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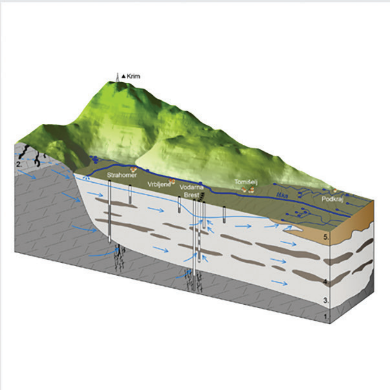
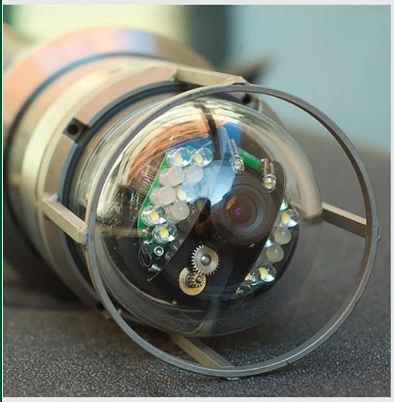
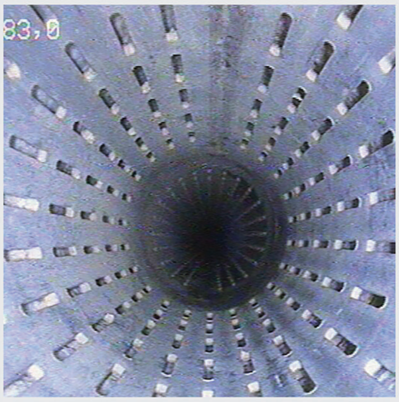


70 geoloških zanimivosti Slovenije





70 Geological Wonders of Slovenia

GeoZS
Geološki zavod Slovenije

ISSN
Tiskana izdaja / Print edition: 0016-7789
Spletna izdaja / Online edition: 1854-620X

GEOLOGIJA

59/1 – 2016

Shaping the future
with the past
70
YEARS
GeoZS
Geološki zavod
Slovenije

GEOLOGIJA	2016	59/1	1-123	Ljubljana

GEOLOGIJA
ISSN 0016-7789

Izdajatelj: Geološki zavod Slovenije, zanj direktor Miloš Bavec
Publisher: Geological Survey of Slovenia, represented by Director Miloš Bavec
Financirata Javna agencija za raziskovalno dejavnost Republike Slovenije in Geološki zavod Slovenije
Financed by the Slovenian Research Agency and the Geological Survey of Slovenia

Vsebina številke 59/1 je bila sprejeta na seji Uredniškega odbora, dne 13. 7. 2016.
Manuscripts of the Volume 59/1 accepted by Editorial and Scientific Advisory Board on July 13, 2016.

Naslov uredništva / Editorial Office: GEOLOGIJA Geološki zavod Slovenije / Geological Survey of Slovenia
Dimičeva ulica 14, SI-1000 Ljubljana, Slovenija
Tel.: +386 (01) 2809-700, Fax: +386 (01) 2809-753, e-mail: urednik@geologija-revija.si
URL: http://www.geologija-revija.si/

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Cena / Price

Posamezni izvod / Single Issue	Letna naročnina / Annual Subscription
Posameznik / Individual: 15 €	Posameznik / Individual: 25 €
Institucija / Institutional: 25 €	Institucija / Institutional: 40 €

Tisk / Printed by: Tiskarna Formatisk d.o.o.

Slika na naslovni strani: Izseki fotografij iz nove knjige z naslovom 70 geoloških zanimivosti Slovenije, ki sta jo uredila N. Rman in M. Novak, ter iz arhivov GeoZS, J. Žaloharja in M. Božovića. Knjigo predstavljamo v tej številki.

Cover page: Sections of photographs from a new book entitled 70 Geological Wonders of Slovenia, edited by N. Rman and M. Novak M., and from archives of GeoZS, J. Žalohar, and M. Božović. The book is described in this issue.

VSEBINA – CONTENTS

GEOLOGIJA *59/1*, 7-22, Ljubljana 2016

http://dx.doi.org/10.5474/geologija.2016.001

Hydrogeochemistry and isotope geochemistry of Velenje Basin groundwater

Hidrogeokemija in izotopska geokemija podzemnih vod Velenjskega bazena

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Prejeto / Received 25. 1. 2016; Sprejeto / Accepted 11. 4. 2016; Objavljeno na spletu / Published online 11. 8. 2016

Key words: hydrogeochemistry, C isotopes, Sr isotopes, groundwater, Velenje Basin, Slovenia
Ključne besede: hidrogeokemija, C izotopi, Sr izotopi, podzemna voda, Velenjski bazen, Slovenija

Abstract

The geochemical and isotopic composition of groundwater in the Velenje Basin, Slovenia, was investigated between the years 2014 to 2015 to identify the geochemical processes in the major aquifers (Pliocene and Triassic) and the water–rock interactions. Thirty-eight samples of groundwater were taken from the aquifers, 19 in the mine and 19 from the surface. Groundwater in the Triassic aquifer is dominated by HCO_3^-, Ca^{2+} and Mg^{2+} with $\delta^{13}C_{DIC}$ values in the range from -19.3 to -2.8 ‰, indicating degradation of soil organic matter and dissolution of carbonate minerals. In contrast, groundwater in the Pliocene aquifers is enriched in Mg^{2+}, Na^+, Ca^{2+}, K^+, and Si, and has high alkalinity, with $\delta^{13}C_{DIC}$ values in the range of -14.4 to +4.6 ‰. Based on the $\delta^{13}C_{DIC}$ values in all the aquifers (Pliocene and Triassic), both processes influence the dissolution of carbonate minerals and dissolution of organic matter and in the Pliocene aquifers, methanogenesis as well. Based on Principal Component Analysis (PCA), and on geochemical and isotopic data we conclude that the following types of groundwater in Velenje Basin are present: Triassic aquifers with higher pH and lower conductivity and chloride, Pliocene, Pliocene 1 and Pliocene 2 aquifers with lower pH and higher conductivity and chloride contents, and Pliocene 3 and Pliocene 2, 3 aquifers with the highest pH values and lowest conductivities and chloride contents. $^{87}Sr/^{86}Sr$ tracer was used for the first time in Slovenia to determine geochemical processes (dissolution of silicate versus carbonate fraction) in Velenje Basin groundwater of different aquifers dewatering Pliocene and Triassic strata. $^{87}Sr/^{86}Sr$ values range from 0.70820 to 0.71056 in groundwater of Pliocene aquifers and from 0.70808 to 0.70910 in groundwater of the Triassic aquifer. This indicates that dissolution of the carbonate fraction prevails in both aquifers, while in Pliocene aquifers, an additional silicate weathering prevails with higher $^{87}Sr/^{86}Sr$ isotope ratios.

