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Analyses of soil, rock and water samples from the location of "French Mines" in the Medvednica Mountain

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Abstract

Historical mining site of the "French Mines" has great potential for promoting geodiversity and educating people about its significance and effects on the environment. In order to get more information about this location, combined preliminary geochemical and hydrogeological explorations were conducted following previous research in this area. Soil, stream sediments, rock and water samples were collected in two occasions and analyses were carried out. In this study, results of these preliminary geochemical and hydrogeological explorations, precisely pXRF (portable X-Ray Fluorescence) spectrometer analyses of soil, stream sediments and rocks, as well as results of in situ measurements and isotopic composition of groundwater and surface water samples are presented. Results suggest that previous mining activities did have significant impact on the overall chemical composition of soil due to elevated Pb, Zn and As contents that are significantly higher than the median value in this part of Croatia. In situ parameters and stable isotopes of water suggest existence of meteoric water.

Keywords: French Mines, Medvednica Mountain, hydrogeology, geochemistry

1. Introduction

According to the Nature Protection Law (OG 80/2013, OG 15/2018, OG 14/2019 and OG 127/2019), geodiversity is the diversity of non-living nature, and it consists of soil, rocks, minerals, fossils, landforms, underground objects, structures, natural phenomena and processes that created them through geological periods and are still creating them today. Considering the above mentioned, geological and related cultural heritage is one of the recognizable elements of the Medvednica Nature Park promoting geodiversity and educating people about its significance.
In this area combined geochemical and hydrogeological explorations were not performed. Considering the previous research, various authors explored different aspects associated with mining in this locality, precisely occurrences of lead and iron ore (**Šinkovec et al. 1988; Jurković, 2005**), geochemical characteristics of stream sediments (**Tomašić, 1997**), trace elements and heavy metal contents in the soil (**Pernar et al. 2008, Perković et al. 2017, Herceg, 2023**). Additionally, detailed speleological explorations were described by Bombardelli (**2003**). The newest research in the wider research area was related to the examination of soil water origin (**Kovač et al., 2022; Kovač et al., 2023**) as well to the usage of portable XRF to measure the influence of salt used during winter periods on the mobility of heavy metals in soil.

With that in mind, preliminary geochemical and hydrogeological explorations were conducted in the location of the "French Mines" on the northern side of Medvednica Mountain. Location was selected for having great potential in educational purposes and as good example of geodiversity and rich mining heritage in Croatia. According to Horvat (**1958**), French count Henri Carion opened these mines and mined galena for some period of time. Since the low amount of ore containing silver could be mined (**Poljak, 1976**), the venture in the end failed and mines were closed. Historically, lenticular and vein ores were mined from Devonian-Carboniferous dolomites. The veins, which align with a southeast-northwest fault system, are mainly composed of galena and quartz, along with smaller quantities of sphalerite, Cu-Fe-As sulphides, carbonates, and secondary weathering products (**Šinkovec et al., 1988**).

The purpose of this research was to get new insight into the geochemical characteristics of soil and sediment, as well to determine water origin. For that purpose, samples of soil, stream sediments, rocks and water were collected, and analyses were carried out.

2. Field and laboratory work

Field work was carried out in two occasions in February 2024. In the first occasion, four mines were located. Although a fifth mine is mentioned in the literature (**Božičević, 1994**), it has not been found. Soil samples were taken at three locations (Figure 1 – locations marked with 1, 2 and 4) and sampling was done with a manual auger in front of each entrance to the mine from a depth of 25 cm. On location marked with 3 (Figure 1) stream sediments were collected in front of the mine because it was located in the stream bed of the Bistra stream. Additionally, in the location marked with 4 (Figure 1) rock samples were collected since it was the only mine which could be entered.

