POTENTIAL INFLUENCE OF A PLANNED LANDFILL ON A HIGH KARST PLATEAU IN SOUTHWESTERN MONTENEGRO TO NEARBY KARSTIC SPRINGS

POTENCIALNI VPLIV NAČRTOVANEGA ODLAGALIŠČA ODPADKOV NA VISOKEM KRASU V JUGOZAHODNI ČRNI GORI NA BLIŽNJE KRAŠKE IZVIRE

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Abstract UDC 556.36:551.435.8:628.472.3(497.16) Micha Horacek, Milan Radulovic, Dejan Jancic, Stefan Wyhlidal & Golub Ćulafić: Potential influence of a planned landfill on a high karst plateau in Southwestern Montenegro to nearby karstic springs

The potential threat of a landfill projected on a high karst plateau in southwest Montenegro is investigated with respect to the subjacent nearby springs. The locality is called Duboki do. As the springs are used for drinking water supply this investigation is urgently needed. For the springs exist two hypotheses concerning their catchment area: I) from the high karst plateau, or II) from a topographically lower area. The stable H- and O-isotope ratios of water samples from the springs are compared with precipitation isotope data, to reveal the catchment area of the springs. The isotope results indicate that the catchment area of the springs is at higher altitude fitting to, and in good agreement with, winter precipitation from the high karst plateau of the planned land-fill locality.

Keywords: isotope hydrology, hydrogen isotopes, oxygen isotopes, d-excess, catchment area, karst hydrology, precipitation.

Izvleček UDK 556.36:551.435.8:628.472.3(497.16) Micha Horacek, Milan Radulovic, Dejan Jancic, Stefan Wyhlidal & Golub Ćulafić: Potencialni vpliv načrtovanega odlagališča odpadkov na visokem krasu v jugozahodni Črni gori na bližnje kraške izvire

Potencialna grožnja odlagališča odpadkov, načrtovanega na visokem krasu v jugozahodni Črni gori, je bila proučena glede na bližnje nižje ležeče izvire. Lokacija se imenuje Duboki do. Ker se izvirska voda uporablja za oskrbo s pitno vodo, je ta raziskava nujno potrebna. Za izvire obstajata dve hipotezi o njihovem zaledju: I) iz visokega krasa in II) iz topografsko nižjega območja. Razmerja stabilnih izotopov vodika in kisika v vzorcih vode iz izvirov smo primerjali s podatki o izotopski sestavi padavin, da bi razkrili zaledje izvirov. Rezultati izotopov kažejo, da je zaledje izvirov na višji nadmorski višini ter prilagojeno zimskim padavinam – in jih dobro prevaja – iz visokega krasa načrtovane lokacije odlagališča odpadkov.

Ključne besede: izotopska hidrologija, izotopi vodika, izotopi kisika, devterijev presežek, povodje, kraška hidrologija, padavine.

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INTRODUCTION

Clean groundwater in abundant quantity is one of the most precious resources in any region of the world. Over-use, contamination and changes in the recharge of groundwater bodies have led to water scarcity and difficulties in water availability or quality in many regions of the world. Accumulation of knowledge about the processes in and around the groundwater is essential for the responsible use, exploitation and protection of this resource.

For the purposes of the waste disposal from the territory of the Herceg Novi municipality at the Boka bay, southwestern Montenegro, the construction of the land-fill "Duboki do" is planned (Figure 1). The site of the projected landfill is located on the high karst plateau above the Boka bay (Figure 2). The altitude of the landfill location is about 1,050 m a.s.l. Since the wider high-altitude area is characterized by large amounts of rainfall (mean annual precipitation range from 3,000 to 5,000 mm (IJC, 2001) and high permeability of the rocks, the region is very rich in groundwater.

The most important groundwater sources in this area are the Opačica spring (about 7 m a.s.l.), which feeds

in the Herceg Novi water-supply system and the Morini spring (5 m a.s.l.), which represents a potential source for supplying a part of the territory of Kotor municipality (Radulović, 1995, 2000; Marić, 1997; Dubljević, 2001; Radulović & Radulović, 2004). Also, there are numerous smaller springs (Dezdarica spring, Česma spring, Bunovići springs and Dragomanovići springs), which are used for the water-supplying of smaller settlements.