Izvleček

Raziskali smo geokemično in izotopsko sestavo podzemnih vod v Velenjskem bazenu, za določitev geokemičnih procesov v glavnih vodonosnikih (pliocenskih in triasnem) in interakcij voda–kamnina med letoma 2014 in 2015. Osemintrideset vzorcev podzemnih vod je bilo odvzetih iz vodonosnikov, od tega 19 iz jame in 19 s površine. V podzemni vodi triasnega vodonosnika prevladujejo ioni HCO_3^-, Ca^{2+}, Mg^{2+} , $\delta^{13}C_{DIC}$ vrednosti pa se gibljejo od -19.3 do -2.8 ‰, kar kaže na razgradnjo organske snovi in raztapljanje karbonatnih mineralov. Podzemna voda pliocenskega vodonosnika je obogatena z Mg^{2+}, Na^+, Ca^{2+}, K^+ in Si in ima višje alkalnosti ter vrednosti $\delta^{13}C_{DIC}$ v razponu od -14.4 do +4.6 ‰. Na $\delta^{13}C_{DIC}$ vrednosti v vseh vodonosnikih (pliocenskih in triasnem) vplivata raztapljanje karbonatnih mineralov in razgradnja organske snovi, v pliocenskih vodonosnikih pa še dodatno metanogeneza. Na osnovi analize glavnih osi (PCA) lahko zaključimo, da imamo v Velenjskem bazenu na osnovi geokemičnih in izotopskih podatkov sledeče tipe podzemnih vod: triasni vodonosnik z višjimi vrednostmi pH in nižjo elektroprevodnostjo ter klorom, pliocenski, pliocenski 1 in pliocenski 2 vodonosniki z nižjim pH in višjo elektroprevodnostjo in vsebnostjo klora, in pliocenski 3 in pliocenski 2, 3 vodonosniki z višjim pH in nizko elektroprevodnostjo in vsebnostjo klora. V tej študiji smo uporabili nov sledilec izotopskega razmerja $^{87}Sr/^{86}Sr$, katerega vrednosti se gibljejo od 0,70820 do 0,71056 v pliocenskem vodonosniku in od 0,70808 do 0,70910 v triasnem vodonosniku. $^{87}Sr/^{86}Sr$ kaže, da v obeh vodonosnikih prevladuje raztapljanje karbonatov, intenzivnejše pa je raztapljanje silikatnih mineralov v pliocenskem vodonosniku z višjim izotopskim razmerjem $^{87}Sr/^{86}Sr$.

Introduction

The Velenje Basin in Slovenia is one of the largest actively mined coal basins in central Europe, producing around 4 million tons of lignite per year (Mihelak, 2010). Large amounts of groundwater are extracted from Velenje Basin aquifers to facilitate underground mining of coal, and coal seam gas outbursts are a serious mine safety concern (Kanduč et al., 2011; Kanduč et al., 2015a). The main problem in the past production years of Velenje lignite mine has been the groundwater standing directly over the main production lignite strata inside the Pliocene's clastic rocks. In the 1970's many groundwater intrusions occurred in the mine. To reduce the hydrostatic pressure during the last four decades, advanced and massive dewatering works have been performed. As a result, constant water pumping in the production area and its surroundings has produced a typical dewatering groundwater cone (Vižintin et al., 2009).

Hydrogeochemistry and stable isotope compositions of groundwater provide critical information regarding water–rock interaction along flow paths, and mixing of distinct groundwater bodies (Cartwright et al., 2012). Groundwater geochemistry, especially where aquifers have contrasting mineralogy, is an effective method of determining regional scale inter-aquifer flow and patterns of recharge (Dogramaci & Herczeg, 2002; Edmunds, 2009; Cartwright, 2010). In this study we use major ion geochemistry and environmental isotopes to constrain geochemical processes in groundwater of Velenje Basin. In addition, characterization of geochemical properties of groundwater may further aid in understanding of hydrocarbon entrapment and mineral deposition, and help in identifying the origin of fluids (Aravena et al., 2003).

Concentrations of dissolved inorganic carbon (DIC) and its isotopic composition ($\delta^{13}C_{DIC}$) are governed by processes occurring in the water system. Changes of dissolved inorganic carbon concentrations result from addition or removal of carbon from the DIC pool (Atekwana & Krishnamurthy, 1998). The major sources of carbon to the groundwater DIC system are the dissolution of carbonate minerals, and soil CO_2 derived from root respiration and from microbial decomposition of organic matter. Constraining water-rock interaction, evapotranspiration, dissolution and precipitation of minerals, ion-exchange and groundwater mixing are all required to understand and manage hydrogeological systems (Cartwright et al., 2007).