In addition to soil, stream sediments and rock samples, water samples were collected at two locations. First sample was taken from the spring zone of the Bistra stream and second sample from the Third Mine (marked 5 and 6 in Figure 1) that was completely flooded. In both locations in situ parameters were measured, precisely, temperature, pH, dissolved oxygen, electrical conductivity, and turbidity. On the second occasion only water samples were collected. Groundwater was sampled on locations 7, 8 and 9, as well as sample from retention on location 10 (Figure 1). In-situ parameters of water samples were measured with the portable multi-parameter Multi 3630 IDS.

Stable isotopes of water (δ^2H and $\delta^{18}O$) were determined at the Laboratory for Spectroscopy of the Faculty of Mining, Geology, and Petroleum Engineering, University of Zagreb, using a Liquid Water Isotope Analyzer (LWIA-45-EP, Los Gatos Research). Data interpretation was done using the Laboratory Information Management System (LIMS for lasers 2015; **Coplen and Wassenaar, 2015**), while the measurement precision of duplicate samples was ±0.19 ‰ for $\delta^{18}O$ and ±0.9 ‰ for δ^2H. All results are presented with respect to VSMOW (Vienna Standard Mean Ocean Water). For the interpretation purposes Local Meteoric Water Line (LMWL) for Zagreb, based on the long-term time series was used (**Krajcar-Bronić et al., 2020**), as well as the newest data from the Velika Gorica site (Figure 2), located in the vicinity of the City of Zagreb. For precipitation sampling, Palmex RS-1 precipitation sampler was used. RS-1 can protect water sample from evaporation and can be used in most hydrology studies (**Gröning et al., 2012; Michelsen et al., 2018**).

