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**THE SUITABILITY OF CARBON ISOTOPE
COMPOSITION AS NATURAL TRACER IN KARST
AQUIFER INVESTIGATIONS**

**UPORABNOST IZOTOPSKE SESTAVE RAZTOPLJENEGA
ANORGANSKEGA OGLJIKA KOT NARAVNEGA SLEDILA V
RAZISKAVAH KRAŠKIH VODONOSNIKOV**

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Izvleček

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Branka Trček & Miran Veselič & Janko Urbanc: Uporabnost izotopske sestave raztopljenega anorganskega ogljika kot naravnega sledila v raziskavah kraških vodonosnikov

Izotopske raziskave so potekale v zaledju kraškega izvira Hubelj na območju Trnovsko-Banjške planote. Spremembe v kemijski in izotopski sestavi vode so bile spremljane od območja napajanja (padavine), preko nezasičene cone do iztoka iz vodonosnika. Posebna pozornost je bila posvečena nezasičeni coni. Rezultati potrjujejo, da je vzorčevana voda v ravnotežju s karbonatno kamnino in da proces raztapljanja karbonatnih kamnin opisuje odprt sistem raztapljanja.

Ključne besede: kraški vodonosnik, hidrogeokemija, naravni izotopi, ogljik, sledenje, Slovenija, Trnovsko-Banjška planota.

Abstract

UDC: 556.34.064

Branka Trček & Miran Veselič & Janko Urbanc: The suitability of carbon isotope composition as natural tracer in karst aquifer investigations

This isotopic research is ongoing in the catchment area of the karstic spring Hubelj in the area of the Trnovsko-Banjška plateau. Changes in water chemistry and carbon isotope composition are monitored from the aquifer recharge area in precipitation water, through the unsaturated zone to the outflow from the aquifer. Special attention is given to the unsaturated zone. The results confirm that the sampled water is equilibrated with the carbonate rock and that the process of carbonate rock dissolution can be described as an open dissolution system.

Key words: karst aquifer, hydrogeochemistry, natural isotopes, carbon, tracing, Slovenia, Trnovsko-Banjška planota plateau.

INTRODUCTION

Our isotopic and hydrogeochemical investigations are directed toward determining groundwater flow and transportation properties of the karst aquifer from the recharge area through the unsaturated zone to the outflow from the aquifer. The transport of infiltrated precipitation water is monitored by measurements of the chemical and isotope composition under different hydrodynamic conditions.

This isotopic research takes place in the catchment area of the karstic spring Hubelj in the area of the Trnovsko-Banjška plateau. Isotopic investigations were performed in this area before (Urbanc 1993, Trček 1997), but they didn't include sampling in the unsaturated zone and only the base flow was sampled. Because of this special attention is given to the unsaturated zone and to short-term sampling (detailed sampling of single precipitation events) in our present work. Base flow sampling is still included and we plan to sample at least two summer storms next year.

The outflow from the aquifer is sampled in the Hubelj spring, while precipitation water and water from the unsaturated zone are sampled 700 m higher in the experimental field site Sinji Vrh. The unsaturated zone is observed in a tunnel about 20 m below the surface.

Water samples are analysed for basic physical and chemical parameters, dissolved organic carbon (DOC), ^{18}O , ^2H and ^{13}C which enable the understanding of geochemical development of groundwater (Person et al. 1991, Hoefs 1997).

The investigations were started this year, hence this paper presents only the first results of the chemical and carbon isotope composition of the analysed waters, enabling a better understanding of carbon geochemistry.

AREA DESCRIPTIONS

The geological and hydrogeological descriptions of the area were written by Jože Janež and Jože Čar (Janež and Čar 1997).

Our investigations take place in the catchment area of the karstic spring Hubelj. The region is a high karst plateau, Trnovski Gozd, in south-western Slovenia. It is in contact with the karst plateaus of Banjšice, Hrušica and Nanos. There are Triassic, Jurassic and Cretaceous carbonate rocks, limestones and dolomites. Carbonate development ends with an erosional discordance that is followed by flysch rocks of the Upper Cretaceous, Palaeocene and Eocene age.

This region has a very complex tectonic structure. The predominant tectonic elements are the extensive and complex overthrusts which were cut by a dense system of subvertical faults.

