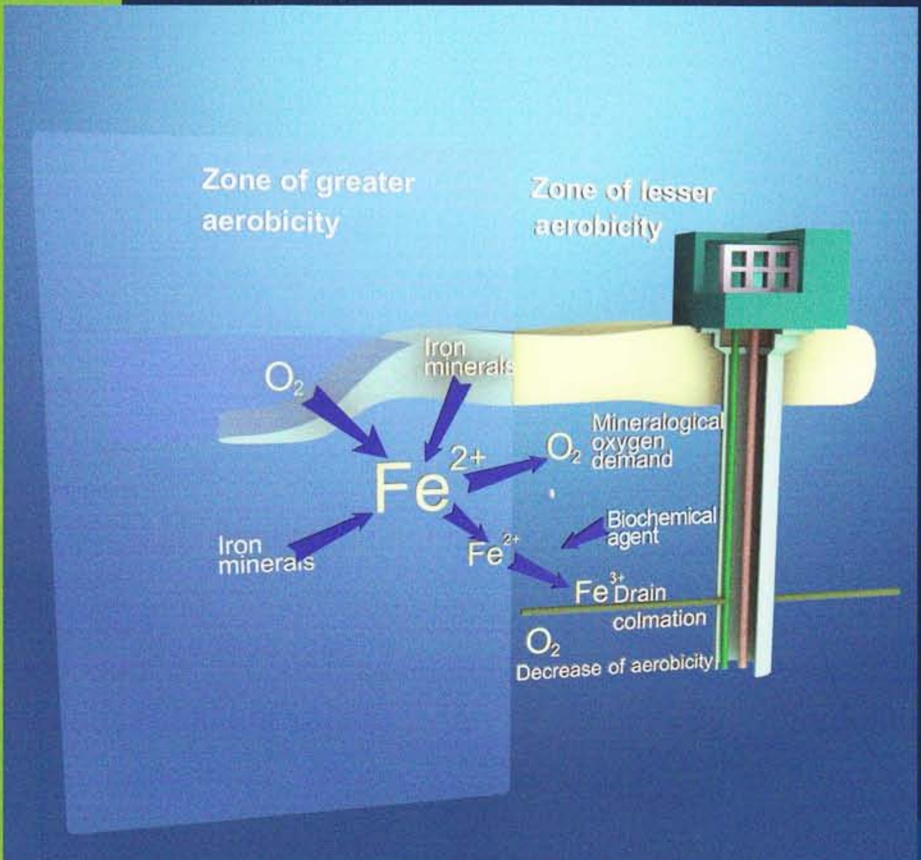
IWA SPECIALIST GROUNDWATER CONFERENCE



PROCEEDINGS

International Water Association

Jaroslav Černi Institute for the Development of Water Resources

Belgrade Water Supply and Sewerage Company

08-10 September 2011, Belgrade, Serbia

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FULL PAPER

WATER QUALITY AS AN INDICATOR OF HYDROGEOLOGICAL CONDITIONS: A CASE STUDY OF THE BELGRADE WATER SOURCE (SAVA/DANUBE CONFLUENCE AREA)

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Abstract: The City of Belgrade receives most of its drinking water supply from the alluvial aquifer of the Sava River. The wells are radial, placed in the lower part of the aquifer, so they partly run below the Sava riverbed. However, the groundwater quality of the wells in one part of the source (near the confluence of the Sava and Danube rivers) was found to differ somewhat from the groundwater quality of the other wells. This gave rise to additional investigations. The results revealed the existence of a deeper, limestone aquifer which is isolated from upper alluvial sediments by a thick layer of clay in most of the terrain. The naturally potential hydraulic contact of the two aquifers was additionally maintained by well operation in this part of the source. According to multiple analyses of groundwater flow using a hydrodynamic mathematical model, a hydrogeological and hydraulic system of groundwater flow was defined in this part of the source. Although the wells are situated adjacent to the river, and some well laterals are below the riverbed, most of the groundwater that flows to the wells is partly from the wider zone of the alluvial aquifer, and partly from the deeper aquifer. At first, the results of hydrochemical investigations showed an unexpected, inverse oxic character of the groundwater in these two aquifers.
Keywords: hydrochemistry, alluvial aquifer, limestone aquifer, geology, Belgrade