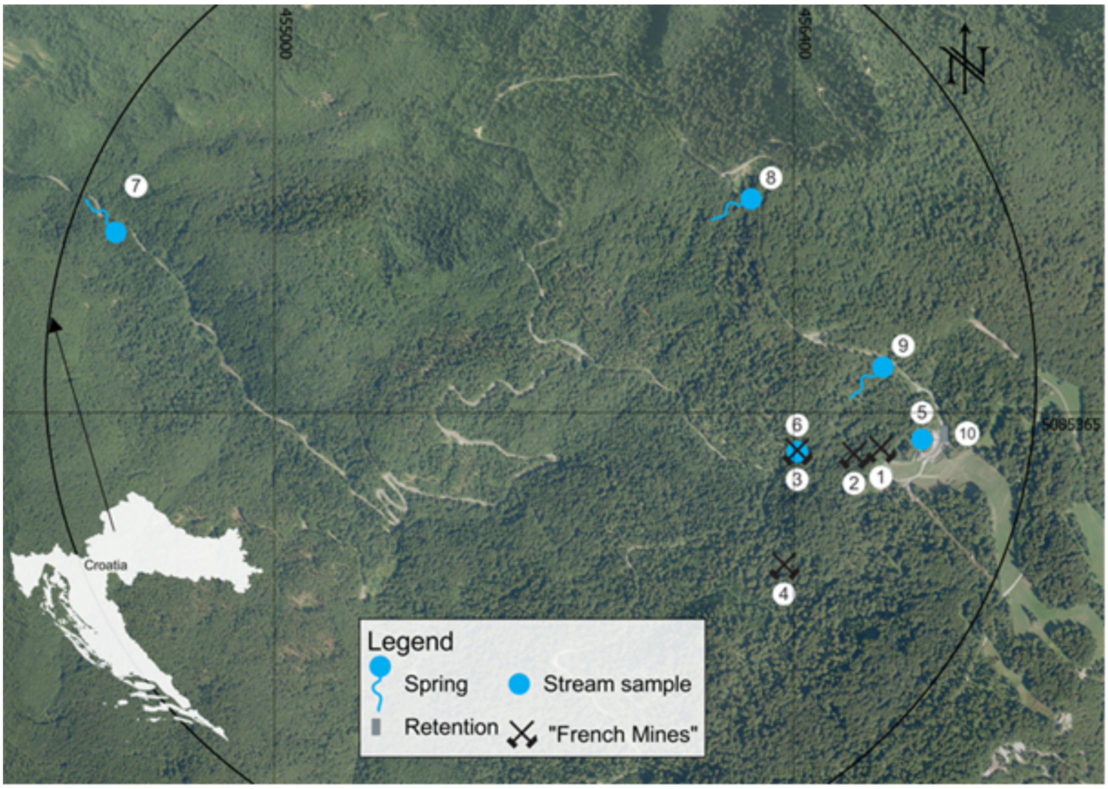

Figure 1: Overview map of the wider research area (northern slopes of Mt. Medvednica with sampling locations marked with numbers 1 to 10)

Figure 2: Location of "French Mines" compared to Velika Gorica site

3. Results and discussion

3.1. Preliminary soil and rock analyses

Considering the geological basemap of the research area (Sheet Zagreb) according to **Šikić et al.** (**1978**) and **Šikić et al.** (**1979**), four major geological units can be differentiated (Figure 3). Devonian-Carboniferous? (D, C?) is represented with orthometamorphites (green schists) and parametamorphites i.e. methamorphosed volcanic-sedimentary complex. Following this, the Aptian-Turonian is represented with volcanic-sedimentary complex ($K_{1,2}$) and diabases and spilites ($\beta K_{1,2}$). The basic characteristic of this complex is the tectogenetic connection of sedimentation and magmatism. Sedimentary rocks are represented with sandstones, shales, marls, cherts and limestones. Palaeocene (Pc) is represented with clastites and limestones. Their occurrence is preserved along the NW slopes of Medvednica Mountain and represented with gray and brownish-gray clayey and sandy marls and sandstones which spatially coincide with the volcanic-sedimentary complex of the older Cretaceous.