Porous karst aquifers are mainly formed in limestones. The main hydrogeological units are the karst aquifer in the catchment area of Hubelj, the karst aquifer of the western part of Trnovski Gozd and Banjšice, the karst aquifer of Hrušica, Črni Vrh plateau and Nanos. The karst aquifer in the catchment area of Hubelj is formed in limestones of Jurassic age.

The karst aquifers are delimited by mainly impermeable flysch rocks and fractured aquifers.

Groundwater springs are located on the erosional base on the impermeable border.

MATERIALS, METHODS AND TECHNIQUES

The outflow of the aquifer is sampled from one fracture at the Hubelj spring.

Water from the unsaturated zone is sampled in a tunnel about 20 m under the surface. There are five sampling stations, each collecting water samples from one or more points. Sampling locations were selected so as to enable the monitoring of impact of different kinds of vegetation cover. Two stations are located under beech forest and the others under grassland. The longitudinal section of tunnel with sampling stations is presented in Fig. 1.

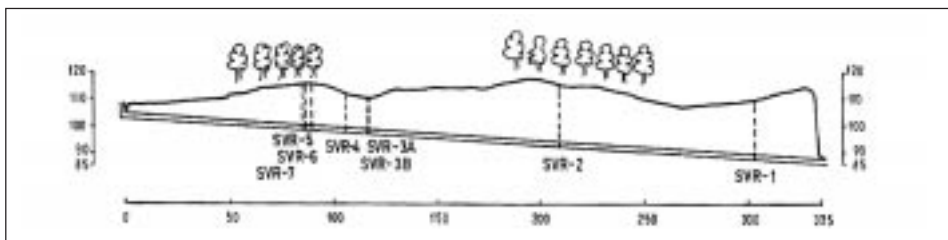
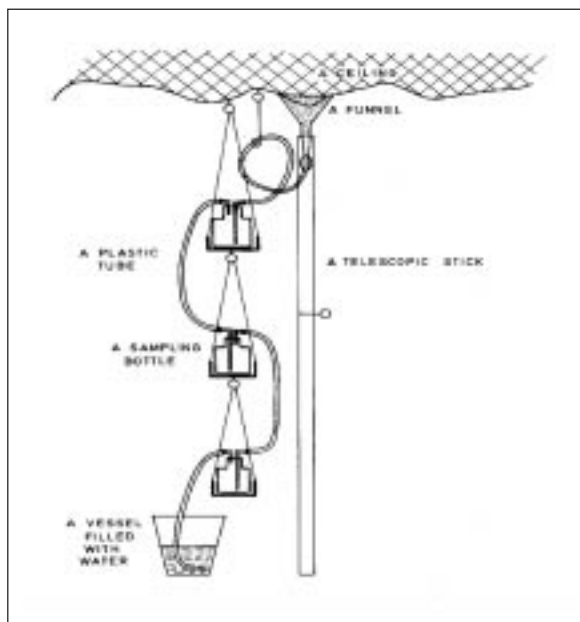


Fig. 1: Longitudinal section of the tunnel.
Sl. 1: Vzdolžni prerez predora.

Sampling point construction is presented in Fig. 2. It is constructed so as to prevent the collected water from being influenced by external effects like evaporation and degassing.



Water from the ceiling of the tunnel is collected with a funnel which is fixed to the ceiling with a telescopic stick and covered with a special waterproof paste. Water flows from the funnel through plastic tubes to the glass sampling bottles. The sampling system ends with a tube which rests in a vessel filled with water. Water from the first bottle is used for laboratory analyses and in situ measurements, while water from other bottles is used mostly for measurements of flow rate and sometimes also for analyses.

Fig. 2: The sampling point in the unsaturated zone.

Sl. 2: Vzorcevalno mesto v nenasičeni coni.