INTRODUCTION

The City of Belgrade is situated at the confluence of the Sava and Danube rivers. Drinking water supply is provided by 99 radial wells, from the alluvial aquifer of the Sava River. The entire Belgrade source is characterized by the following hydrochemical parameters: oxygen concentrations about 0.3 mg/L, iron ions about 2 mg/L, oxidation/reduction potential about 110 mV, and ammonium ions about 0.6 mg/L. This represents a poor aerobic to poor anaerobic environment, with low oxygen concentrations and increased iron and ammonium ion concentrations (Dimkić et al., 2011).

However, it was determined that the well water quality in one part of the source (near the confluence of the Sava and Danube rivers) differs from the water quality of the alluvial aquifer. Exploratory boring revealed the existence of limestone sediments below the alluvial aquifer. These two series of sediments are separated by an impermeable clay layer (Fig.1).

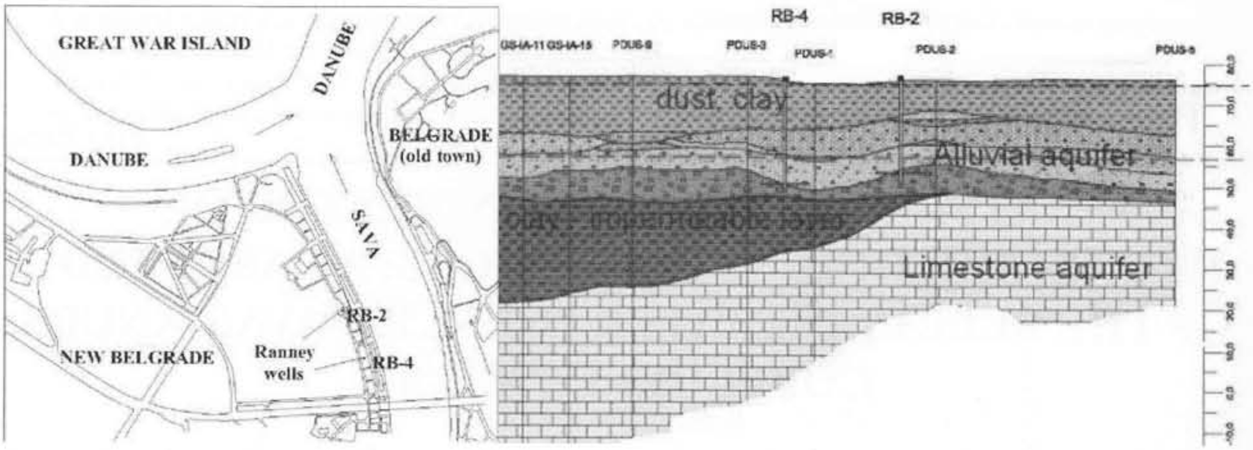

Figure 1: a) A part of the Belgrade source – Sava/ Danube confluence;
b) Lithological section along the left bank of the Sava River.

Contrary to the left bank, limestone sediments are exposed on the ground surface along the right bank of the Sava River ("Old Town" in Fig.1a) and from that point they extend eastward. This area represents the main recharge area for the limestone aquifer.

The role of the Sava River is very interesting in groundwater abstraction in this part of the source. Although the well laterals are placed directly below the riverbed, the results of hydrodynamic investigations and well water quality tests show that the water in the wells does not predominantly originate from the river. Further investigations showed that the well water was a blend of groundwaters from two aquifers.