The use of strontium isotopes in hydrogeological studies has many applications. First, minerals that interact with groundwater and surface water exhibit a wide and predictable range of $^{87}Sr/^{86}Sr$ ratios. ^{87}Sr is produced by the decay of ^{87}Rb with a half-life of 48.8 Ga (Faure, 1991). Strontium derived from K-rich minerals such as biotite and K-feldspar, have high $^{87}Sr/^{86}Sr$ ratios, minerals such as plagioclase that have lower K/Ca ratios will contain strontium with moderate $^{87}Sr/^{86}Sr$ ratios, while the strontium in Ca-rich minerals such as calcite or gypsum, have low $^{87}Sr/^{86}Sr$ ratios that remain essentially unchanged over time (Faure, 1991; Mcnutt, 2000). The geochemical and isotopic composition of carbon and $^{87}Sr/^{86}Sr$ isotopes of groundwater in the Velenje Basin, combined with mineralogical information, are applied to investigate the groundwater–rock interactions and geochemical processes that contribute to understanding the generation and source of coal seam gases, namely carbon dioxide and methane (Kanduč et al., 2012; Sedlar et al., 2014; Kanduč et al., 2015A).

Study area

The Velenje Basin and associated coal mines are situated in the NE part of Slovenia (Fig. 1). It is situated at the junction of the WNW–ESE trending Šoštanj fault and the E—W trending Periadriatic zone, bounded to the south by the Smrekovec fault segment. The Šoštanj and Smrekovec faults were generated by the collision of continental plates. In general, two hydrogeological systems can be distinguished in the Velenje coal mine (Fig. 1): (1) Plioquaternary and Pliocene aquifers, each composed of gravel, sand and silt, which are further divided to upper, middle and lower aquifers. Below the latter aquifers, Triassic carbonates are present as a basement of the basin. The upper aquifers are schematically divided into Plioquaternary alluvial sediments (not analyzed in this study) and at least three parts of the Pliocene aquifers (Pliocene 1, Pliocene 2, Pliocene 3) and (2) carbonate aquifers, which are further divided into Lower Triassic (Scythian) limestone and dolomite, Anisian dolomite and limestone, and Miocene Lithotamnium limestone (Vižintin et al., 2009 & references therein). Pliocene and Pliocene 2, 3 aquifers were introduced due to the fact that in some cases, it was not possible to attribute the water to a single aquifer, so a combination of all (Pliocene) or two aquifers (Pliocene 2, 3) was used instead. Hydrogeological properties of these dolomites are presented in detail in the works of Verbovšek & Veselič (2008) and Verbovšek (2008a, 2008b). Groundwater recharging the Velenje Basin is drained by hanging filters to prevent inrush of water into the mine. The average discharge of water from Pliocene sands is 800 l/min, while that from Triassic limestone aquifers is 3400 l/min (Supovec et al., 2012a, 2012b). In the Velenje coal basin, the shallow aquifers are part of the Quaternary and Pliocene sections. Pliocene aquifers are further classified as aquifers above the coal 0–20 m (Pl-1), aquifers 20–80 m above the coal, Pl-2, and upper Pliocene aquifers (Pl-3) (Fig. 1).