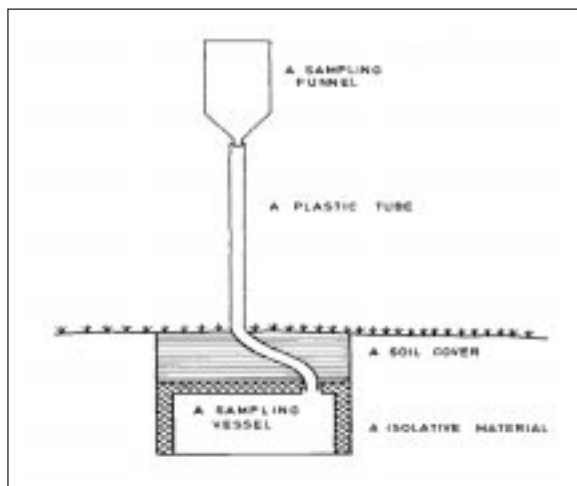


Fig. 3: The precipitation water sampling station.
Sl. 3: Postaja za vzorčevanje padavin.

Precipitation water is sampled in the experimental field site above the tunnel. The sampling station is presented in Fig. 3. Water flows from a standard precipitation sampler through a plastic tube to the sampling vessel. The vessel is buried about 50 cm below the surface to prevent water from evaporating and freezing.

Sampling takes place once a month to get an impression of the experimental field site and the base flow. In situ measurements include temperature, conductivity and pH data. Basic chemical analyses were made in Geological Survey's laboratory with standard titrimetric methods (Greenberg et al. 1992). Carbon isotope analyses were made at the

Jožef Stefan Institute on a Europa 20-20 spectrometer with an ANCA TG module. Analytical and in situ data were used in the geochemical reaction model PhreeqC (Charlton et al. 1997) to calculate equilibrium values of different parameters.

RESULTS AND DISCUSSION

The results of the laboratory analyses and the in situ measurements of the water are presented in charts in Fig. 4, providing conductivity, pH, temperature, alkalinity and ^{13}C data.

Alkalinity values range from 1,5 to 2,5 meq/l. Values of the carbon isotope composition of the water range from -8 to -16‰. They reflect the isotopic composition of soil CO_2 in the recharge area of the aquifer and the isotopic composition of carbonate rocks which were dissolved during infiltration. Previous investigations in the research area show that the average values of carbon isotope composition of soil CO_2 are from -18 to -23 ‰ while the average value of carbon isotope composition of limestones is + 1,2 ‰ (Urbanc 1993, Trček 1997).

The relationship between carbon isotope composition and alkalinity is showed in Fig. 5. Lower alkalinity values reflect lower values of soil CO_2 partial pressure, higher values of soil CO_2 carbon isotope composition, and lower values of soil temperature (Trček, 1997). Hence the values of carbon isotope composition of sampled water are higher at lower alkalinity values and vice-versa. Factors that control the partial pressure and carbon isotope composition of soil CO_2 (soil temperature, vegetation cover, soil type, etc) also indirectly control alkalinity and carbon isotope composition of sampled water. A response in a sampling point depends upon mixing processes and residence time of water in the aquifer.

Data from Fig. 4 were used in the computer program PhreeqC (Charlton et al. 1997) to calcu-