GEOLOGY AND HYDROGEOLOGY

The geology in the area of the Sava's mouth consists of several members:

- Tertiary sediments, noted on the right bank (limestone, clay and marl). The limestone is of a riverbank nature, cracked and with a characteristic spongy porosity.
- Quaternary sediments, whose lower zone is made up of lacustrine-fluvial formations (gravel, gravel-sandy sediments, clayed in the bottom part), and whose upper zone is represented by alluvial sediments of the Sava River (a sandy-gravel complex with clay lenses).
- The final member is represented by dusty sand and sandy-marsh clay, with occasional peat. Their role is of extreme importance for defining the aerobic character of the alluvial aquifer, because they prevent the ingress of atmospheric oxygen, except in the narrow well zone, where groundwater levels are much lower.

In the hydrogeological sense, in the area along the left and right banks of the Sava River there are two types of aquifers: an aquifer within the alluvial sediments and an aquifer formed in limestone (Geozavod, 2003).

HYDRODYNAMIC MODEL INVESTIGATIONS

A hydrodynamic simulation of groundwater flow in the wider area of this part of the source was used for analysis of the groundwater flow mechanism, and also of the hydrodynamic relationship of these two aquifers. The model, consisting of six schematized layers (Fig.2), represents a complicated mechanism of groundwater flow in this part of the Belgrade source. The two aquifers, each with its own features, are in indirect hydraulic contact and form one hydrodynamic unit. The Sava River, in this part of its course, flows over a fault zone whose hydraulic role in groundwater flow remains unknown for the time being. Based on model tests, it was assumed that some of the river water is in contact with the alluvial aquifer, partly by infiltration through the (considerably) colmated riverbed, and partly through limestone on the right bank, at the very point of the confluence (lacking a clayey interlayer of alluvial and limestone sediments).

Measurements of groundwater levels during operational monitoring of the source and occasional well tests indicated an indisputable hydraulic contact between the two aquifers (Pušić, 2003).

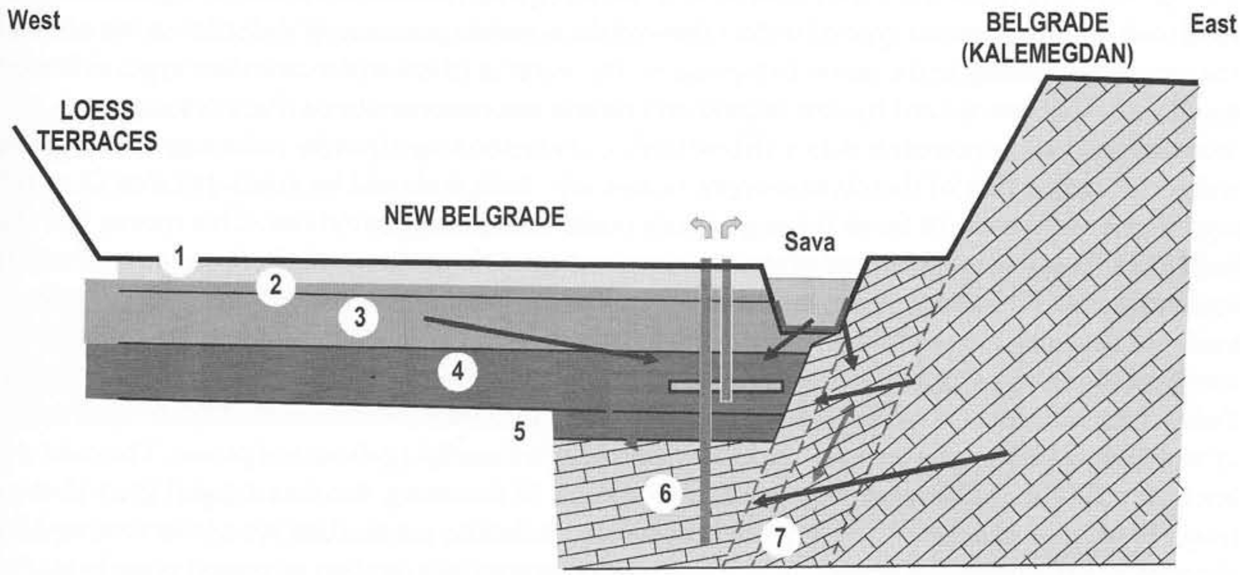

Figure 2: Modeled groundwater flow directions and aquifer layers at the Sava's mouth; Key: 1 – roof, impermeable layer, 2-4 – alluvial aquifer, 5 – clayey interlayer, 6 – limestone aquifer, 7 – fault zone.