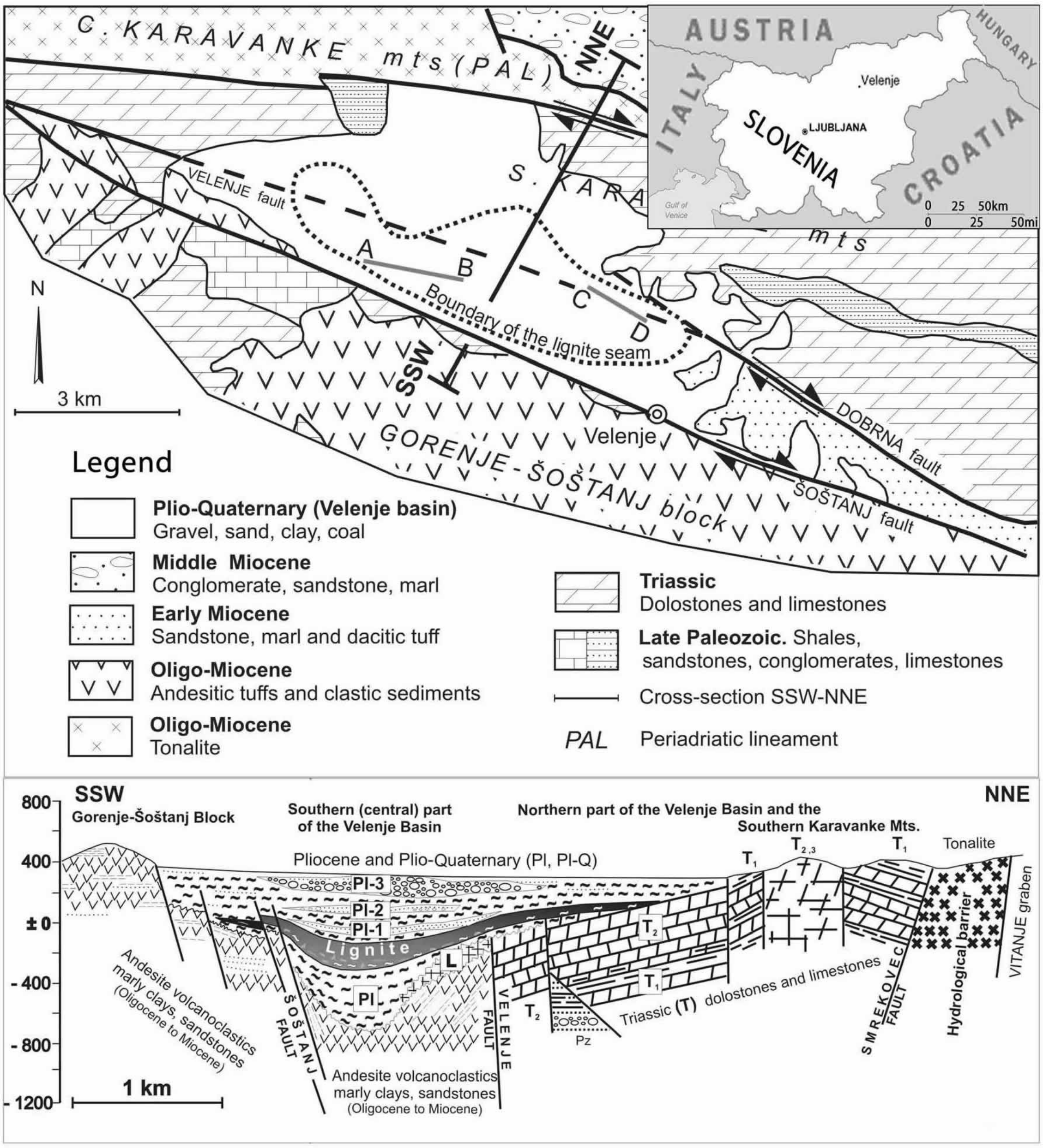


Fig. 1. Geological sketch map (Brezigar et al., 1988) of the Velenje Basin with a NNE–SSW cross section. Main aquifers are Pliocene (Pl_1, Pl_2 and Pl_3), and Triassic (T_1, T_2 and $T_{2,3}$) dolostones (prevailing) and limestones. Other Triassic and Paleozoic (Pz) lithologies are composed of relatively impermeable strata and therefore do not include significant aquifers. Profiles A–B and C–D show the locations of groundwater sampling in the study of Kanduč et al. (2014).

Materials and methods

In a previous study (Kanduč et al., 2014), only 14 groundwater samples were taken seasonally in Velenje Basin for geochemical and isotope characterization. Due to complex groundwater flow paths in the Velenje Basin, a more dense sampling network was established for investigation, in detail of spatial variability in hydrogeochemistry and isotope geochemistry.

Location of groundwater sampling location is presented on Figure 2. In this study, following locations of groundwater dewatering Triassic and Pliocene strata were sampled: groundwater dewatering Triassic strata (15 locations), Pliocene 2 (10 locations), Pliocene (1 location), Pliocene 1 (9 locations), Pliocene 3 (2 locations), Pliocene 2, 3 (1 location) (Fig. 2).

Samples were taken from: a) overflow piezometers from the surface, b) groundwater samples sampled with Solinst sampler and c) mine wells. Groundwater samples were taken wherever possible since the complete Velenje Basin is subsiding due to mining activity and piezometers are sheared. Altogether 38 samples were taken, 19 from the mine and 19 from the surface. Temperature, pH and electrical conductivity were measured in the field. Some groundwater samples (sampling b) were sampled with a Discrete Solinst Sampler (Kanduč et al., 2014, 2015a), modified for depth measurements and for sampling from depths to almost 400 m. Sample aliquots collected for

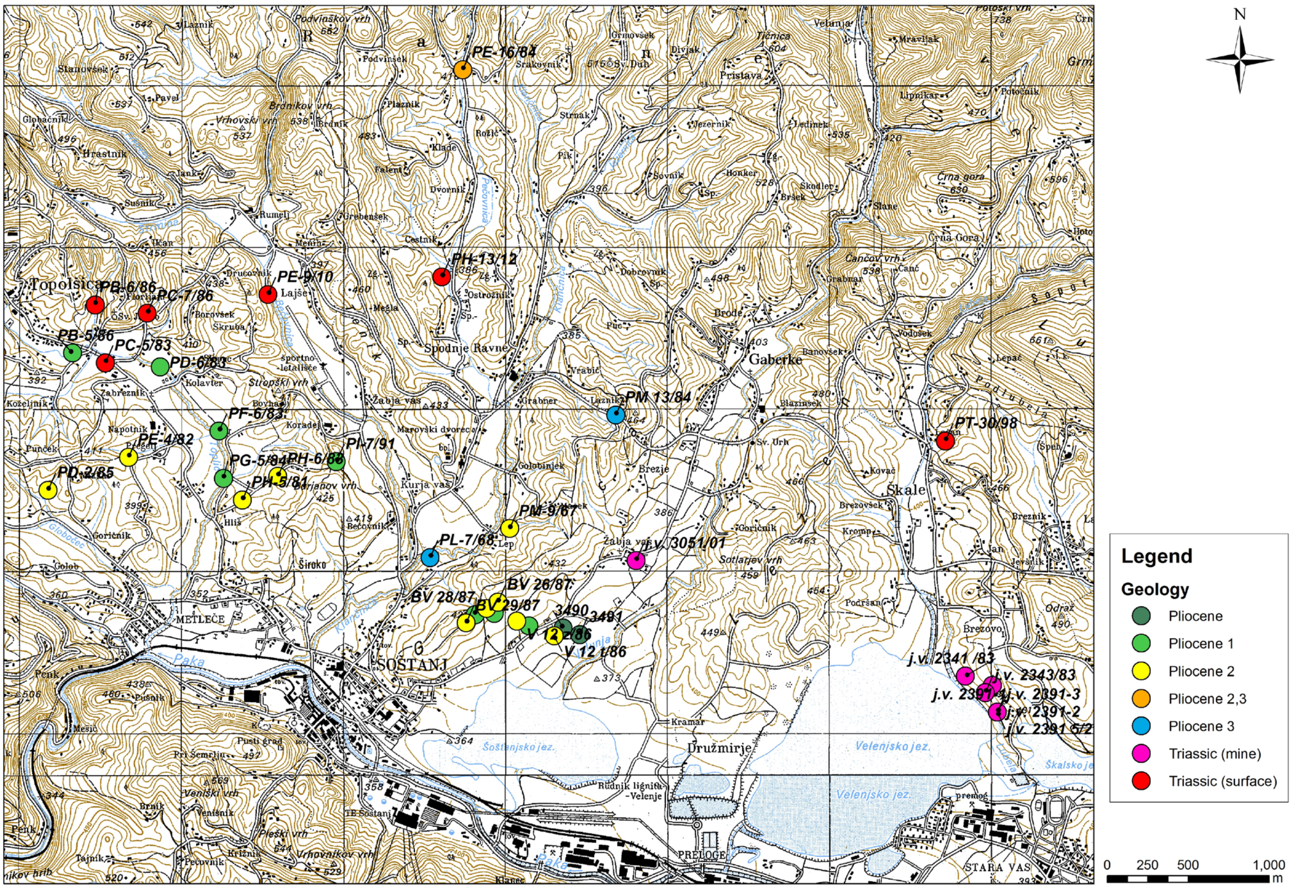


Fig. 2. Sampling locations (38 samples) of groundwater between years 2014 and 015 and located in the Velenje Basin: (a) overflow piezometers (red color) (b) groundwater sampling from the surface of Pliocene aquifers (green, yellow, and brown) and (c) from mining wells (purple color).