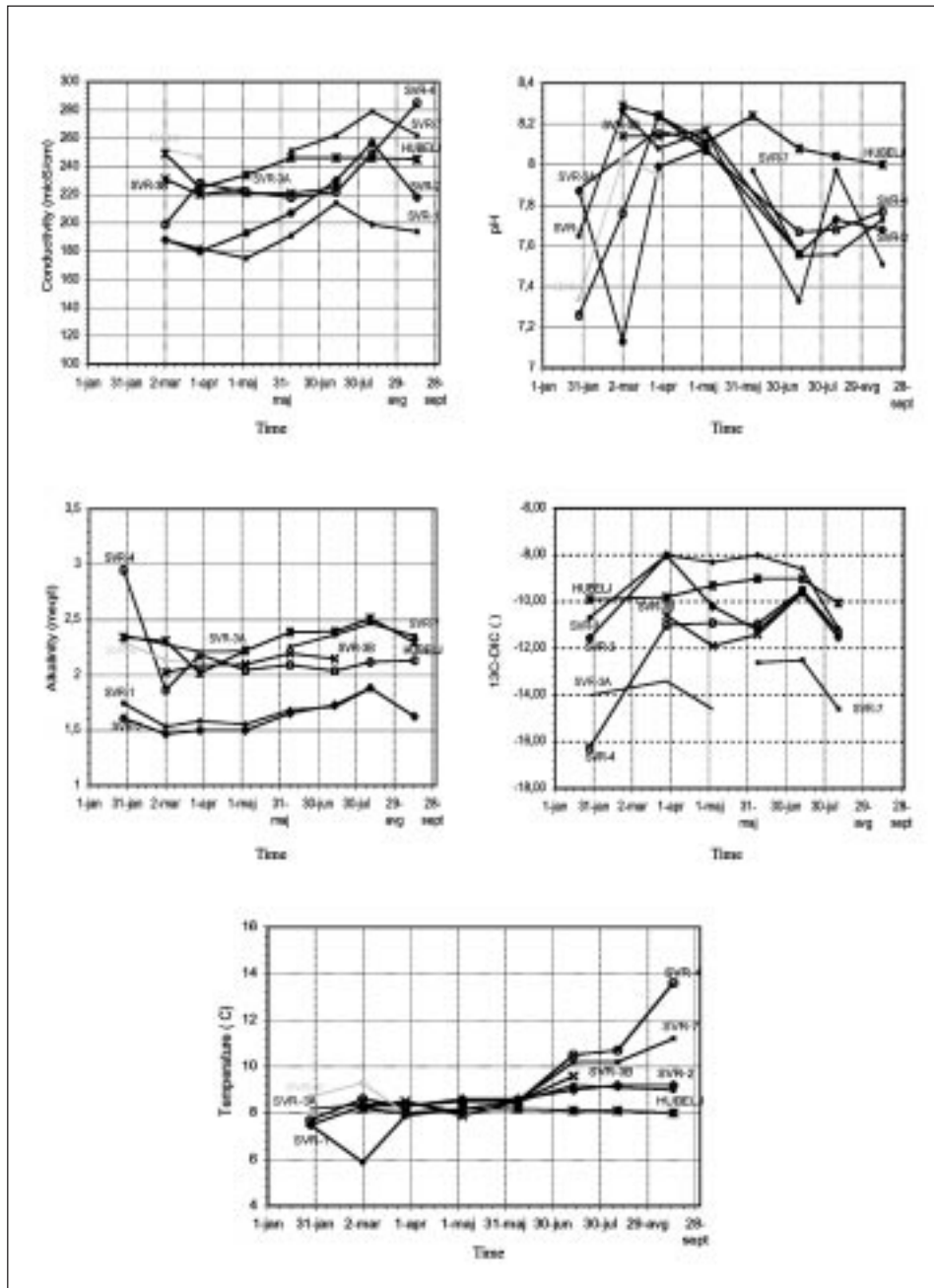


Fig. 4: Results of laboratory analyses and in situ measurements of sampled water.
 Sl. 4: Rezultati laboratorijskih analiz vzorcev vode in in-situ meritev.

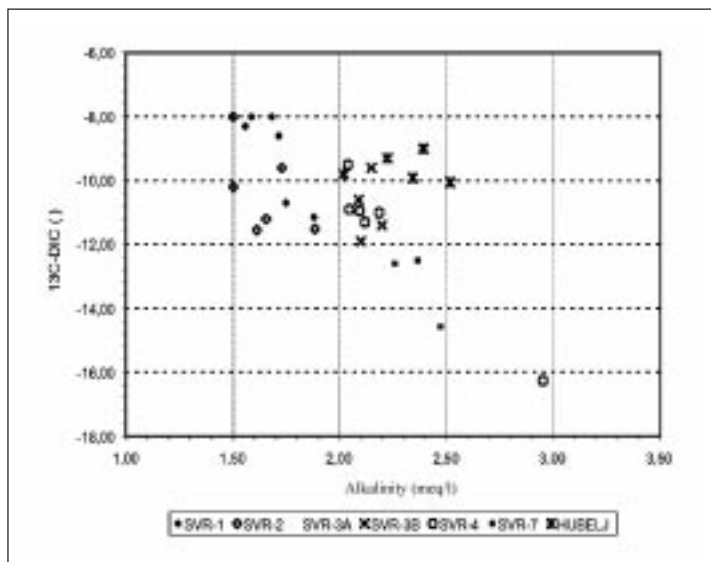
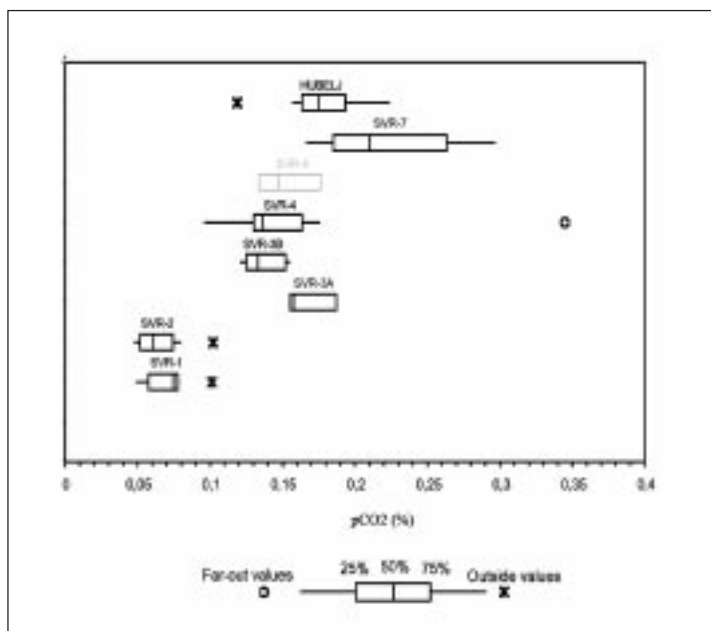