The crucial question is whether a leakage of waste water from the projected landfill can pollute the nearby springs (Figure 3), which are located below the high karst plateau near the coast. According to one hypothesis (I), the recharge area of the springs is on the Karst plateau with an average altitude of about 1,100 m a.s.l. (Figure 3), covering the wider area of the proposed landfill location. Another hypothesis (II) claims that the recharge zone of these springs is situated in the background of Morinj bay on a terrain with an average altitude of about 500 m a.s.l. (Figure 3). These two zones are divided by impervious Flysh sediments, so the main question is whether the water infiltrating the Karst plateau at 1,100 m a.s.l., at the projected locality of the landfill, flows below the Flysch



Figure 1: Map of Montenegro (ME) showing the localities where the precipitation has been collected and location of projected Duboki do landfill.

barrier towards the springs. Generally, it is necessary to determine the recharge zones of the karstic springs used for water supply in this area, to investigate which of them are at risk of being contaminated by the planned landfill or other anthropogenic activities.

During previous investigations, an artificial tracer (uranine) was injected into the borehole B3 at Duboki Do. However, the tracer did not appear in any of the surrounding springs (Šućur, 2015; Doklestic, et al., 2015). It was assumed that the tracer went to submarine springs and that therefore the tracer was not noticed. Montenegrin largest submarine spring is the Sopot Spring, which is located around 11 km east of Duboki Do in the Risan Bay.

Stable isotope patterns in water can give information about the origin of the water, the catchment area, altitude etc. of a spring or water body, the reservoir size, the residence time and further information (Clark & Fritz, 1997). The origin of water can be identified by

comparison of the stable isotope patterns of the ground-water body and possible meteoric (or river-) origins. Stable isotopes in precipitation are influenced by several fractionation processes, the magnitude of which in temperate climates depends mainly on temperature and altitude (temperature and altitude effects, Dansgaard, 1964) and the distance from the coast (continent effect, Gat & Gonfiantini, 1981). These result in typical isotope values and seasonal patterns for different catchment areas and allow the discrimination of water samples and therefore provide the basis for assessing the mean altitude of the catchment (Reischer et al., 2015).

Thus, using Isotope ratio mass spectrometry (IRMS) measurements could favor one of two selected hypotheses. To our knowledge this is the first study on isotope hydrology in Montenegro, besides some preliminary investigations by Horacek et al. (2019). Preliminary results have been published in Radulovic et al., 2019.

LOCALITY, GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The landfill is planned at the high karst plateau northeast of Herceg Novi, at an altitude of 1,050 m a.s.l. (Figure 1). Herceg Novi is situated at the outer part of Boka bay (southwest Montenegro). The location Duboki Do is situated in a karst doline (sinkhole). Coordinates of the site are 42°29'56.73" N; 18°35'12.55" E.

Geological investigation of borehole B3 in the Duboki do doline showed a ca. 4m thick layer of clayey soil in the above the bedrock. The subsoil geology of the Duboki do locality consists of carbonate rocks (Jurassic limestone and dolomite) (Antonijević et al., 1973; Mirković et al., 1985), which are characterized by high permeability, covering a wide area. The water table was reached at 11.6 m in the borehole B3 on 6th December 2014. Impervious Flysh sediments extend along a narrow zone from Morini bay on the east to the western border of the research area.

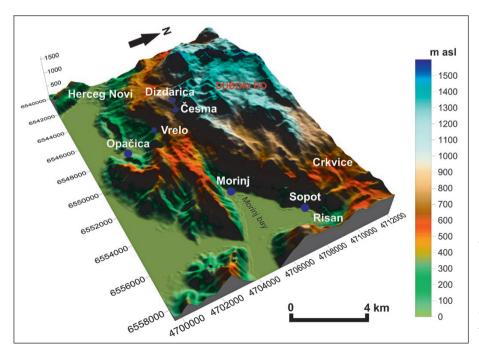


Figure 2: Digital elevation model of the wider area of Duboki do doline. The eastern tongue of the Morinj bay is the Risan bay (Risan), where the submarine Sopot spring is located close to the coast. "Herzeg Novi" and "Crkvice" indicate the location of these two towns.