Additionally, the results of model tests showed with a high degree of reliability that the aquifer within the limestone sediments extends beyond the riparian zone to the west. This fact is especially favorable given that the limestone in this area is covered by a thick layer of clay and thus very well protected from potential pollution from the ground surface. These results are important because of the possibility to provide additional amounts of groundwater if the city's water demand increases.

GEOCHEMISTRY

The presence of heavy metals in samples of rock material from the alluvion and limestone was determined by geochemical analyses, in order to assess the possibility of transfer of certain toxic elements into the groundwater under favorable oxidation-reduction and acid-base conditions. The analyses encompassed As, Zn, Cd, Al, Fe, Mn, Cr, Pb, Ni, Mo and Sb. The results of these analyses did not reveal an unusual load of toxic chemical elements (As, Cd, Cr, Pb, Ni, Mo, Sb). Characteristic of alluvial sediments in this part of the source were iron (0.42 to 2.58 %) and manganese (105 to 1800 ppm), such that elevated concentrations of these elements may be expected in the groundwater, especially under favorable anaerobic conditions. The concentrations of all toxic elements were much lower in the limestone samples than in the alluvial sediments.

HYDROCHEMISTRY

Hydrochemical investigations encompassed the determination of physical features and chemical and microbiological compositions of both groundwater and river water (Table 1) (Papić and Rakić, 2003). The gray areas in Table 1 show characteristic hydrochemical parameters of the given aquifer. Based on a large number of analyses of groundwater sampled from the alluvial sediments in the area of the Sava's mouth, the water was found to be poorly mineralized (TDS about 450 mg/L) and exhibited slight alkalinity (pH about 7.4). The cation content was dominated by calcium ions, followed by magnesium and potassium. The hydrogeochemical genetic coefficient Ca/Mg (meq) was 1.5 to 2.5, indicating the existence of calcite and dolomite in the sediments. X-ray tests of the alluvial sediments confirmed the presence of dolomite, quartz, calcite and feldspar. Hydrochemical tests (calcium-magnesium type of water) showed the possible presence of dolomite in the alluvial sediments. According to the anion composition, the water is of the hydrocarbonate type, followed by chlorides, characterized by low sulfate and nitrate ion concentrations. As a consequence, the oxidation/reduction potential is low (Eh~40 mV), characterizing a poorly reducing environment, and the concentration of dissolved oxygen is also low. Still, it should be noted that iron (3 to 6.5 mg/L) and manganese (0.56 to 0.9 mg/L) ions occur in high concentrations. This means that the Fe(II)/Fe(III) system determines oxidation/reduction conditions, due to the high concentrations of these elements in the sediments, as already mentioned. Based on the ions of the so-called nitrate triad, the groundwater of this aquifer is characterized by high concentrations of the ammonium ion (5 to 10 mg/L) of organogenic origin, and low concentrations of nitrate ions (1.7 to 4.5 mg/L). Concerning other elements, groundwater sampled from piezometers contained a high concentration of zinc (up to 14.5 mg/L), as a result of the construction material (galvanized pipes). This was not the case with the wells, since they are made of steel. In summary, the investigated groundwater from the alluvial sediments is of the hydrocarbonate-calcium, magnesium type, characterized by elevated concentrations of ammonium, iron and manganese ions, and an increased organic matter content ($KMnO_4$ above 12 mg O_2/L), which occur naturally in these sediments. The selected group of hydrochemical parameters indicates, as in many other water sources in alluvial sediments, the presence of elements-followers (Fe-Mn-NH_4^+) and organic substances. Microbiological analyses determined the presence of Bacillus sp.