Fig. 5: Relationship between carbon isotope composition and alkalinity of sampled water.

Sl. 5: Zveza med izotopsko sestavo raztopljenega anorganskega ogljika in alkalnostjo vode.



late equilibrium values of physical and chemical parameters of the water. The study of measured and calculated values show that the sampled water is in equilibrium with carbonate rock. Calculated values of partial pressure of soil CO_2 are presented in Fig. 6. They fall in the same range as values of previous investigations in the Trnovsko-Banjška plateau (Trček, 1997). The results of the present and previous investigations confirm that the process of carbonate rock dissolution can be described as the open dissolution system (Trček 1997).

Fig. 6: Calculated values of partial pressure of soil CO_2 .
Sl. 6: Izračunani parcialni tlaki talnega CO_2 .

CONCLUSIONS

The analyses of the previous and present data enable a better understanding of carbon geochemistry and thus the geochemical development of the groundwater studied. They confirm that the sampled water is in equilibrium with carbonate rock, that the carbonate rock dissolution occurs under open system conditions, and that the total dissolved inorganic carbon isotope composition of sampled waters can be used to draw conclusions about climatic and vegetation properties of aquifer recharge areas.

Previous and future results of isotopic investigations will give additional information about the flow system and transport phenomena in karst aquifers. They enable a better estimation of aquifer vulnerability, which is a basic prerequisite for sustainable groundwater management.

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Povzetek

Izotopske raziskave potekajo v zaledju Hublja na območju Trnovsko-Banjške planote. Z raziskavami želimo preučiti tokovni sistem podzemne vode in transportne procese v kraškem vodonosniku od območja napajanja, preko nezasičene cone, do iztoka iz vodonosnika. Transport infiltrirane padavinske vode sledimo s pomočjo kemijske in izotopske sestave vode. Iztok iz vodonosnika smo vzorčevali na izviri Hubelj, padavine in vodo iz nezasičene cone pa 700 m višje, na raziskovalnem poligonu blizu Sinjega vrha. Posebna pozornost je namenjena nezasičeni coni, ki se opazuje v tunelu okoli 20 m pod površino in kratkotrajnemu vzorčevanju (natančno vzorčevanje posameznega hidrološkega dogodka).

Naslednje leto bosta natančno vzorčevani dve poletni nevihti, zato predstavljamo prve rezultate fizikalno-kemijske in izotopske sestave mesečno vzorčevane vode. Podatke smo modelirali z računalniškim programom Phreeqc. Študij predhodnih in sedanjih rezultatov raziskav na Trnovsko-Banjški planoti omogoča boljše razumevanje ogljikove geokemije in geokemijskega razvoja podzemne vode. Potrjuje, da je vzorčevana voda v ravnotežju s karbonatno kamnino, da poteka raztapljanje karbontanih kamnin pod pogoji odprtega sistema in da odseva izotopska sestava skupnega anorganskega ogljika vzorčevane vode klimatske in vegetacijske pogoje na območju napajanja vodonosnika.