Geological Investigations with Dye-tracing Technique and Trace Elements in Water and Sediments, Biokovo Mt (Croatia)

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Abstract

Makarski Vrutak, Orašje, Grebice, Podgorski Vrutak and Izbitac are the gravity springs in the Split – Dalmatia County, Republic of Croatia. They are tapped and included in the local water supply system. Submarine spring Klokun and spring Blace are not part of the local water supply system. Inflow area of these typical karstic springs is composed of the Mesozoic carbonate rocks and minor part of Eocene age flysch deposits. Occurrences of the springs are related to the fault contacts of carbonate rocks and flysch deposits. Biokovo Mt lies in SE Europe in the North Mediterranean region, directly by the eastern Adriatic Sea coast. It is part of the geotectonic zone of the Outer Dinarides. Its relief is the result of tectonically disturbed deposits of Jurassic and Cretaceous limestones, which favoured the development of surface and underground karst features.

The aim of this study was to investigate geological characteristics of this watershed with dye-tracing technique and trace elements in water and sediments, presenting one of the most typical karstic areas in the world.

Ground water flow is established with dye-tracing technique. First dye-tracing was done with 3.12 kg Uranine which was poured into the pit Mala Marija on the location Lađena. Observed springs are situated on the Adriatic coast and on the slopes of the Biokovo Mt at the distance of 1.82 – 8.8 km from the Mala Marija pit. The apparent velocity of the groundwater flow for spring Orašje is 0.20 cms^{-1} and for Grebice is 0.48 cms^{-1}.

The second dye-tracing was done with 5.0 kg Uranine which was poured into the Saranač pit on the location Saranač. Observed springs are situated on the Adriatic coast and on the slopes of the Biokovo Mt at the distance between 6.07 and 6.96 km from the Saranač pit. There is no confirmed connection between the Saranač pit and springs Grebice, Podgorski Vrutak, Izbitac, Blace and submarine spring Klokun by ground water analysis.

First dye tracing was partially effective and second dye tracing was ineffective.The reason of this ineffectivness might be due to a geological barrier, probably some immanent ore mineralization.

For the first time, concentrations of 6 dissolved and total trace elements were determined in groundwater samples of this region, using voltammetry. Their concentrations were extremely low, up to three orders of magnitude lower than Croatian standards for drinking water. This supports our earlier finding that water from Biokovo Mt springs is of an extreme quality.

The mass fractions of 60 elements were determined in 3 representative spring sediments. Highest measured concentrations of some heavy metals in sediments ($mgkg^{-1}$) are: lead 5440, chromium 118, manganese 935, zinc 116 and barium 238. It is assumed that lead in sediments is of natural origin, as a result of ore mineralization. This could lead to conclusion that in the deeper layers of Biokovo Mt some Triassic or even Paleozoic magmatic or metamorphic rocks might be present, what would explain elevated concentrations of many metals in sediments. Indicators of mineralization in the groundwater and sediments samples suggest possible Pb-Zn ore-associations, what is supported by mineralogical analysis.

Keywords : *Biokovo Mt (Dalmatia, Croatia); Karstic springs; Dye-tracing technique; Trace elements in water and sediments; Mineralogy.*

Introduction

The aim of this study was to investigate geological characteristics of Biokovo Mt. watershed with dye-tracing technique and trace elements in water and sediments, presenting one of the most typical karstic areas in the world. It is a part of the Dinaric Mt. and the Dinaric karst is the «locus typicus» of karst. Also, the Biokovo Mt. with its gravity springs is very important as drinking water supply.

There is a long tradition of using hydrogeological and geochemical methods like tracer technique which is a tool for solving problems associated with resources and management of groundwater and pollutants in water.

First detailed report about water supply of this area was provided by Štambuk-Giljanović (2002). Čakarun et al. (1990) have described zones of sanitary protection in professional report but war in Croatia stopped administrative procedure. The observed terrain was a subject of extensive hydrogeological investigations for the first time during the 2007, 2008 and 2009 and results have been described in professional report (3). Those last hydrogeologycal investigations have shown that investigated area is characterized by slope relief (area of Saranač Pit - location Saranač 800 m a.s.l.; area of Mala Marija Pit – location Lađena 1440 m a.s.l.; top of the Biokovo Mt 1762 m a.s.l.) composed of high hills and karst dolines. Stretching of the geological structure is northwest-southeast, typical for this part of the Croatian karst terrains; it is called «Dinaric» after the mountain Dinara (4). Dinaric karst is characterized by very deep and irregular karstification mainly predisposed by tectonics, compression, reverse faults and overthrusting structures (5).

Study area

Geographic position and geomorphological characteristics of Biokovo Mt

Biokovo Mt is situated in South Eastern part of Europe close to the Eastern Adriatic coast. Study area of this paper includes Biokovo Mt ridge of the southern part of mountain and it is a part of geotectonic zone of outer Dinarides (6).

Very typical for this area is a karst with sinkholes, caves and pits. The area is characterized by deep karst, where vertical circulation of groundwater prevails. There are no permanent water courses and occasional water courses are also rare and are formed only in the events of heavy rains. Groundwater is emerging at the surface in the form of springs called "vrulje", which are formed at the contact of limestones with flysch along the coast line at the SW edge of study area.

Heterogeneous relief (Fig. 1), expressed elevation differences on a small area and geological basis with formed typical karstic relief in the zone of so called deep karst are basic determinants of studied area in the southern part of Biokovo Mt.

a)

b)

c) d)

Figure 1. Heterogeneous relief of the investigated area

Climate characteristics of Biokovo Mt

The continental side of Biokovo Mt belongs to the transitional climate type between maritime and continental influence, while the coastal side belongs to maritime climate type. According to Köppen climate classification, larger area belongs to temperate warm pluvial climate (C class climate), while parts above 1200 – 1500 m a.s.l. are belonging to snow-forest climate (D class).