chemical analysis (major, trace elements, $^{87}Sr/^{86}Sr$) were immediately passed through 0.45 µ PTFE membranes, which were leached with 1-2 ml of dilute clean HCl, then 2–4 ml of MilliQ water (Millipore) and finally 1–2 ml of the sample itself before collecting the sample filtrate. For cations, $^{87}Sr/^{86}Sr$ and trace element analysis, 30 ml LDPE (Nalgene) bottles were used. The bottles were filled with 10 % HCl leaving some headspace and placed in in a zip lock bag in an oven at 70 °C for one day. The bag was then tightened and left for a second day. The bottles were then rinsed repeatedly with MilliQ water, and filled completely with MilliQ water and capped the bottles. They were finally emptied in a dust free place (fume cupboard) and left until dried. Samples for $\delta^{13}C_{DIC}$ analysis were stored in glass vials filled to the top, with no headspace. Total alkalinity was measured within 24 h of sample collection by Gran titration (Gieskes, 1974) with a precision of ±1 %. Major anions (Cl^-, SO_4^{2-} and NO_3^-) were analyzed (with ± 2 % precision) with a Dionex Ion Chromatograph (IC) Model 3000, using an AS23 analytical column in the Hydrology and Water Resources Department at the University of Arizona (UA).

Major and trace elements (Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}) in water were determined using a quadrupole inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7500ce) with a double-pass spray chamber, PTFE 100 L/min nebulizer, platinum cones and sapphire injector within a quartz platinum-shielded torch. The instrument is located in a filtered air positive pressure lab and sample handling and chemistry was routinely performed on laminar flow benches. External calibration curves for all the elements reported were prepared from 1,000 mg/L single element standard solutions in HNO_3 (Inorganic Ventures). Both the samples, blanks and the calibration solutions were prepared in 2.4 % HNO_3 (BDH Aristair Plus). Standard Reference Material (SRM) 1643e ("Trace Elements in Water", National Institute of Standards and Technology, USA) was prepared at 1:20 dilution and run together with blanks, samples and calibration curve. Indium at a concentration of 20 ppb was added to the calibration curve, reference material, samples and blanks as internal standard. Samples were diluted in 1:5 and run with inductively coupled plasma mass spectrometer (MC-ICPMS) in blocks of five samples, two blanks and one SRM. This analysis were performed at University of Utah.

The stable isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) was determined on Europa scientific TG isotope ratio mass spectrometer coupled with a ANCA-TG preparation module. Phosphoric acid (100 %) was added (100-200 µl) to a septum tube, then purged with pure He. The water sample (1 ml) was then injected into the septum tube and CO_2 measured directly from the headspace. Two standard solutions of Na_2CO_3

(Carlo Erba and Scientific Fisher) with known $\delta^{13}C_{DIC}$ values of -10.8±0.2 ‰ and -4.8±0.2‰ were used to calibrate $\delta^{13}C_{DIC}$ measurements (Spötl 2005; Kanduč, 2006). This analysis were performed at Jožef Stefan Institute.

Isotopic analysis of strontium was performed using an inductively coupled plasma mass spectrometer (MC-ICPMS) Neptune (ThermoFisher Scientific) at the Department of Geology and Geophysics, University of Utah. Purified fractions, with a strontium concentration around 30 ppb, were introduced in the mass spectrometer through a PTFE nebulizer, quartz double-pass spray chamber, quartz torch and nickel cones.

Results and discussion

Groundwater geochemistry of Velenje Basin groundwater

The pH of groundwater in the Triassic aquifers ranged from 6.8 to 8.7 and, in the Pliocene aquifers from 6.6 to 9.7 (Table 1). Dissolved oxygen (DO) was not measured in this study due to risk of explosion (from elevated methane concentration), but it ranges from 10 to 30 % in groundwater dewatering Pliocene strata and from 60 to 80 % in groundwater dewatering Triassic strata (Kanduč et al., 2014). Conductivity ranged from 205.4 to 4410 µS/cm in groundwater dewatering Pliocene strata, and from 232.8 to 4330 µS/cm in groundwater dewatering Triassic strata (Table 1). Only in one sample (j.v. 3051/01, Fig 2), from dewatering Pliocene strata, was very high conductivity found (Table 1). The very high alkalinities can be contributed to by the methanogenesis process, that occurs in the Pliocene groundwaters and are discussed below.