Table 1: Selected hydrochemical parameters of groundwater and river water

Aquifer / Parameter	Alluvial		Limestone		Radial well	River
	Piezometer	Well	Piezometer	Well		
T°C	17	13.5	15.7	17	15	
pH	7.4	7.4	8	7.2	7.3	7.5
Eh ,mV	36	38	244	275	188	
O_2, mg/l	0.1	1.5	5.2	3	0.8	5.5
TDS, mg/l	450	400	550	535	430	280
$KMnO_4$, mg/l	14	12.8	6	2	4	5-25
NH_4^+, mg/l	10	5.5	0.1	0.01	0.6-1	0.3-1
NO_2^-, mg/l	0.01	0.01	0.8	0.02	0.02	0.01-0.05

Parameter \ Aquifer	Alluvial		Limestone		Radial well	River
	Piezometer	Well	Piezometer	Well		
NO_3^-, mg/l	1.7	4.5	40	40	3 - 25	10
SO_4^{2-} ,mg/l	1.5	2	40	55	25	20
Fe , mg/l	3.1	6.5	0.05	0.02	0.55	0.04
Mn, mg/l	0.56	0.9	0.03	0.01	0.27	0.001
As, mg/l	0.007	0.05	0.002	0.002	0.01	0.006
Sr, mg/l	0.4	0.4	0.8	0.9		
Zn, mg/l	14.5	0.01	0.3	0.02		
Ca/Mg, meq	2.3	1.6	1.6	1.55	1.6	
Bacteriology[1]	1	1	2	2	1 , 2	3

[1] *1 – Bacillus sp.; 2 – E. coli; 3 – Enterobacter sp., Aeromonas sp.*

Hydrochemical investigations of the limestone groundwater showed that, based on physical properties, the temperature was somewhat elevated, up to 17°C. The groundwater was found to be poorly mineralized, with a TDS level of about 500 mg/L, which was somewhat higher than for the alluvial groundwater. The oxidation/reduction potential ranged from 218 to 345 mV, which was indicative of an oxidation medium, and oxygen concentrations varied from 3 to 6 mg/L. Calcium, magnesium and potassium ions dominated the macro-component content. The genetic coefficient Ca/Mg (meq) of about 1.5 suggested that the water originated from limestone, even parts of dolomitic limestone. This type of aquifer is characterized by elevated sulfate (about 40 mg/L) and nitrate (about 40 mg/L) concentrations. Regarding the ions of the nitrate triad, the concentrations of ammonium ions (0.01 mg/L) and nitrate ions (0.02 mg/L) were low. Organic content determined as $KMnO_4$ demand was about 2 mg O_2/L, and significantly lower than in the alluvial groundwater. Regarding other elements, elevated concentrations of strontium (up to 1 mg/L) were detected, which are a consequence of its presence in carbonate rocks (strontianite). The concentrations of iron (0.02 mg/L) and manganese (0.01 mg/L) were low, regardless of the presence of these elements in the limestone and the oxidation environment within them. Microbiological analyses detected the presence of coliform bacteria.

The water quality of the radial wells in this part of the source was characterized as poorly mineralized (TDS about 430 mg/L), with temperatures around 15°C and an oxidation/reduction potential of about 190 mV, which are somewhat lower than in the case of the limestone groundwater. Oxygen concentrations were about 1 mg/L, iron concentrations 0.5 mg/L, and manganese concentrations 0.27 mg/L. The water is of the hydrocarbonate-calcium, magnesium type, and the concentrations of sulfate (25 to 37 mg/L) and nitrate (3 to 25 mg/L) are elevated. Ammonium ions are present in concentrations up to 1 mg/L, and KMn04 demand is about 4 mg O_2/L. The genetic coefficient Ca/Mg (meq) of about 1.6 indicated that the water is genetically bound to limestone and dolomitic limestone. This groundwater occasionally revealed the presence of Enterobacter sp., Aeromonas sp., and other bacterial species.