The mean annual precipitation on the coastal side is 1043 mm and in the highest northern parts of Biokovo Mt range from 2000 mm to 2500 mm. Precipitation is mostly in the form of rain and in winter rarely in form of snow.

The annual amplitude of air temperature is ranging between 15˚C and 20˚C. In the highest parts of the mountain mean temperatures in January range between 0ºC and 4ºC, while absolute minimal temperature could be lower than -25ºC.

Geological and tectonic setting of the southern part of the Biokovo Mt

Most of the Makarski Vrutak, Orašje, Grebice, Podgorski Vrutak, Izbitac, Blace and submarine spring Klokun catchment areas are composed of Mesozoic carbonate sedimentary rocks and minor part of Eocene age flysch deposits, as well as some various types of Quaternary sediments. In Fig. 2 is presented hydrogeological map of part of investigated area. The Mesozoic carbonate rock formation is completed with Jurassic and Cretaceous limestones and subordinate dolomites. Upper Jurassic limestones form the cores of anticlines. The Paleogene formation is completed with Paleocene-eocene breccias, Eocene limestones and Eocene flysch (clastic rocks). The Paleocene-eocene rocks are transgressive over Upper Cretaceous sedimentary rocks and form the cores of anticlines. Their base is composed of breccias, breccias limestones and calcarenites. Clastic Paleogene rocks – the Eocene flysch – is composed of marls, calcisiltites, and clayey limestones. These deposits form the cores of synclines and are usually eroded. Flysch deposits are extended along the coastline and play a crucial role in forming the Makarski Vrutak, Orašje, Grebice, Podgorski Vrutak, Izbitac, Blace springs and submarine spring Klokun as they separate the permeable, freshwater saturated carbonate rock from the sea. These deposits have hydrogeological function and act as total or hanging barriers for the karst groundwater. Quaternary deposits (clays, sandy clays, «terra rossa» and sippar) covering karstified limestones and dolomites and also Eocene deposits. Rare Quaternary deposits can occur both in the sinkholes «terra rossa» and on the steep part of the seaward side of the coastal range forming the rockfalls. In the watersheds it is quite thin and discontinuous and with no hydrogeological relevance regarding groundwater flow.

Geological structures in the surveyed area extend mostly NNW-SSE or NW-SE. From the structural-geological point of view the terrain is composed of several anticlines and synclines. These follow the so-called «Dinaric» stretching (NW-SE), parallel to the coast. The investigated area is a heavily faulted terrain with predominantly dip-slip movements which is tectonically disturbed by joints and reverse faults of different size and importance. Some of them are not visible at outcrops (3).

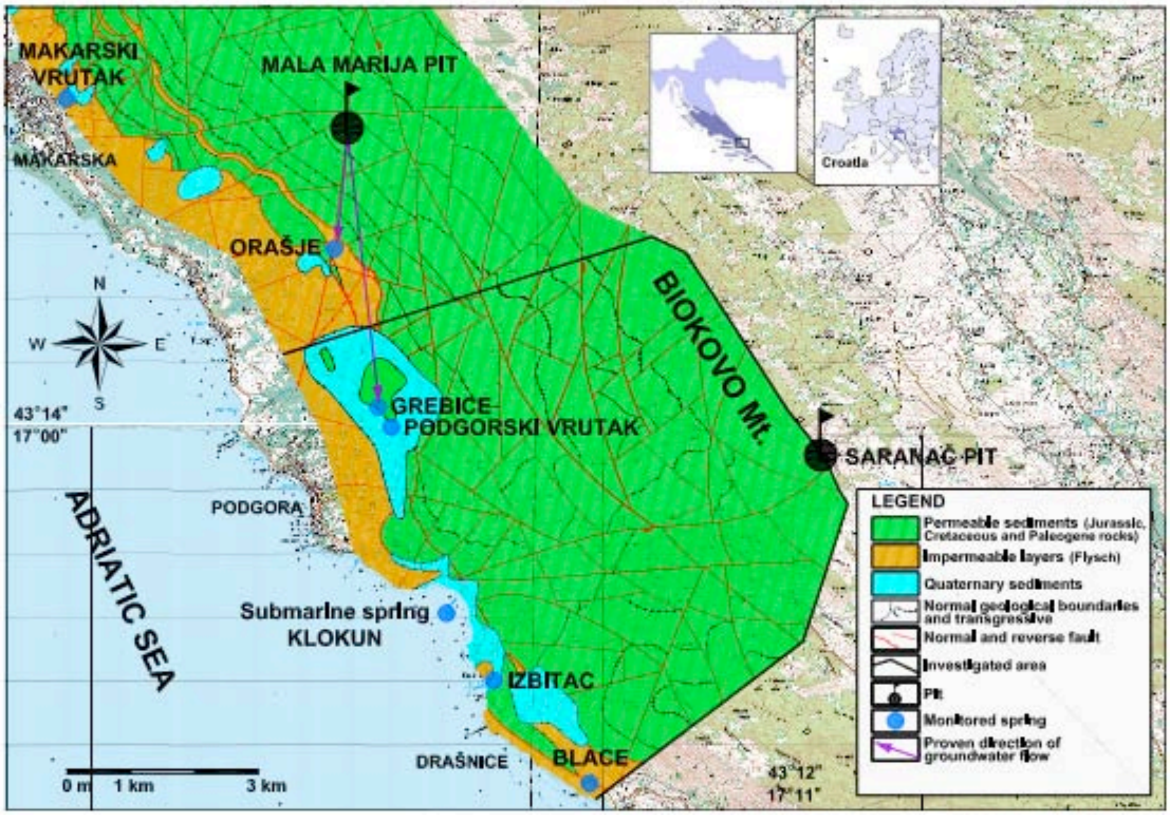

Figure 1. Hydrogeological map of part of investigated area

Hydrogeological setting of the southern part of the Biokovo Mt

From microlocation standpoint springs Makarski Vrutak is situated near Makarska town, Orašje is situated near Tučepi settlement, Grebice and Podgorski Vrutak are situated near the settlement Podgora, while springs Izbitac and Blace are situated near the settlements Drašnice and Igrane. Submarine spring Klokun is situated near settlement Drašnice on the Adriatic coast, Croatia. Inflow area of this typical karst springs is composed of the Mesozoic carbonate rocks and in minor part of Eocene age flysch deposits. Occurrences of the springs are related to this fault contact (3). Simple geology of the Mesozoic carbonate rocks and Eocene flysch deposits covered by a sippar might have enabled formation of a secondary geochemical halo.