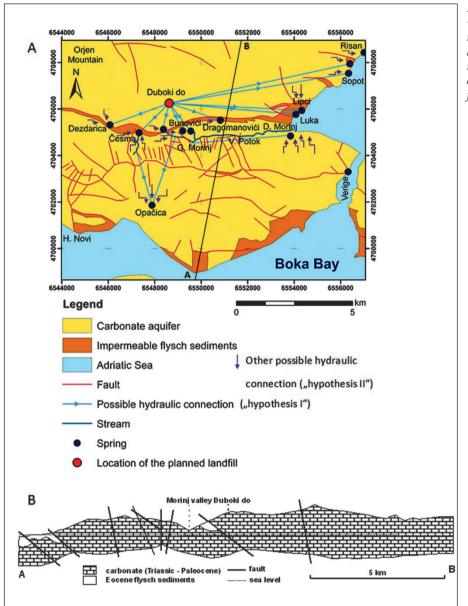
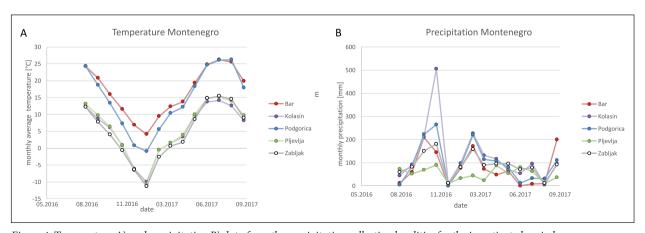


Figure 3: Map of possible ground-water flow directions (indicating the recharge areas of the spring for hypothesis I and II) from the location of landfill Duboki do, with a cross section depicting the simplified geological situation.



 $Figure\ 4:\ Temperature\ A)\ and\ precipitation\ B)\ data\ from\ the\ precipitation\ collection\ localities\ for\ the\ investigated\ period.$

Along this Flysch zone there are many small springs at higher altitudes (Figures 2, 3). Although the terrain generally is very permeable, the conditions of groundwater flow within a Karst aquifer are very complex. By the application of the conventional hydrologic methods in this terrain, it

was not possible to reliably determine the recharge area of karstic springs (Šućur, 2015; Doklestic et al., 2015), nor to identify the groundwater flow directions from the location of landfill (Šućur, 2015; Doklestic et al., 2015).

SAMPLING AND ANALYTICAL METHODS

Precipitation water samples have been collected throughout one year (from September 2016 to September 2017) as monthly samples from the following localities: Bar (5 m a.s.l.), Podgorica (32 m a.s.l.), Kolašin (954 m a.s.l.), Žabljak (1,456 m a.s.l.) and Pljevlja (770 m a.s.l.), see Figure 1. There are not precipitation samples available for all months, as during some months there was no precipitation at some stations. Information about weather data (air temperature, precipitation) during the investigated period is shown in Figures 4A, B.

Spring samples have been collected in July 2017 from the following sources: Česma, Vrelo, Donji Morinj, Opačica (Zelenika).

The stable isotope composition of precipitation,

surface and spring water samples were analysed using the isotope mass spectrometer Thermo Finnigan DeltaPlusXL equipped with automatic equilibration lines and the Picarro L1115-i Isotopic Liquid Water and Water Vapor Analyzer (laser spectroscopic analyser, CRDS) at the Austrian Institute of Technology (AIT) in Tulln. All results are reported as relative abundance (δ^2H and $\delta^{18}O$, respectively) of the isotopes 2H and ^{18}O in per mill (‰) with respect to the international standard VSMOW (Vienna Standard Mean Ocean Water). The accuracy of measurement is better than $\pm 1.0\%$ for δ^2H and $\pm 0.1\%$ for $\delta^{18}O$. Calibration of the mass spectrometer and CRDS was accomplished using VSMOW, GISP, and SLAP standards (Reischer et al., 2015).