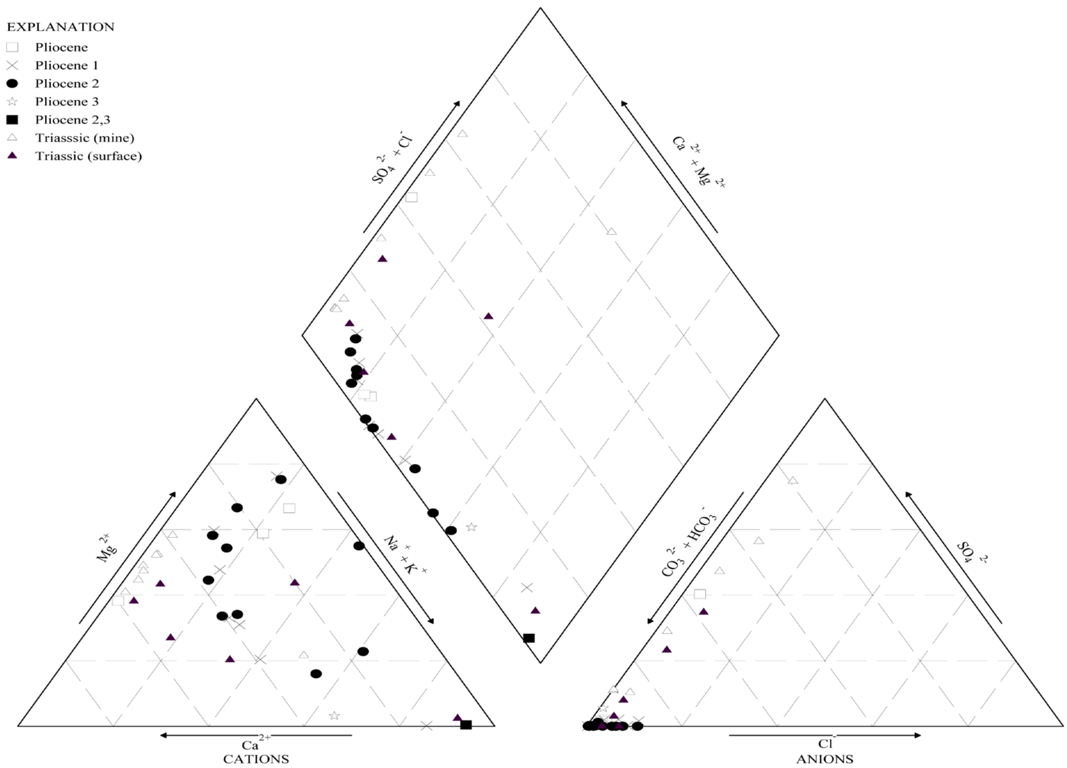


Fig. 3. Piper plot showing the major cation and anion geochemistry of the Velenje Basin groundwater.

Principal component analysis (PCA), based on correlation matrix was used to examine the variation of selected environmental variables (temperature, pH, conductivity, Na^+, K^+, Cl^-, Mg^{2+}, Ca^{2+}, nitrate (NO_3^-), sulphate (SO_4^{2-}) and HCO_3^- ions and $\delta^{13}C_{DIC}$) measured in 38 samples of Velenje Basin groundwater. The CANOCO software package (Ter Braak & Šmilauer, 2002) was applied, and the results presented as an ordination diagram, on which points represent samples and arrows the measured parameters.

Chemical speciation of the carbonate system- e.g. partial pressures of CO_2 (pCO_2), saturation indices of calcite ($SI_{calcite}$) – was evaluated using water composition, pH, alkalinity, and temperature as inputs to the PHREEQC speciation program and employing thermodynamic computations (Parkhurst & Appelo, 1999).

Concentrations of major and minor ions in Velenje Basin groundwater dewatering Pliocene strata and Triassic strata are presented on Figure 3. Groundwater in the Triassic aquifer is dominated by HCO_3^-, Ca^{2+}, Mg^{2+} (mostly water types Ca-Mg-HCO_3 and Mg-Ca-HCO_3), while groundwater in the Pliocene aquifers is enriched in Mg^{2+}, Na^+, Ca^{2+}, K^+ and Si. Total alkalinity of Pliocene aquifers ranges from 1.95 to 44.1 mM in groundwater dewatering Pliocene strata and from 1.3 to 10.4 mM in groundwater dewatering Triassic strata (Table 1). The highest alkalinity

Table 1. List of sampling locations with geochemical parameters (T, pH, conductivity) and selected major ion concentrations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Sr^{2+}, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}) and isotopic composition of Sr^{2+} and dissolved inorganic carbon ($^{87}Sr/^{86}Sr$ and $\delta^{13}C_{DIC}$) in Velenje Basin groundwater during the sampling period 2014–2015.