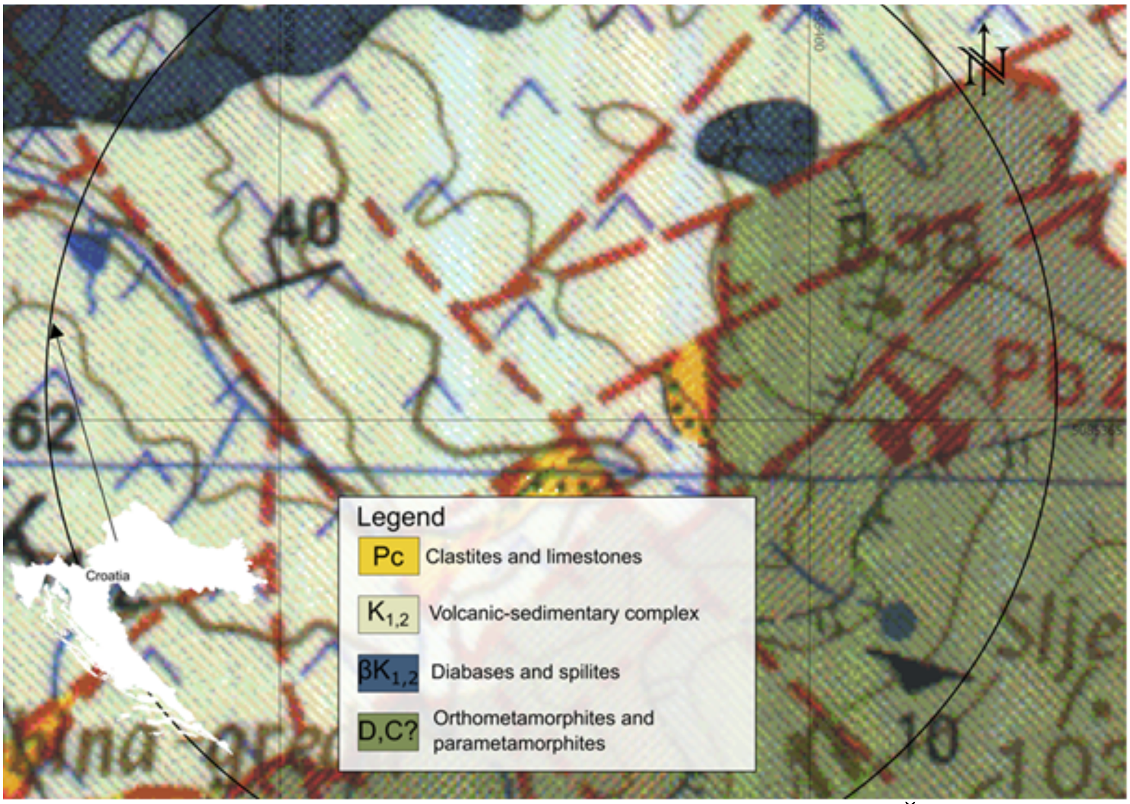

Figure 3: Geological map of the research area (modified according to **Šikić et al., 1978**)

Results of portable XRF analysis on four soil samples and two different types of mineralization in fourth mine, in the form of major and selected trace elements, aree given in Table 1. Four soil samples were taken in front of entrances to the mines, while the two additional samples represent two types of mineralisation in fourth mine (oxidative malachite mineralization and reductive galena mineralization). Typical elevated Ca and Mg contents are in line with carbonate rocks surrounding the mines. Silicon values are in line with occurrences of quartz which is hosting the mineralisation. Lead and zinc values are elevated in almost all cases, with values for Pb ranging from 160.00 up to 10976.40 ppm, and for Zn from 34.0 up to 278.20 ppm. Malachite and galena samples from fourth mine exhibit different chemistry than the rest of the samples. Malachite sample shows elevated Cu (81222.80 mg/kg = 8.12 %) and Fe (14.60 %), with also extreme enrichment of As (5586.20 mg/kg). Galena sample exhibits significantly elevated Pb (10976.60 kg/kg = 1.09 %) and S (1.56 %).

Measured contents of Pb (160.00– 10976.40 mg/kg, average 2863.40 mg/kg) and Zn (34.00 – 278.20 mg/kg, average 157.03 mg/kg) are significantly over the medium values for Pb and Zn in soil. The global average content of Pb in soils and sediments of Central Croatia is 25 mg/kg (**Halamić and Miko, 2009**). Same authors discovered that Pb in the central part of Croatia ranges from 13 to 198 mg/kg, with a median value of 25 mg/kg. In the central part of Croatia values of Zn are within the range of 27 – 362 mg/kg, with median value of 61 mg/kg. These values are significantly lower than the values obtained in this study. Elevated values are well in line with previous mining activity that was occurring in the study area during the 18th and 19th century as a part of quest for silver ore discovery.

Interestingly, arsenic values are also extremely elevated (42.00 – 5586.20 mg/kg), well above the range established by Halamić and Miko (**2009**) in Geochemical Atlas of Croatia (1.8 – 59 mg/kg). Possible reason is that arsenic mineralisation, such as arsenopyrite (FeAsS) can sometimes occur simultaneously with galena, or rather that up to 0.7% of As can be replacing Pb in galena (**George, 2013**).

Two samples from the fourth French mine, representing primary (galena) and secondary (malachite) mineralisation differ with regard to Pb, S, Cu and As. Arsenic content in malachite is most interesting. All studies analysing occurrence of malachite report very little, or no arsenic within malachite. Therefore, this could indicate that another mineralisation is present. It is proposed, that based on elevated Fe contents, occurrence of arsenopyrite is present here. As previously mentioned, arsenopyrite can sometimes occur alongside galena mineralisation, which might be the case here.