Based on sediment quality test results, a comparative analysis of surface water and groundwater within the alluvial and limestone sediments allowed for an assessment of the conditions under which the chemical composition and hydrochemical conditions were formed in this part of the Belgrade source. The software used for geochemical calculations of the hydrochemical component included SOLMINEQ.GW (Kharaka et al., 1999) and PHREEQC (Parkhurst et al., 1999) (Table 2).

Table 2: Saturation index values (SI) of selected minerals

Aquifer / Mineral phase	Alluvial		Limestone		Radial well
	Piezometer	Well	Piezometer	Well	
Calcite	0.42	0.36	0.35	0.38	0.28
Dolomite	0.01	0.03	0.04	0.12	-0.17
Fe $(OH)_3$	1.5	1.61	-0.36	-0.69	1.19
Magnesite	-0.48	-0.41	-0.39	-0.34	-0.52
Quartz	0.27	0.46	0.3	0.16	-
Rhodochrosite-Mn	0.06	0.23	-1.29	-1.76	-0.26
Siderite-Fe	-0.26	0.03	-2.1	-2.5	-0.76
Smithsonite-Zn	0.71	-2.51	-1.07	-2.2	-
Strontianite-Sr	-0.02	-0.03	0.19	0.24	-

According to thermodynamic stability calculations of the investigated groundwater in relation to mineral phases, separate conditions were noted within alluvial sediments and limestone in this part of the Belgrade source. The groundwater of the alluvial sediments was found to be in balance with dolomite, siderite and strontianite. The values of the saturation index (SI) were higher from the balanced for the minerals calcite, $Fe(OH)_3$, quartz and rhodochrosite. Mineralogical and petrographical analyses confirmed, among other things, the presence of so-called plated grains. These are grains that are petrogenic (quartz, carbonates and others), covered with iron and manganese oxides. This was reflected in the chemical composition of the groundwater, which is of the hydrocarbonate-calcium and magnesium type, with elevated concentrations of iron and manganese favored by a reducing medium with low Eh values. Besides this, concentrations of ammonium ions were elevated as a consequence of the presence of organic matter in the sediments ($KMnO_4$ higher than 12 mg/L). A possible answer to the question regarding the origin of the calcium and magnesium composition of the groundwater in the alluvial sediments could lie in aquifer drainage into the Sava limestone and gravel, where the limestone complex is below the river deposits.

The groundwater within the limestone sediments was over-saturated in relation to calcite, dolomite, quartz and strontianite. The water is of the hydrocarbon-calcium, magnesium type, with strontium (about 1 mg/L) which is also present in strontianite in limestone. The groundwater was found to be unsaturated in relation to siderite, $Fe(OH)_3$, and rhodochrosite, and the concentrations of iron and manganese were low.

The water tapped by the radial wells was unsaturated in related to dolomite, siderite and rhodochrosite, and over-saturated in relation to calcite and $Fe(OH)_3$, and with groundwater from the alluvial sediments. Based on the chemical composition, the water was found to be of the hydrocarbonate-calcium, magnesium type.

What do the results of analytical determinations and thermodynamic calculations indicate? The schematic of the hydrochemical conditions which characterize the groundwaters within the alluvial sediments and limestones, presented in Figure 3, clearly shows the influence of the limestone on the chemical composition of the water tapped by the radial wells.