RESULTS

Results are shown in Table 1 and Figures 5-7.

Precipitation from the coastal and lowland region (Bar, Podgorica) show significantly higher isotope values (Figure 5 and Figure 6) than the precipitation from the high-altitude hinterland localities (Kolašin, Žabljak), with Pljevlja station showing a "continental" pattern of low values in winter (similar to the high-altitude stations) and high values in summer (similar to the lowland stations). Annual averages from Bar are -24.1‰ and -3.5% for δ^2 H and δ^{18} O isotope values respectively, from Podgorica -26.4% and -3.9%, from Kolašin -43.0% and -6.6‰, from Žabljak -44.7‰ and -6.7‰ and from Pljevlja -43.0% and -5.7% for $\delta^2 H$ and $\delta^{18} O$ isotope values, respectively (for our sampling period, without taking into account the monthly volumes). Differences in isotope values between low- and high hinterland sample stations seems to be largest during autumn and spring. The seasonal variation in isotope values, with elevated values in summer and low values in winter can be observed in the data as well.

One sample showing exceptionally high (and positive) H- and O- isotope values in summer from the Podgorica sampling site might belong to an individual pre-

cipitation event or evaporation before sample collection, due to the elevated Deuterium excess-value, and is eliminated from the data set.

Results from the four springs investigated (Figure 7, Table 1) give low isotope values around -60% for hydrogen and lower than -9% for oxygen isotopes. Most of the analyzed water samples (precipitation and spring water, Figure 7) lie close to the Global Meteoric Water Line (GMWL; Craig, 1961). The (summer) samples with the highest isotope values, however, show a trend towards the side right of the GMWL, which indicates significant influence of evaporation. The relationship between d²H and d18O is the deuterium excess (d), globally defined as $d = \delta^2 H - 8 \delta^{18} O$ (Dansgaard, 1964) and adapted for Middle Europe (Austria) as $d = \delta^2 H - 7.88 \delta^{18}O$ (Humer et al., 1995). Deuterium excess of spring and river water usually ranges from 9 to 13 (Reischer et al., 2015) and the value increases with altitude (Schotterer et al., 1993; Holko, 1995; Gonfiantini et al., 2001, Rank et al., 2016). Low values usually are a sign for partial evaporation of the water sample (Horvatincic et al., 2005). The uncertainty of the deuterium excess is ±1.3 (combined uncertainties of $\delta^2 H$ and $\delta^{18} O$ measurements).

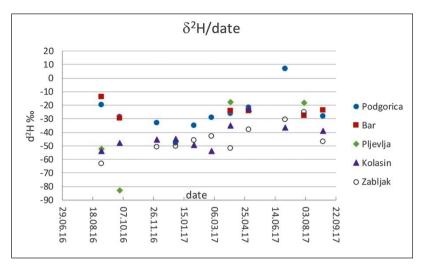


Figure 5: Diagram showing d²H-isotope values in precipitation from different localities versus time.

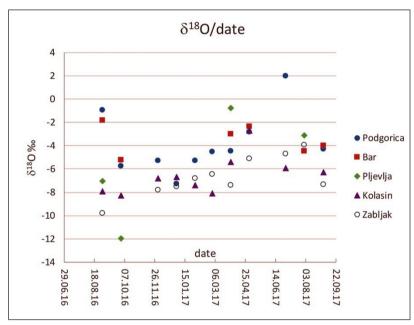


Figure 6: Diagram showing d¹⁸O-isotope values in precipitation from different localities versus time.

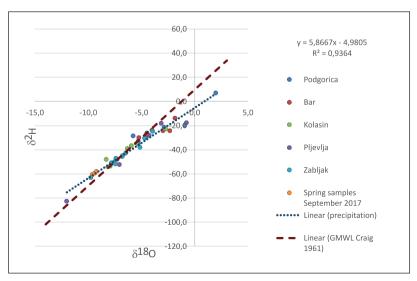


Figure 7: Diagram showing δ^2H and $\delta^{18}O$ isotope values of all analyzed water samples (precipitation and spring water) together with linear equation (Linear) of precipitation samples and R^2 , and with Global Meteoric Water Line (Linear (GMWL Craig, 1963)). Samples with highest isotope values dominantly plot on right side of GMWL and thus indicate evaporation effects. Spring water samples fit to regional water line (Linear (precipitation)).