Observed gravity springs are very important for Split – Dalmatia County, Republic of Croatia. They are tapped and included in the local and regional water supply system. Relations between minimal and maximal discharge of two of those springs are typical for karsts conditions. The spring Izbitac shows untypical behavior for the karst springs. Results are presented in Table 1. Ratio between minimum and maximal discharge was 1:4.4 and this spring has no karst features. This theory confirmed extremely low recession coefficient of base flow (α =0,009). The reason could be some natural barrier in the hinterland, slowing and limiting groundwater flow (3).

Table 1. Values of Electrolytic Conductivity (EC), Total Dissolved Solids (TDS), Concentration of hydrogens ions in a solution (pH), Temperature (T), Min. discharge (ls^{-1}) and Max. discharge (ls^{-1}) (measured each day during 2007 to 2009 and June 2011) (3)

Spring	Parameters	Range of measured values	Mean value	Min. discharge (Ls^{-1})	Max. discharge (Ls^{-1})
Makarski Vrutak	EC (μScm^{-1})	304 - 327	316	3.89	400
	TDS (mgl^{-1})	216 - 232	224		
	pH	7,17 - 7,57	7.37		
	T (°C)	13.60 – 14.09	13.85		

Orašje	EC (μScm^{-1})	229 - 233	231	0.96	60
	TDS (mgl^{-1})	163 - 165	164		
	pH	7,71 - 8,07	7.89		
	T (°C)	12.68 – 12.98	12.83		
Grebice	EC (μScm^{-1})	245 - 257	251.0	2.3	63
	TDS (mgl^{-1})	174 - 183	178.5		
	pH	7.5 - 7.95	7.725		
	T (°C)	11.92 - 12.65	12.25		
Podgorski Vrutak	EC (μScm^{-1})	250 - 259	254.5	3.7	74
	TDS (mgl^{-1})	178 - 184	181.0		
	pH	7.18 - 7.71	7.445		
	T (°C)	12.11 - 12.28	12.2		
Izbitac	EC (μScm^{-1})	357 - 368	362.5	4.76	21
	TDS (mgl^{-1})	254 - 261	257.5		
	pH	7.18 - 7.68	7.43		
	T (°C)	14.9 - 15.0	14.95		

Materials and methods

Hydrogeological tracing

In general, the most practical, convenient, safe, available and satisfactory technique to provide information for the management and protection zoning of karst water sources is dye tracing.

Toward estimated values for the first and second dye tracing the total discharge of all springs under observation was 0.5 m^{3}s^{-1}. According to calculations for the first dye tracing values between 2.2 and 4.4 kg and for the second dye tracing values between 3.5 and 4.2 kg Na-fluoresceine were received.

At the time of the first dye tracing on 27th March 2008, 3.12 kg Na-fluoresceine with 1.5 kg NaOH were injected into the Mala Marija Pit (1260 m a.s.l.). The monitoring of the observed springs lasted for 30 days (3). Also, at the time of the second dye tracing on 4th June 2010, 5.0 kg Na-fluoresceine with 2.0 kg NaOH were injected into the Saranač Pit (725 m a.s.l.). The monitoring of the observed springs lasted for 45 days. Larger quantity of dye Na-fluoresceine was used because the results of first dye tracing with Na-fluoresceine in this area was less successful, what indicated larger adsorption processes during the transport of the tracer.

Dye tracing was done in a humid period during the time with high water level because the velocities of the groundwater are then the biggest.

Before the tracer injection, 1 m^3 of water was poured into the Saranač Pit and after injection tracer was washed with 10 m^3 of water. Water samples were measured using Perkin Elmer LS 55 Luminescence Spectrometer (USA) and limit of quantification was 0.0001 mgL^{-1} (7).

Sampling and determination of elements in water

Water samples for measurements of six ecotoxic trace metals Cu, Cd, Pb, Zn, Co and Ni were collected in pre-cleaned high-density polyethylene (HDPE) bottles (0.5 L). Concentrations of total metals were measured in unfiltered water samples. Total dissolved fractions (hereafter named dissolved) were determined after filtration under nitrogen pressure through 0.45 μm cellulose nitrate membrane filters (Sartorius, Göttingen, Germany). Prior to analysis, unfiltered and filtered water samples for determination of trace metals were acidified with Suprapur® nitric acid (Merck, Darmstadt, Germany) to a pH < 2 and UV irradiated for 24 hours (150 W mercury lamp, Hanau, Germany).