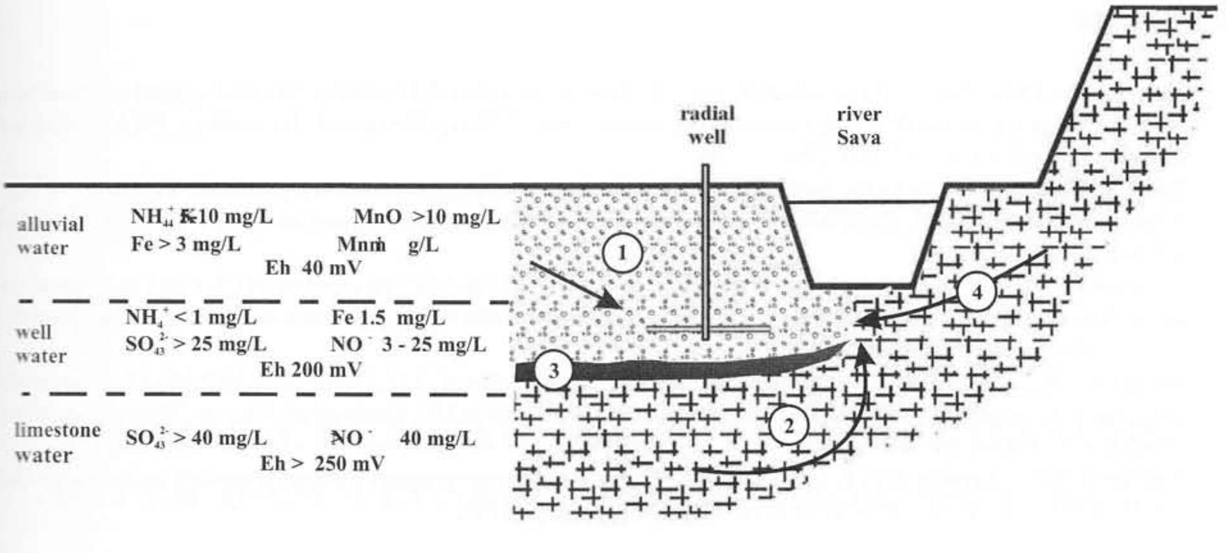

Figure 3: Schematic of hydrochemical conditions and groundwater flow.
Key: 1 – alluvial sediments, 2 – limestone; 3 –impermeable interlayer; 4 – groundwater flow directions.

The zone tapped by the radial wells is characterized by the following hydrochemical parameters of the alluvial and limestone groundwaters: Eh about 200 mV, iron less than 1.5 m/L, manganese about 0.3 mg/L, and ammonium ion about 1 mg/L. Elevated concentrations of sulfates and nitrates are also indicative of a large similarity with the composition of the limestone groundwater. During abstraction, potassium and chloride ion concentrations slightly increase, which is attributable to their presence in the deeper reaches of the limestone sediments, assuming that there is a fault that allows the two types of aquifers, alluvial and limestone, to come in contact.

CONCLUSION

The investigations undertaken in one part of the Belgrade water source, in the zone of the Sava's mouth, indicated a special character of the well water drawn from the alluvial aquifer. The groundwater quality was used as an indicator of hydrogeological relationships in this part of the source. Hydrochemical investigations and calculations showed that the groundwater tapped from the alluvion was loaded with ammonium, iron and manganese ions and organic matter, with low oxygen concentrations and a low oxidation/reduction potential, which are characteristic of a poorly reducing medium. The limestone groundwater exhibited characteristic elevated sulfate and nitrate concentrations, with an increased oxidation/reduction potential which defines an aerobic environment. Based on the oxidation/reduction conditions, it can be concluded that there is an inverse aerobic feature in this part of the Belgrade source, as the shallow alluvial groundwater is less aerobic (Eh about 40 mV) than the deeper groundwater in the limestone aquifer (Eh greater than 250 mV). The water tapped by the radial wells, with regard to its chemical composition and aerobic state, is under the influence of both the alluvial and the limestone aquifer, i.e. it is a blend of these waters (Eh about 200 mV, elevated concentrations of sulfate and nitrates).

Hydrodynamic model tests confirmed previous assumptions and indicated the direction in which the limestone aquifer extends beyond the study area.

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