Table 1: $\delta^2 H$ and $\delta^{18} O$ isotope values and d-excess of analysed water samples (precipitation and spring water).

Sampling locality	Sampling date	δ²H [‰] vs.VSMOW	δ^{18} O [‰] vs.VSMOW	D-excess
Bar	Sep.16	-14.2	-1.8	0.3
	Oct.16	-30.0	-5.2	11.7
	Apr.17	-24.4	-3.0	-0.5
	May 17	-24.4	-2.3	-5.8
	Aug.17	-27.7	-4.4	7.8
	Sep.17	-24.1	-4.0	7.9
Kolasin	Sep.16	-54.1	-7.9	9.3
	Oct.16	-48.1	-8.3	18.2
	Dec.16	-45.4	-6.8	8.8
	Jan.17	-44.9	-6.7	8.7
	Feb.17	-49.5	-7.4	9.8
	Mar.17	-54.2	-8.1	10.7
	Apr.17	-35.0	-5.4	8.4
	May 17	-23.1	-2.7	-1.7
	Jul.17	-36.6	-5.9	10.7
	Sep.17	-39.3	-6.3	11.1
Pljevlja	Sep.16	-52.6	-7.0	3.6
	Oct.16	-82.9	-12.0	12.9
	Apr.17	-17.9	-0.8	-11.8
	Aug.17	-18.4	-3.1	6.6
Podgorica	Sep.16	-20.1	-0.9	-12.7
	Oct.16	-28.7	-5.8	17.5
	Dec.16	-33.1	-5.3	9.0
	Jan.17	-48.2	-7.3	9.8
	Feb.17	-35.2	-5.3	7.1
	Mar.17	-29.2	-4.5	7.0
	Apr.17	-26.4	-4.4	9.1
	May 17	-21.8	-2.8	0.9
	Jul.17	6.8	2.0	-8.9
	Sep.17	-28.2	-4.3	5.8
Zabljak	Sept. 2016 + Oct. 2016	-63.6	-9.8	14.5
	Dec.16	-50.9	-7.8	11.7
	Jan.17	-50.5	-7.5	9.7
	Feb.17	-45.9	-6.8	8.3
	Mar.17	-43.2	-6.4	8.2
	Apr.17	-52.0	-7.4	7.2
	May 17	-38.2	-5.1	2.8
	Jul.17	-30.8	-4.7	6.7
	Aug.17	-25.1	-3.9	6.3
	Sep.17	-47.0	-7.4	11.8
Spring Cesma	Sep.17	-60.9	-9.6	15.6
Spring Vrelo	Sep.17	-60.6	-9.6	15.9
Spring Donjia	Sep.17	-59.4	-9.4	15.6
Spring Zelenika	Sep.17	-58.3	-9.2	15.1

The precipitation samples of the present study show a wide range of values from -12.7 to +18.2. The lowest values are from samples from spring to autumn. They might have some evaporation component, and/or represent individual single rain events, which might

have very variable deuterium excess values (Rank and Papesch, 2005). The highest values (17.5 and 18.2) come from Podgorica and Kolašin October samples. The spring water samples have very similar d values ranging from 15.1-15.9.

DISCUSSION

The precipitation isotope values from the coastal and lowland Bar and Podgorica sites are similar to published data from Dubrovnik (Horvatincic et al., 2005), the latter values are slightly more depleted, though. However, these published values are from an earlier period and thus not directly comparable, as more recent values are not available. Precipitation values from mountain collection sites (Kolašin, Žabljak) and far inland Montenegro (Pljevlja) show lower isotope values on average than the marine influenced lowland, as expected due to altitude and continent effects.