Table 1: Results of pXRF analyses. Bolded values for Cu, Pb, Zn, As and Ag represent values above maximum detected values in Central Croatia according to **Halamić and Miko** (**2009**)

Elemental Composition	**Concentration**	**Location number**					
		1	2	3	4	4 - galena	4 - malachite
Si	%	19.9	20.92	22.95	19.76	40.92	7.14
Ti	%	0.56	0.76	0.56	0.43	b.d.l.	b.d.l.
Al	%	8.71	7.89	7.13	8.06	0.2	1.7
Fe	%	6.9	9.21	5.76	5.27	0.59	14.6
Ca	%	9.46	7.4	8.61	12.15	0.85	21.31
Mg	%	4.14	3.94	4.76	3.62	b.d.l.	8.19
Mn	%	0.63	0.61	0.17	0.42	0.02	0.64
K	%	2.94	2.25	2.38	3.81	0.18	0.44
P	%	0.13	0.14	0.08	0.13	b.d.l.	0.08
S	%	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.56	b.d.l.
Cu	ppm	86.2	**1213**	70.2	271.6	**1233.8**	**81222.8**
Ba	ppm	284.33	217	209	229	210	375.25
Pb	ppm	**991.8**	**1060.4**	**160**	**3111**	**10976.4**	**880.8**
Zn	ppm	**154.8**	**239.8**	**107.4**	**128**	34	**278.2**
As	ppm	**190.2**	**304.8**	**42**	**199.4**	**256**	**5586.2**
Ag	ppm	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	**119.5**

Abbreviation: b.d.l. – below detection limit

3.2. Preliminary water analyses

Temperature, pH, dissolved oxygen, electrical conductivity, and turbidity were measured on six locations and are given in the Table 2 and shown in the Figure 1. In general, sampling locations can be divided into surface water sampling point (location 10), groundwater sampling points (locations 5, 7, 8 and 9) and sample form Third Mine (location 6). Values of pH vary from

6.779 in the surface water from the retention to 7.945 in the Third Mine. Electrical conductivity was highest in the Volarski Spring closest to the "French Mines" with value of 921 µS/cm and lowest again in the Retention, 203 µS/cm. Highest value of dissolved oxygen was measured in surface water, at location 10 (10.60 mgO_2/l) and lowest in the spring on location 7 (4.21 mgO_2/l). Water temperature varied from 6.5 °C to 10.6 °C, and turbidity from 0.35 to 9.15.

During the first sampling, in situ parameters were measured in the spring zone of the Bistra stream (location 5) and in the Third Mine (location 6). Although, at the time the Bistra stream was not in direct contact with the mine shaft, it is clear that during high water levels the stream submerges the mine. As shown in Table 2 (locations 5 and 6) main difference is observed in pH, electrical conductivity, and turbidity. Water from the Third Mine had higher values of electrical conductivity (533 µS/cm compared to 368 µS/cm) as well as higher pH values (7.945 compared to 7.496). It was expected for the pH values to be lower than the ones measured, since water flow through mineralised rock zones where mining exposes rocks to oxidation usually causes lower pH values (**Fetter, 2018**). Water from the mine shaft also had higher turbidity than a flowing stream (4.84 compared to 0.99).

During the second sampling, in situ parameters were measured on retention (location 10) as well as on the three springs (locations 7, 8 and 9). Spring on location 7 is in literature (**Šikić, 1979**) determined as a mineral water spring and it is called Sulphuric Spring. It has pH value of 7.583 which is higher compared to Oštrica Spring and Volarski Spring with values 6.848 and 7.412. Electrical conductivity varies from 560 µS/cm for Sulphuric spring to 921 µS/cm for Volarski Spring and 896 µS/cm for Oštrica Spring. Dissolved oxygen had similar values on Oštrica Spring and Volarski Spring (10.47 and 10.51 mgO_2/l) and significantly lower for Sulphuric Spring (4.21 mgO_2/l). This could be an indication of O_2-consuming reactions such as decay of organic matter or oxidation of sulphide minerals (**Weight, 2008**). Temperature and turbidity are similarly grouped. For Oštrica Spring and Volarski Spring temperature was measured 8.7 °C and 8.9 °C and turbidity 0.35 and 0.68. Water temperature on location of Sulphuric Spring was 10.6 °C and turbidity was 4.46 which is again higher than two previously mentioned locations.