The electrochemical method used for measuring Cd, Pb, Cu and Zn in water samples was differential pulse anodic stripping voltammetry (DPASV), while Ni and Co were measured by differential pulse cathodic stripping voltammetry (DPCSV). The standard addition method was used for determination of trace metal concentrations. Uncertainties (±) of trace metal concentrations in water samples were given as 95% confidence intervals. Trace metal concentrations in water samples were measured on the ECO Chemie μAUTOLAB multimode potentiostat (Utrecht, The Netherlands) connected with a three-electrode system Metrohm 663 VA STAND (Metrohm, Herissau, Switzerland). A hanging mercury drop was used as a working electrode with a drop surface of 0.25 mm^2. A platinum wire was used as a counter electrode and Ag|AgCl as a reference electrode. Limit of detection (3σ), LOD, obtained in acidic Milli-Q® (Millipore, Billerica, USA) water were 0.5, 1, 5 and 5 ng L^{-1} for Cd, Pb, Cu and Zn, respectively and for Co and Ni LOD were 1 and 10 ng L^{-1}, respectively.

Quality control of the applied voltammetric methods was verified by determining trace metal concentrations in River Water Reference Material for Trace Metals (SLRS-5), of National Research Council Canada. All measured metal concentrations were within 5 % of certified values.

Sampling and determination of elements in sediments

Sediment samples were air-dried in a shade for several days and then sieved, using three standard sieves, Fritsch (Germany), of diameters 2000, 500 and 63 μm. Fine fraction (<63 μm), which is easily transported and usually used in environmental studies, was further analyzed.

Determination of major elements in stream sediments (fraction <63 μm) was performed in commercial laboratory ACTLABS, Ontario, Canada, using FUS-XRF method and equipment for irradiation beam (WDS, XRF, ARL 8410) and program 4C. Concentrations are expressed as percentages of related oxides. Following standards were used: DNC-1, W2, SY-3, SGR-1 and BE-N.

Multielemental analysis was performed in ACTLABS laboratory in fraction <63 μm, using ICP-MS (Inductively Coupled Plasma Mass Spectroscopy), with program «Ultratrace 2». The procedure was as follow: 0.5 g of sample is dissolved in aqua regia at 90ºC in a microwave digestion unit. The solution is diluted and analyzed using a Perkin Elmer SCIEX ELAN 6100 ICP-MS instrument. For analysis the following reference materials were used: USGS GXR-1, GXR-2, GXR-4 and GXR-6, which were analyzed at the beginning and after analyzing each series of samples. Elements Ti, P and S were analyzed with ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) using a Perkin Elmer OPTIMA 3000 ICP spectrophotometer.

Although this digestion is not total, its use is justified because the international standard methods for determining action limits are based on aqua regia leach (8).

Mercury was determined also in ACTLABS, using the same solution prepared from sediment fraction <63 μm for ICP-MS analysis. Program 1G-Hg-CV was used and international standards SO-2, GXR-4, GXR-2 and GXR-1. It is performed using CV-AAS method (Cold Vapor Atomic Adsorption Spectrometry). Hg is oxidized in solution till the state of stable divalent ion. Its concentration is determined using Hg vapor, which is adsorbed at wave length of 253.7 nm, besides reducing of Hg (II) in evaporating state (Hg°) using $SnCl_2$. Argon is running through the mixture of sample and reducing solution, which transports Hg atoms into adsorption cell, which is situated in beam of atomic adsorption spectrophotometer. According to Beer's law, emission intensity which is being adsorbed is proportional to concentration of Hg atoms in emission beam of λ = 253.7 nm.

Determination of mineralogical composition of sediments

Mineralogical composition of sediments (fraction <63 μm) was determined by X-ray diffractometer Philips, X-Pert MPD (start position: 82Q: 4.01; end position: 82Q: 62.99; generator settings: 40 kV, 40 mA). Crystalline phases were identified using a Powder Diffraction File (1997) and computer program X'Pert High score 2002, Philips. Semi quantitative mineralogical composition was determined as described in Boldrin et al. (1992).

Results and discussion

Hydrogeological tracing

The Na-fluoresceine was injected in the Mala Marija Pit and was later measured in five springs: Makarski Vrutak, Orašje, Grebice, Podgorski Vrutak and Izbitac. Dye was observed in two of those springs: Orašje (concentration 0.0024 mgL^{-1}, max concentration 0.0086 mgL^{-1}) and in Grebice (concentration 0.0010 mgL^{-1}, max concentration 0.0156 mgL^{-1}). Only five grab samples had the Na-fluoresceine in concentration >0.0001 mgL^{-1}. Exact data about distances from the pit and groundwater velocities could be found in Table 2. The analysis of the Na-fluoresceine dye tracer was carried out at the Croatian Geological Survey, Zagreb. According to calculations the recovery of injected tracer was 0.12 % and available discharge of the Grebice spring was 5 Ls^{-1} (3).

Table 2. Obtained data of dye tracing of the Mala Marija Pit during March and April 2008 (3)

Spring	Distance from the Mala Marija Pit (m)	Hours (h)	Apparent maximum velocity (cms^{-1})	Conc. (mgl^{-1})	Hours (max conc.) (h)	Apparent dominant velocity (cms^{-1})	Max conc. (mgl^{-1})
Makarski Vrutak	4793	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Orašje	1820	245	0.21	0.0024	252	0.20	0.0086
Grebice	4465	245	0.51	0.0010	258	0.48	0.0156
Podgorski Vrutak	4627	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Izbitac	8800	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not determined

Apparent velocity for the spring Orašje was 0.21 cms^{-1} and for the spring Grebice was 0.51 cms^{-1}. It was interesting that apparent velocities were under the calculated values reported by Jones (1977) and Milanović (1979).

Also, the second dye tracing was done with Na-fluoresceine. Na-fluoresceine was inserted in the Saranač Pit and five springs were observed: Grebice, Podgorski Vrutak, Klokun, Izbitac and Blace. No one grab sample had a Na-fluoresceine in concentration >0.0001 mgL^{-1}.

It is hard to admit that the investigation area of the southern part of the Biokovo Mt (Saranač area) does not belong to the Grebice, Podgorski Vrutak, submarine spring Klokun or Izbitac springs catchment area (7).