The $\delta^2 H$ and $\delta^{18} O$ isotope values from the investigated springs are very low. They do not fit at all with the data from the coastal and lowland region (Bar and Podgorica) and are also lower than most of the precipitation data from the high-altitude hinterland, but do fit with their high-altitude winter precipitation values. Thus, most likely the water from the investigated springs originates from winter precipitation at higher altitudes. The catchment area(s) of these springs seem to dominantly receive precipitation during the winter period (as snow, based on the water isotope signatures of the investigated samples) and are supplied throughout the year with this winter precipitation dominated water, perhaps due to melting of the snow during a longer period from spring to early summer. Furthermore, the deuterium excess values of the four springs investigated, which are very similar, show very high values. The Mediterranean Sea is a landlocked marine water body where, especially in winter, continental air masses impinge on seawater under conditions of large humidity deficit, a strong temperature contrast between air and water and isotopic disequilibrium between the atmospheric moisture and the water body (Gat & Dansgaard, 1972). Therefore winter precipitation originating from the Mediterranean Sea is characterized by distinctly higher d-excess values, reflecting the specific source conditions during water vapour formation.

The deuterium excess can be used to identify vapour source regions (Gat et al., 2003). The spring water samples have d-excess values ranging from 15.1-15.9 which indicates a water vapour source from the Mediterranean Sea during the winter months. Combined

with the $\delta^2 H$ and $\delta^{18} O$ isotope values the spring water samples are interpreted as coming from a high-altitude catchment and representing winter precipitation.

As all spring water samples are very similar, a common catchment area and similar to identical retention time for the springs investigated seems likely. An origin of the water of the investigated springs from the hinterland of the Morinj bay and thus the location of the catchment area(s) at lower (ca. 500 m a.s.l.) altitude is, based on our isotope results, very unlikely. Therefore, hypothesis II can be rejected and hypothesis I, assuming the high karst plateau of the wider Duboki do area/ region, is likely. However, due to the depleted isotope and the high d-excess values, we want to introduce working hypothesis III, assuming the origin of the investigated spring water samples from a catchment area of even higher altitude than Duboki do. A possible area might be Orjen Mountain, several kilometers further inland to the North of Duboki do. Due to sampling problems spring water samples were only collected once in summer 2017. This limits the study to a one-point or snap-shot view of the situation, and thus there also is the possibility that hypothesis I still might be valid for other times of the year. Therefore, further studies investigating the spring water and precipitation from potential catchment areas over an at least one year interval are required to tackle this question. At present, an origin of the water of the springs nearby Duboki do from the planned land fill area cannot be ruled out.

This result has serious implications with respect to the municipal water supply utilizing springs around the future land fill. Once in operation, the landfill poses a potential and continuous threat to the quality and innocuousness of the springs and their water. To prevent the supply with contaminated tap water (and thus also the contamination of the water line), the springs used for municipal water supply need to be closely and constantly monitored for their water quality, to detect any decrease in quality and potential health threat in time. If the landfill becomes leak it might contaminate the springs. Depending on the severity of the leakage and dilution the spring water used for tap water supply will require disinfection, filtration and maybe additional

processes (e.g. dilution) to maintain an acceptable water quality. Water contamination of springs not used for water supply might not directly negatively impact on

humans but will negatively influence the ecosystem and nature.

CONCLUSIONS

To solve the pressing question whether the construction of a new waste dump north of Herzeg Novi at ca. 1000 m altitude in a sinkhole (named Duboki do) in a karst mountainous area poses a threat for nearby karst water springs due to the risk of contamination, a stable isotope investigation of spring and precipitation water samples has been performed. The stable isotope results of samples from springs in the Herceg Novi region, compared with isotope data of precipitation from various stations in Montenegro, demonstrate an origin of the spring water samples from a high-altitude catch-

ment area receiving mainly winter precipitation, as the Duboki do locality. Thus, an origin from the Duboki do area cannot be ruled out and is the likely one of the two presented working hypotheses, with the other hypothesis of an origin of the spring water from a lower altitude area seeming much less probable. However, as an isotope record over a longer period for the investigated springs has not been produced, uncertainties remain, if the springs might be fed from a catchment area of even higher altitude, and thus further studies covering a longer sampling period are necessary.

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