Table 2: Results of in-situ measurements of water samples

Location number	Location name	Date	pH	Electrical conductivity (µS/cm)	Dissolved oxygen (mgO_2/l)	Temperature (°C)	Turbidity (NTU)
5	Spring zone Bistra	8.2.2024	7.496	368	10.38	8.5	0.99
6	Third Mine	8.2.2024	7.945	533	9.96	8.6	4.84
7	Sulphuric Spring	19.2.2024	7.583	560	4.21	10.6	4.46
8	Oštrica Spring	19.2.2024	6.846	896	10.47	8.7	0.35
9	Volarski Spring	19.2.2024	7.412	921	10.51	8.9	0.68
10	Retention	19.2.2024	6.779	203	10.60	6.5	9.15
Average			7.344	580	9.36	8.6	3.41
Minimum			6.779	203	4.21	6.5	0.35
Maximum			7.945	921	10.60	10.6	9.15

Stable isotope composition of all water is very similar (Figure 4). However, these preliminary results show grouping of spring zone Bistra and Sulphuric Spring, Oštrica Spring with Third Mine and Volarski Spring with Retention. Spring zone Bistra and Sulphuric Spring isotope composition suggest existence of the slightly different water with possible influence of Bistra stream on Sulphuric Spring. Grouping of Oštrica Spring and Third Mine suggests that water from the mine is not only from the Bistra stream, while grouping of Volarski spring and Retention is expected due to their morphology location and water which is probably coming from higher altitudes and flowing from northeast to southwest. However, in order to get more reliable results at least one year of isotope research is necessary, where sampling must be done in at least monthly sampling period. Additionally, these results should give relevant information for designing future sampling network. In general, all samples present meteoric water and are located slightly above the LMWL Zagreb, and between isotopic composition of precipitation which fell in December 2023 and January 2024 in the area of the Velika Gorica City. Results suggest that precipitation from February didn`t have a lot of influence on surface and groundwater samples taken within this research.