First and second dye tracing with Na-fluoresceine show that dye tracing with Na-fluoresceine in this area was less or completely inefficient.

According to the presented results it is obvious that dye tracing experiments can be either successfully or less successfully used in simultaneous investigations of hydrokarst systems. The major advantage of Na-fluoresceine tracer is extremely low detection limit. Also, represented results from the first dye tracing indicate larger adsorption processes during the transport of the tracer. The possible adsorption was to be seen in connection with some type of natural mineralization, in this case relatively high lead concentration in sediment. The second dye tracing with Na-fluoresceine, in investigating area, was inefficient. The reasons for that can be: geological settings, tracer was less conservative than expected (huge level of dye sorption), low mass of Na-fluoresceine, high rainfall (on 21st June 2010 which was 309 mm) and huge dilution of Na-fluoresceine in the mountain aquifer. Possibly monitoring of the tracer test was terminated prematurely because assumed effective porosity was too low and hydraulic conductivity was too high. In addition, measured concentrations were too low to be used for quantitative interpretation because dispersivity values were underestimated, ratio of anisotropy and/or principal directions of anisotropy were «misevaluated», location of the grab sampling was incompatible with the actual flow pattern, vertical component of hydraulic gradient was neglected or «misevaluated», instrument detection level was too high and etc.

The Na-fluoresceine should not be the adequate tracer because of possible strong sorption properties or nonconservative behavior due to adsorption onto ore or mineralisation deposits. In this case it is necessary to use larger amounts of Na-fluoresceine approximately two to three times more (12) and even more because for the second dye tracing it is used double amount than it was necessary for the karstified aquifers. Mather et al. (1969), Merritt and Angerman (1972) also have reported much less success using Na-fluoresceine to study old mine workings. Sorption of dye in ores is in contrast to their behavior in karstified limestone aquifers (15).

Trace elements in spring waters

Voltammetric measurements for Zn, Cd, Pb, Cu, Ni and Co are performed and results are presented in Table 3.

Concentrations of all studied elements were extremely low, up to three orders of magnitude lower than Croatian standards for drinking water, what supports our earlier finding that water from Biokovo Mt springs is of an extreme quality. The difference between the nonfiltered and filtered fractions shows the amount of trace elements bound to particulate matter of sizes greater than 0.45 micrometers. The origin of these particles was not investigated within the present paper.

It is obvious that in some springs and for some of measured elements differences between NF and F values are higher than in the other springs, what could indicate that in some springs amount of particulate matter is higher than in other springs. That is especially visible in Izbitac spring, where majority of measured elements have much higher values in NF than in F water samples. In Izbitac spring is especially interesting situation in sample taken in June 2011, as Pb concentration in NF water sample is about 25 times higher than in F sample. In this spring extremely high concentrations of Pb in sediments were found, so we assume that such drastic difference in values between NF and F water samples are caused by presence of particles rich with Pb.It is known that Pb has a strong adsorption affinity for natural particles. In Izbitac spring situation is similar with all other measured elements, but differences are not so drastical as for Pb. Makarski Vrutak spring has in June 2011 sample rather high differences between NF and F samples for Zn, Cd and Pb, while Orašje has the same situation with those elements in November 2011. In Blace spring, sample taken in November 2011. shows Zn concentration in NF water sample significantly higher than in F sample.

Table 3. Concentrations of trace elements (with standard deviation in the second column for each element) in spring waters obtained by voltammetric method

Uzorak		Zn (ng/l)		Cd (ng/l)		Pb (ng/l)		Cu (ng/l)		Ni (ng/l)		Co (ng/l)	
Makarski Vrutak (June 2011)	F	39,41	2,92	0,95	0,53	2,23	2,03	27,72	1,51	48,29	3,90	7,81	0,63
	NF	64,72	2,80	3,13	0,27	5,25	0,72	33,03	1,61	60,56	5,96	10,55	0,34
Makarski Vrutak (November 2011)	F	85,00	5,80	1,39	0,10	2,05	1,00	62,30	7,30	66,11	7,40	7,46	0,98
	NF	89,00	8,70	5,70	1,20	2,11	0,40	73,40	7,90	76,28	3,40	7,99	0,79
Orašje (June 2011)	F	83,82	4,23	2,25	0,65	3,84	0,79	106,01	5,59	60,36	2,65	8,51	0,53
	NF	96,67	4,36	5,02	0,38	8,13	1,48	127,79	2,41	66,03	4,17	10,55	0,58
Orašje (November 2011)	F	67,30	7,30	0,50	0,08	1,49	1,32	63,60	6,40	57,80	2,08	7,01	0,46
	NF	83,90	5,20	2,48	0,95	4,47	0,86	73,20	6,70	62,56	4,69	8,75	0,63
Grebice (June 2011)	F	50,41	2,65	3,82	1,05	3,24	1,84	31,38	1,45	46,63	5,08	8,17	0,71
	NF	55,45	0,65	4,71	0,71	4,16	0,47	43,88	2,39	56,46	3,72	10,37	0,89
Grebice (November 2011)	F	93,90	8,30	1,19	0,11	2,38	0,18	51,80	9,90	42,93	3,91	8,14	0,41
	NF	106,00	9,00	1,19	0,28	8,64	0,78	53,10	3,20	78,34	2,68	11,64	0,86
Podgorski Vrutak (June 2011)	F	97,54	4,43	4,39	0,57	6,73	1,21	94,65	7,40	67,48	2,32	8,64	0,53
	NF	98,98	4,23	4,41	0,10	10,63	0,49	115,49	6,01	90,67	3,84	12,40	0,40
Podgorski Vrutak (November 2011)	F	92,30	8,40	0,91	0,50	1,85	0.96	46,70	5,70	42,14	2,34	7,21	0,35
	NF	121,00	10,00	1,76	0,85	5,50	0,04	84,50	14,00	59,53	3,85	10,00	0,40
Izbitac (June 2011)	F	45,69	2,01	1,21	0,51	0,86	0,32	47,44	3,52	64,83	4,19	9,61	0,54
	NF	89,30	7,86	2,40	0,19	21,26	2,19	77,41	3,49	121,43	4,28	21,88	1,17
Izbitac (November 2011)	F	104,00	8,00	2,10	0,98	3,81	1,57	115,00	23,00	52,38	2,74	8,16	0,29
	NF	111,00	6,00	2,43	0,51	11,70	0,80	116,00	19,00	51,58	6,59	9,63	0,59
Blace (June 2011)	F	176,75	7,66	2,27	0,58	12,11	0,81	242,24	4,33	127,54	6,30	12,38	0,80
	NF	185,61	9,70	3,80	0,53	19,28	1,01	258,35	9,85	137,22	3,85	14,78	0,67
Blace (November 2011)	F	52,30	7,00	1,18	0,55	5,32	1,07	68,60	0,00	64,90	12,40	8,14	0,61
	NF	131,00	16,00	2,30	0,10	6,11	1,12	91,30	6,30	68,80	8,90	8,43	0,76