Sample number	Date of sampling	Geology	T (°C)	Cond (µS/cm)	pH	Total alkalinity- (mM)	Total alkalinity- (mg/l)	Na^+ (mM)	Na^+ (mg/l)	Mg^{2+} (mM)	Mg^{2+} (mg/l)	K^+ (mM)	K^+ (mg/l)	Ca^{2+} (mM)	Ca^{2+} (mg/l)	Sr^{2+} (mM)	Sr^{2+} (mg/l)
V 12 t/86	1.4.2014	Pliocene 2	19.4	3340	6.63	42.4	2586.4	4.55	104.65	12.65	307.39	0.25	9.77	3.92	157.19	0.013	1.13
3490	1.4.2014	Pliocene	19.7	2305	6.85	28.0	1708	4.93	113.39	7.14	173.50	0.15	5.86	1.05	42.1	0.003	0.26
j.v. 2346 T/84	1.4.2014	Triassic	16.8	933.6	7.35	5.97	364.17	0.10	2.3	1.39	33.77	0.03	1.17	2.17	87.0	0.003	0.26
j.v. 2370 T/88	2.4.2014	Triassic	17.8	455.0	7.32	1.32	80.52	0.05	1.15	0.55	13.36	0.01	0.39	0.65	26.0	0.002	0.17
j.v.2343/83	2.4.2014	Triassic	16.6	759.6	7.35	5.65	344.65	0.095	2.185	1.66	40.33	0.03	1.17	1.67	66.96	0.005	0.43
BV 28/87	1.4.2014	Pliocene 1	17.3	1117	7.00	12.0	732	1.80	41.4	2.48	60.26	0.11	4.30	1.75	70.17	0.005	0.43
j.v.2391 5/2	2.4.2014	Triassic	14.2	581.4	7.38	5.45	332.45	0.14	3.22	1.43	34.74	0.02	0.78	1.21	48.52	0.002	0.17
j.v. 3051/01	1.4.2014	Triassic	26.7	4330	6.81	10.4	634.4	22.02	506.46	4.94	120.0	0.48	18.76	6.69	268.3	0.044	3.85
V 12 v/87	1.4.2014	Pliocene 1	18.7	2244	6.92	27.2	1659.2	2.41	55.43	6.90	167.67	0.20	7.82	3.35	134.3	0.009	0.78
j.v.2391-2	2.4.2014	Triassic	14.1	581.0	7.42	5.42	330.62	0.13	2.99	1.42	34.51	0.02	0.78	1.50	60.2	0.002	0.17
j.v. 2391-1	2.4.2014	Triassic	14.3	581.3	7.42	5.39	328.79	0.13	2.99	1.39	33.77	0.02	0.78	1.19	47.7	0.002	0.17
j.v. 2391-3	2.4.2014	Triasic	14.1	579.8	7.33	5.09	310.49	0.14	3.22	1.48	35.96	0.02	0.78	0.97	38.9	0.002	0.17
j.v. 2341/83	2.4.2014	Triassic	16.1	1094	7.39	6.30	384.3	0.173	3.979	2.06	50.05	0.03	1.17	2.86	114.7	0.004	0.35
BV 29/87	1.4.2014	Pliocene 2	18.5	2298	6.85	27.1	1653.1	3.31	76.13	7.59	184.4	0.23	8.99	0.72	28.9	0.006	0.52
BV 27/87	1.4.2014	Pliocene 2	16.4	900.7	7.22	9.64	588.04	1.43	32.89	1.92	46.65	0.09	3.51	1.62	64.9	0.005	0.43
V12z/86	1.4.2014	Pliocene 2	18.2	2252	6.89	27.1	1653.1	2.51	57.73	6.75	164.0	0.21	8.21	3.48	139.5	0.008	0.70
3491	1.4.2014	Pliocene	19.9	1848	6.80	21.6	1317.6	4.09	94.07	5.63	136.81	0.12	4.69	1.84	73.8	0.006	0.52
BV 26/87	1.4.2014	Pliocene 2	17.7	1200	7.19	14.2	866.2	1.87	43.01	3.25	78.97	0.12	4.69	1.73	69.4	0.006	0.52
j.v. 3378-K/08	1.4.2014	Pliocene 1	19.3	4410	6.88	44.1	2690.1	6.71	154.33	16.63	404.1	0.32	12.51	1.65	66.2	0.007	0.61
PC-5/83	6.6.2014	Triassic	15.7	616.2	8.14	5.26	320.86	5.78	132.94	0.08	1.94	0.06	2.34	0.21	8.42	0.001	0.08
PB-6/86	6.6.2014	Triassic	14.1	851.1	7.00	8.77	534.97	2.86	65.78	0.88	21.38	0.11	4.30	1.96	78.6	0.005	4.38
PH-13/12	6.6.2014	Triassic	16.2	232.8	8.66	1.50	91.5	0.80	18.4	0.53	12.87	0.067	2.61	0.24	9.6	0.0008	0.07
PT-30/98	6.6.2014	Triassic	14.0	469.9	7.80	4.70	286.7	0.41	9.43	1.21	29.4	0.048	1.87	1.35	54.1	0.006	0.52
PC-7/86	6.6.2014	Triassic	16.6	433.4	7.92	4.22	257.42	0.80	18.4	0.61	14.8	0.040	1.56	1.24	49.7	0.005	0.43
PE-9/10	6.6.2014	Triassic	14.9	388.3	7.57	2.74	167.14	0.16	3.68	0.79	19.19	0.063	2.46	1.18	47.3	0.005	0.43
PH-5/81	25.5.2015	Pliocene 2	16.1	1979	7.50	22.6	1378.6	4.95	113.85	3.02	73.38	0.186	7.27	3.27	131.1	0.011	0.96
PM13/84	26.5.2015	Pliocene 3	16.4	311.1	9.68	3.23	197.03	2.00	46	0.04	0.97	0.017	0.66	0.49	19.6	0.0029	0.25
PE-16/84	26.5.2015	Pliocene 2,3	16.4	205.4	9.68	1.95	118.95	1.82	41.86	0.004	0.097	0.02	0.78	0.05	2.0	0.00034	0.029
PG-5/84	26.5.2015	Pliocene 1	18.0	2276	7.42	27.6	1683.6	6.82	156.86	3.51	85.29	0.19	7.42	4.30	172.4	0.013	1.13
PM-9/67	27.5.2015	Pliocene 2	15.9	1667	8.17	18.9	1152.9	10.2	234.6	1.92	46.65	0.092	3.59	1.36	54.5	0.0125	1.09
Pl-7/68	27.5.2015	Pliocene 3	16.9	639.0	9.55	7.59	462.99	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
PH-6/83	27.5.2015	Pliocene 2	17.6	1061	8.40	11.9	725.9	2.52	57.96	1.67	40.58	0.08	3.12	2.01	80.6	0.007	0.61
Pl-7/91	1.6.2015	Pliocene 1	15.8	1744	8.90	6.29	383.69	3.87	89.01	0.004	0.0972	0.51	19.94	0.36	14.4	0.002	0.17
PF-6/83	1.6.2015	Pliocene 1	17.9	1883	7.73	22.1	1348.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.	n.a.
PD-6/83	1.6.2015	Pliocene 1	25.1	1811	7.45	20.6	1256.6	7.39	169.97	1.85	44.95	0.00012	0.00046	3.54	141.9	0.011	0.96
PB-5/86	2.6.2015	Pliocene 1	14.3	2617	7.69	30.5	1860.5	6.17	141.91	3.99	96.95	0.51	19.94	4.71	188.9	0.018	1.57
PD-2/85	2.6.2015	Pliocene 2	15.9	1300	8.00	8.01	488.61	3.30	75.9	0.49	11.9	0.06	2.34	0.90	36.1	0.0003	0.02
PE-4/82	2.6.2015	Pliocene 2	16.9	1117	8.10	12.4	756.4	1.52	34.96	1.02	24.8	0.11	4.30	0.017	0.68	0.008	0.70