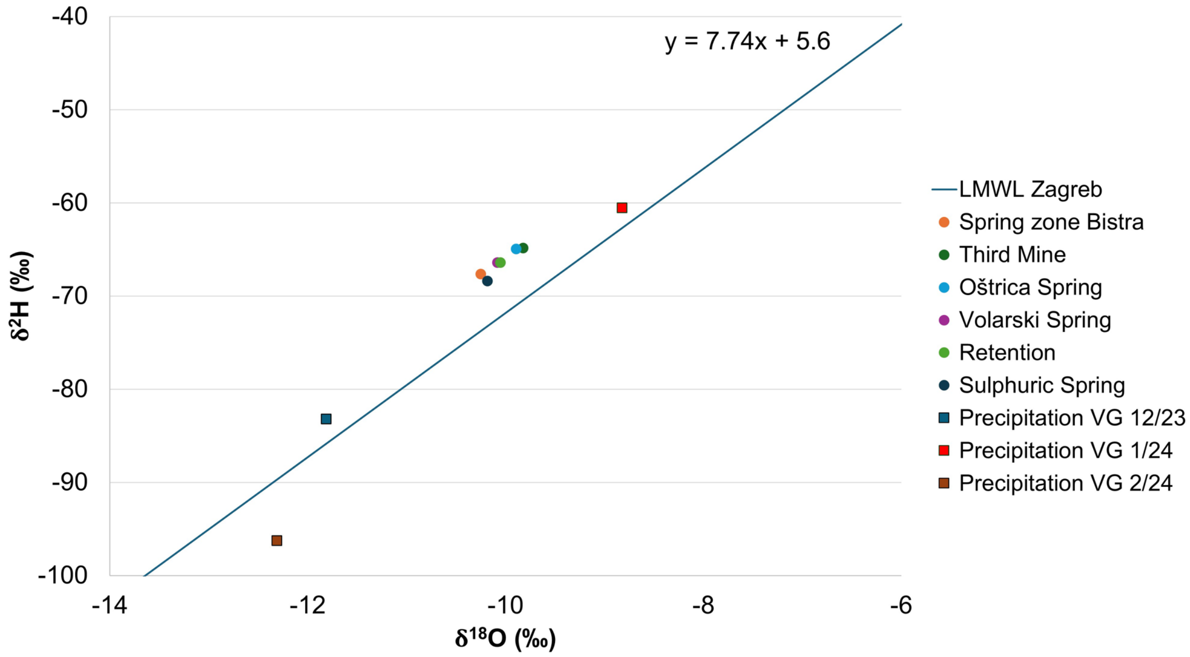

Figure 4. Isotopic composition of sampled water with respect to LMWL Zagreb and precipitation from Velika Gorica site in the period from December 2023 till February 2024

5. Conclusions

Combined geochemical and hydrogeological analyses were conducted in Medvednica Nature Park, mostly targeting zones in close vicinity of previously recognized French Mines. Based on the results obtained within this study, it can be concluded that previous mining activities did have significant impact on the overall chemical composition of soil.

Elevated Pb, Zn and As contents, significantly higher than the median valued in this part of Croatia, were discovered in all analysed sampled, suggesting intensive mining activities took place in this area. Furthermore, preliminary water stable isotope composition analyses suggest that water present in the Third Mine is the consequence of mixing between Bistra stream and groundwater. Also, variations in electrical conductivity, pH values and dissolved oxygen indicate that morphological and geological properties condition the diversification of the physio-chemical properties of the collected water samples which is also indicated with their preliminary grouping according to their stable isotope composition.

It is proposed that future studies include sequential extraction analysis to determine in what soil phases are heavy metals accumulating, as well as water chemistry in order to determine hydrogeochemical facies and ability for heavy metals to mobilize further in the environment, especially in groundwater. To conclude, all the above represents a significant insight into the consequences of historical mining and, in general, anthropogenic impact on the environment. Therefore, the location of the French Mines can be an excellent example of an insight into Croatia's rich mining heritage and geodiversity of the Medvednica Nature Park, which should be investigated in much more detail within the future research.

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Sažetak

Analiza uzoraka tla, stijena i vode s lokacije Francuskih rudnika na Medvednici

"Francuski rudnici" na Medvednici imaju veliki potencijal za promicanje georaznolikosti i edukaciju ljudi o njezinom značaju i učincima na okoliš. Kako bi se dobilo više informacija o ovome lokalitetu, provedena su preliminarna geokemijska i hidrogeološka istraživanja. U dva navrata prikupljeni su uzorci tla, potočnog sedimenta, stijena i vode te su provedene analize. U ovome radu prikazani su rezultati ovih preliminarnih geokemijskih i hidrogeoloških istraživanja, točnije pXRF (portable X-Ray Fluorescence) spektrometrijske analize tla, potočnih sedimenata i stijena, kao i rezultati in situ mjerenja i izotopnog sastava uzoraka podzemne i površinske vode. Rezultati pokazuju da su prethodne rudarske aktivnosti imale značajan utjecaj na ukupni kemijski sastav tla zbog povišenog sadržaja Pb, Zn i As koji su značajno viši od srednjih vrijednosti u ovom dijelu Hrvatske. In situ parametri i stabilni izotopi vode upućuju na postojanje atmosferske vode.

Ključne riječi: Francuski rudnici, Medvednica, hidrogeologija, geokemija

Author`s contribution

Borna-Ivan Balaž (1) (expert associate) participated in field sampling, laboratory analyses and wrote most of the manuscript. **Tomislav Brenko** (2) (assistant) participated in field sampling, laboratory analyses and wrote most of the manuscript. **Zoran Kovač** (3) (associate professor) participated in data processing and laboratory analyses, results interpretation and editing of the manuscript **Stanko Ružičić** (4) (associate professor) participated in data processing and editing of the manuscript.