From results presented in Table 3 it can be suggested that springs Makarski Vrutak and Izbitac show similarities.

Elemental composition of sediments

Results of ICP-MS analysis of 60 elements in three selected sediments (from captured springs) are presented in Table 4. Distribution and behavior of several selected most significant elements will be discussed and more details could be found in Matić et al. (2011).

Lead (Pb) is found to be most interesting among investigated elements, as its concentrations are extremely high (highest value of 5440 ppm is measured in Izbitac spring). At other two investigated springs concentrations are also significantly high. According to sediment quality criteria (British Columbia, Canada legislative), all three springs regarding Pb concentrations in sediments belong to heavily contaminated sediments which could cause significant toxic effects (>250 ppm). Lead concentrations found by us are comparable to those obtained by Pavlowsky et al. (2010) in «The Old Lead Belt», a historic Pb-Zn mining district within St. Francois County in Southeast Missouri, which was a leading producer of lead worldwide from 1869 to 1972. There they treated all sediments with concentrations >400 as contaminated. Although such Pb concentrations in sediments pose a potential health risk, elevated concentrations of Pb luckily have not been found in spring waters. As Biokovo Mt is composed mostly of carbonate rocks, prevailing water type is slightly alkaline. Because of that heavy metals from the sediments have not been released and dissolved in liquid phase, but it deserves further research and possible monitoring. It is assumed that lead in sediments might be of natural origin, as a result of ore mineralization, what is additionally supported in mineralogy chapter. Zinc (Zn) concentration is also highest in Izbitac spring (116 ppm), what according to USA federal criteria belongs to moderately contaminated sediments (90-200 ppm). Spring Podgorski Vrutak (110 ppm) belongs also to the same category, while third observed spring Grebice in Gornja Podgora (86.7 ppm) is slightly below the limit value for moderately contaminated sediments. All those values are comparable to those measured in mostly karstic Kupa River drainage basin (also from Dinaric part of Croatia), where mean value for Zn in sediments is 61 ppm, while highest concentration measured in this drainage basin is 229 ppm (17). It is assumed that zinc in sediments is also of natural origin, as a result of ore mineralization and its behavior is similar to that of lead.

Copper (Cu) concentrations are equal in Izbitac and Podgorski Vrutak springs (38.2 ppm), while in Grebice spring is slightly lower (34.3 ppm). Concentrations in first two springs are slightly above those causing moderately toxic effects (USA standards), while concentration in Grebice spring could cause minimal toxic effects.

Nickel (Ni) has highest concentration at Izbitac spring (134 ppm), slightly lower at Podgorski Vrutak (124 ppm), while the lowest concentration is measured at Grebice spring (67.1 ppm). Concentrations obtained at two first springs could cause significant toxic effects according to standards of British Columbia, Canada (75 ppm), while concentration at the third spring is slightly lower than this concentration.

Chromium (Cr) has highest concentration at Izbitac spring (118 ppm), what is slightly above the value that could cause significant toxic effects according to British Columbia legislative, Canada (110 ppm). At Podgorski Vrutak ,Cr concentration is somehow lower (96.7 ppm), while at Grebice spring is the lowest (50.4 ppm). Those two values are above the concentration that might cause minimal toxic effects (26 ppm) according to British Columbia legislative, Canada.

Iron (Fe) has similar concentrations at Izbitac and Podgorski Vrutak springs (2.69 and 2.56 % respectively), while concentration is a bit lower at Grebice spring (1.91 %). Those values are comparable to mean values from the whole Kupa River drainage basin (1.9 ppm), reported by Frančišković-Bilinski (2007). Concentrations at first two springs are slightly above value that might cause minimal toxic effects (2.12%) according to British Columbia legislative, Canada.

Manganese (Mn) has completely different behavior than previously described elements. Its highest concentration of 935 ppm is measured at Podgorski Vrutak spring, while Izbitac and Grebice springs have lower, almost identical concentrations (786 and 754 ppm respectively). All those values are above the value that might cause minimal toxic effects (460 ppm) according to British Columbia legislative, Canada. The value obtained at Podgorski Vrutak is only slightly lower than the value that could cause significant toxic effects (1100 ppm) according to British Columbia legislative, Canada. The highest concentration of Mn in Biokovo Mt sediments is higher than mean value for the whole Kupa River drainage basin (617 ppm), reported by Frančišković-Bilinski (2007). It is interesting to mention that highest concentrations of Mn from the Kupa River drainage basin are found in the area influenced by strong Middle Triassic volcanism characterized by ophiolite belt, while concentrations in the carbonate part of this drainage basin are significantly lower. So, this could lead to conclusion that in the deeper layers of Biokovo Mt some Triassic or even Paleozoic magmatic or metamorphic rocks might be present, what would explain elevated concentrations of many metals in sediments.

Cadmium (Cd) concentrations are almost the same at Izbitac and Podgorski Vrutak springs (0.5 and 0.48 ppm respectively), while at Grebice spring is somehow higher (0.71 ppm). According to legislative of Ontario and British Columbia, Canada, which have lowest tolerance threshold for Cd in sediments, only at Grebice spring some minor toxic effects might be present (0.6 ppm).

Barium (Ba) concentration is the highest at Podgorski Vrutak spring (238 ppm). After that follow Grebice (133 ppm) and Izbitac (89.8) springs. Those concentrations are comparable to mean values from the whole Kupa River drainage basin (232 ppm), reported by Frančišković-Bilinski (2007), but are significantly lower than maximal values (5790 ppm) from this drainage basin (18). All those concentrations are higher than USA federal legislative value for heavily contaminated sediments (60 ppm). When microelements in sediments exist in much higher concentrations than their natural levels (geochemical anomalies), it often points to precious ore occurrences (19).

Table 4. Elemental analysis of sediments collected from three captured springs on Biokovo Mt, obtained by ICP-MS method

Element	Unit	Det. Limit	min. recommended value (ppm)	max. recommended value (ppm)	Grebice	Podgorski Vrutak	Izbitac
Hg	ppb	5	0.2	2	69	91	68
Li	ppm	0.1	0.003	0.01	27.5	34.8	47.7
Be	ppm	0.1			1.6	1.3	1
B	ppm	1			17	16	27
Na	%	0.001			0.033	0.041	0.045
Mg	%	0.01			0.58	1.08	1.18
Al	%	0.01			2.4	2.58	2.76
K	%	0.01			0.33	0.37	0.51
Ca	%	0.01			23.5	16.3	15.1
V	ppm	1			44	56	63
Cr	ppm	0.5	26	110	50.4	96.7	118
Mn	ppm	1	460	1100	754	935	786
Fe	%	0.01	2.12	4.38	1.91	2.56	2.69
Co	ppm	0.1	50	50	12.9	18.3	20.5
Ni	ppm	0.1	35	75	67.1	124	134
Cu	ppm	0.01	16	110	34.3	38.2	38.2
Zn	ppm	0.1	< 90	> 200	86.7	110	116
Ga	ppm	0.02			5.51	6.17	7.07
Ge	ppm	0.1			< 0.1	< 0.1	< 0.1
As	ppm	0.1	3	33	4.5	6	4.5
Se	ppm	0.1	1	1	1	0.9	1.1
Rb	ppm	0.1			40.8	42.1	41.8
Sr	ppm	0.5			150	256	246
Y	ppm	0.01			13.8	13.6	11.6

Zr	ppm	0.1			4.5	4.7	4.3
Sc	ppm	0.1			2.3	5.9	5.9
Pr	ppm	0.1			3.7	4.1	3.8
Gd	ppm	0.1			2.8	3.2	3
Dy	ppm	0.001			2.16	2.52	2.17
Ho	ppm	0.1			0.4	0.5	0.4
Er	ppm	0.1			1.1	1.3	1
Tm	ppm	0.1			0.2	0.2	0.1
Nb	ppm	0.1			0.7	< 0.1	< 0.1
Mo	ppm	0.01	4	4	0.43	0.57	0.6
Ag	ppm	0.002	0.5	0.5	0.165	0.095	0.134
Cd	ppm	0.01	0.2	10	0.71	0.48	0.5
In	ppm	0.02			0.03	0.04	0.04
Sn	ppm	0.05			1.06	1.08	0.94
Sb	ppm	0.02	200	500	0.2	0.16	0.22
Te	ppm	0.02			0.17	0.24	0.47
Cs	ppm	0.02			3.27	3	2.9
Ba	ppm	0.5	< 20	500	133	238	89.8
La	ppm	0.5			17.2	16.4	17.3
Ce	ppm	0.01			33.9	37	32.7
Nd	ppm	0.02			14.2	16.6	15.2
Sm	ppm	0.1			2.7	3.3	3
Eu	ppm	0.1			0.6	0.7	0.6
Tb	ppm	0.1			0.4	0.4	0.4
Yb	ppm	0.1			0.9	1	0.8
Lu	ppm	0.1			0.1	0.1	0.1
Hf	ppm	0.1			< 0.1	< 0.1	< 0.1
Ta	ppm	0.05			< 0.05	< 0.05	< 0.05
W	ppm	0.1			< 0.1	< 0.1	< 0.1
Re	ppm	0.001			0.001	0.002	0.002
Au	ppb	0.5			9	2.5	4
Tl	ppm	0.02			0.48	0.47	0.24
Pb	ppm	0.01	31	250	293	1290	5440
Bi	ppm	0.02			0.2	0.2	0.23
Th	ppm	0.1			1.5	4.4	6.2
U	ppm	0.1			0.7	0.7	0.8

Mineralogical composition of sediments

Semi-quantitative mineralogical composition of sediment fraction <63 μm from three springs (Grebice, Podgorski Vrutak and Izbitac) of Biokovo Mt basin is performed by comparing relative intensities of strongest peaks of every present mineral whose strongest peak was present within diffractograms.

Presented sediment samples are complex mixtures of minerals, with dominant calcite in each sample. This was expected for a typical karstic region, such as Biokovo Mt, where limestone rocks prevail.

Quartz is second abundant mineral. In sediments of Izbitac and Podgorski Vrutak springs there is approximately the same amount of quartz (about 70% of calcite amount), while Grebice spring sediment has significantly lower amount of quartz (about 38% of calcite amount). This indicates presence of some non-carbonate rock formations in the drainage area of Izbitac and Podgorski Vrutak springs, while Grebice spring is predominantly under carbonate influence.

Among feldspars, plagioclases were confirmed in all three studied sediments. Podgorski Vrutak is richest with plagioclases (almost 15% of calcite amount), while in Grebice they are least abundant, what supports its carbonate predominance.

From clay-mica group of minerals illite-montmorillonite was confirmed in all studied sediment samples. It is more abundant in Izbitac and Podgorski Vrutak springs than in Grebice spring. Similar situation is with muscovite, belonging to the same mineral group. Presence of clay-mica group of minerals could indicate existing of shales and other argillaceous rocks in drainage areas of Izbitac and Podgorski Vrutak springs.

From mica minerals biotite was determined in samples from Podgorski Vrutak (about 3% of calcite amount) and Grebice (weak peak), while in Izbitac spring sample biotite was not determined.

A significant finding of semi-quantitative mineralogical analysis is presence of strontianite, a rare carbonate mineral from aragonite group. It is present in sediment samples of Izbitac and Podgorski Vrutak springs in significant amounts (6-7% of calcite amount), while in Grebice spring it was not determined. In waters of Biokovo Mt increased levels of Sr at some locations were found and discovery of strontianite mineral could explain its origin as natural.

Mineralogical analysis of separated dark particles showed presence of Magnesium diiron (III) oxide (01-089-3084), OF Magnesium Iron, Silicate , Ringwoodite ferroan (00-021-1258), of Galena (00-005-0592). It was also discovered possible presence of unexpected mineral Ramdohrite bismuthian, lead sulfide $Ag_4Pb_6(Sb, Bi)_{11}S_{24}$ what could explain extreme Pb concentrations measured in sediment samples of Izbitac and Podgorski Vrutak springs. In Grebice spring it was not determined. Discovery of Ramdohrite bismuthian mineral could explain its origin as natural as a result of ore mineralization (7).

Mineral goethite was also confirmed by semi-quantitative mineralogical analysis in sediment samples of Izbitac and Podgorski Vrutak springs and in the Grebice spring it was not determined.

Celestite, strontium sulfate is often associated with strontianite and it has the same structure as barite. In waters of Biokovo Mt springs also higher concentrations of Ba were determined, which could be of natural origin, due to mineralogy of the region.

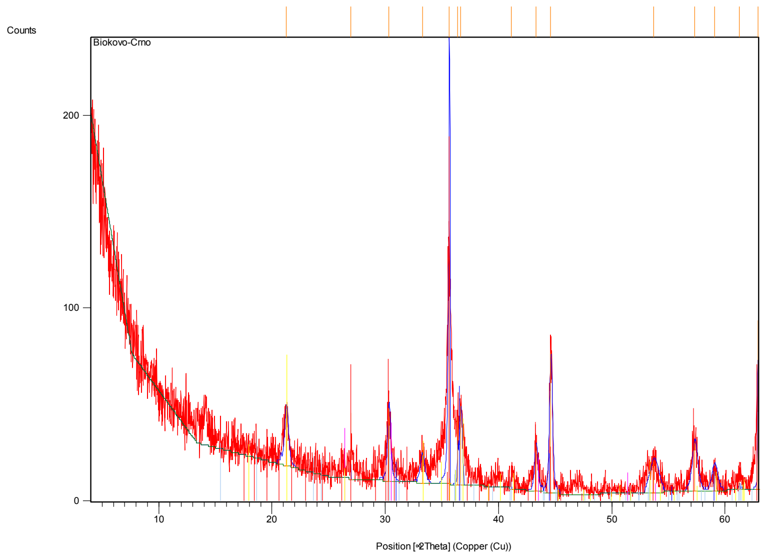

Figure 3. Semi-quantitative mineralogical analysis of black particles separated from sediment sample of Izbitac spring. XRD pattern of mineral Ramdohrite bismuthian is at:

Pos. [°2Th.] = 44.6075; d-spacing [A] = 2.03136; Rel. Int. [%] = 62.18; Matched by = 00-042-1416

Conclusions

This paper showed interesting and partly unexpected results of different way of tracing techniques. Dye tracing with Na-fluoresceine was less efficient or inefficient. In first dye tracing campaign apparent velocities were below or close to lower limit of the results of other investigations in world karst regions. Second dye tracing was completely inefficient. The Na-fluoresceine is not detected in the sampled springs but still the possibility for a hydraulic connection between the Saranač Pit, the underlying limestone aquifer and some of the observed springs cannot be excluded.

Concentrations of dissolved metals in the groundwater water from Biokovo Mt. springs are of extremely high quality. Their concentrations were about three orders of magnitude lower than Croatian standards for drinking water, what supports our earlier findings.

Elemental composition of sediments showed extremely high concentrations of lead. A significant finding of semi-quantitative mineralogical analysis is presence of strontianite, ramdohrite bismuthian and goethite in sediment samples of Izbitac and Podgorski Vrutak springs while in Grebice spring it was not determined. It is assumed that lead in sediments might be of natural origin, as a result of possible ore mineralization. That could lead to conclusion that in the deeper layers of Biokovo Mt some Triassic or even Paleozoic magmatic or metamorphic rocks might be present, what would explain elevated concentrations of many metals in sediments. Indicators of mineralization in the groundwater and sediments samples indicate possible Pb-Zn ore-associations. According to the presented results it is obvious that it is necessary to carefully perform dye tracing in the karst areas with hidden mineralization or ores.

Continuation of mineralogical analyses of dark particles in studied sediments of Biokovo Mt springs is suggested. Also model laboratory experiments of adsorption of Na –fluoresceine traces on isolated iron and lead minerals is suggested to solve the problem of the insufficiency of its use as a tracer in karst environment.

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