Sample number	Date of sampling	Geology	Cl^- (mM)	Cl^- (mg/l)	SO_4^{2-} (mM)	SO_4^{2-} (mg/l)	NO_3^- (mM)	NO_3^- (mg/l)	pCO_2 (ppm)	$\delta^{13}C_{DIC}$ (‰)	$^{87}Sr/^{86}Sr$
V 12 t/86	1.4.2014	Pliocene 2	3.51	124.6	n.a.	n.a.	0.11	6.82	575439.9	-3.4	0.70919
3490	1.4.2014	Pliocene	0.87	30.88	0.31	29.8	n.a.	n.a.	245470.9	-0.9	0.70910
j.v. 2346 T/84	1.4.2014	Triassic	0.38	13.49	2.14	205.4	0.005	3.1	16595.9	-9.7	0.70822
j.v. 2370 T/88	2.4.2014	Triassic	0.29	10.29	1.04	99.8	n.a.	n.a.	4265.8	-10.9	0.70808
j.v.2343/83	2.4.2014	Triassic	0.20	7.1	1.19	114.2	n.a.	n.a.	15848.9	-10.7	0.70818
BV 28/87	1.4.2014	Pliocene 1	0.35	12.4	0.12	11.5	0.005	0.31	75857.8	-3.5	0.70931
j.v.2391 5/2	2.4.2014	Triassic	0.25	8.87	0.32	30.7	0.038	2.35	14125.4	-11.9	0.70846
j.v. 3051/01	1.4.2014	Triassic	3.19	113.2	20.2	1939.2	n.a.	n.a.	107151.9	-19.3	0.70869
V 12 v/87	1.4.2014	Pliocene 1	3.13	111.1	0.25	24	0.07	4.34	489778.8	-2.3	0.70925
j.v.2391-2	2.4.2014	Triassic	0.007	0.24	0.33	31.7	0.0006	0.0372	12989.3	-10.3	0.70846
j.v. 2391-1	2.4.2014	Triassic	0.007	0.24	0.32	30.7	0.030	1.86	12589.3	-11.4	0.70845
j.v. 2391-3	2.4.2014	Triasic	0.007	0.24	0.32	30.7	0.045	2.79	14791.1	-12.5	0.70843
j.v. 2341/83	2.4.2014	Triassic	0.56	19.88	3.07	294.7	n.a.	n.a.	15848.9	-9.5	0.70842
BV 29/87	1.4.2014	Pliocene 2	1.54	54.67	n.a.	n.a.	0.105	6.51	229086.8	-2.8	0.70923
BV 27/87	1.4.2014	Pliocene 2	0.18	6.39	0.06	5.8	0.002	0.124	36307.8	-3.5	0.70938
V12z/86	1.4.2014	Pliocene 2	3.26	115.7	n.a.	n.a.	0.063	3.906	208929.6	-1.2	0.70925
3491	1.4.2014	Pliocene	0.53	18.82	0.18	17.3	0.0079	0.4898	213796.2	0.0	0.70907
BV 26/87	1.4.2014	Pliocene 2	0.94	33.4	n.a.	n.a.	1.11	6.82	56234.1	-2.0	0.70820
j.v. 3378-K/08	1.4.2014	Pliocene 1	2.71	96.2	0.50	48	0.11	6.82	331131.1	-2.0	0.70924
PC-5/83	6.6.2014	Triassic	0.38	13.5	n.a.	n.a.	n.a.	n.a.	2041.7	-7.9	0.70912
PB-6/86	6.6.2014	Triassic	0.29	10.3	n.a.	n.a.	n.a.	n.a.	44668.4	-2.8	0.70862
PH-13/12	6.6.2014	Triassic	0.18	6.4	0.44	42.2	n.a.	n.a.	169.8	-6.9	0.70834
PT-30/98	6.6.2014	Triassic	0.20	7.1	0.21	20.2	n.a.	n.a.	3715.4	-8.0	0.70904
PC-7/86	6.6.2014	Triassic	0.19	6.7	0.07	6.72	n.a.	n.a.	2691.5	-9.6	0.70868
PE-9/10	6.6.2014	Triassic	0.201	7.1	0.44	42.2	0.0002	0.0124	3801.9	-6.7	0.70835
PH-5/81	25.5.2015	Pliocene 2	0.145	5.1	0.0139	1.33	n.a.	n.a.	34673.7	2.6	0.70958
PM13/84	26.5.2015	Pliocene 3	0.024	0.9	0.0961	9.2	n.a.	n.a.	46.8	-9.1	0.70972
PE-16/84	26.5.2015	Pliocene 2,3	0.023	0.8	0.002	0.192	n.a.	n.a.	15.8	-14.4	0.71056
PG-5/84	26.5.2015	Pliocene 1	0.2431	8.6	0.012	1.152	n.a.	n.a.	51286.1	4.3	0.70958
PM-9/67	27.5.2015	Pliocene 2	0.2913	10.4	n.a.	n.a.	n.a.	n.a.	6309.6	1.0	0.71002
Pl-7/68	27.5.2015	Pliocene 3	0.090	3.2	0.0065	0.624	0.003	0.186	398.1	1.0	n.a.
PH-6/83	27.5.2015	Pliocene 2	0.0697	2.5	n.a.	n.a.	n.a.	n.a.	2990.9	0.3	0.70975
Pl-7/91	1.6.2015	Pliocene 1	0.58	20.6	0.0059	0.56	n.a.	n.a.	398.1	-12.5	0.70867
PF-6/83	1.6.2015	Pliocene 1	0.187	6.6	n.a.	n.a.	n.a.	n.a.	n.a.	4.6	n.a.
PD-6/83	1.6.2015	Pliocene 1	0.547	19.4	0.00017	0.016	n.a.	n.a.	39810.7	1.8	0.70949
PB-5/86	2.6.2015	Pliocene 1	0.098	3.5	0.003	0.28	n.a.	n.a.	31623.8	4.3	0.70926
PD-2/85	2.6.2015	Pliocene 2	0.032	1.1	0.00078	0.074	n.a.	n.a.	4168.7	-0.3	0.70943
PE-4/82	2.6.2015	Pliocene 2	0.43	15.3	0.0019	0.18	n.a.	n.a.	5248.1	1.6	0.70942

n.a. - not analysed

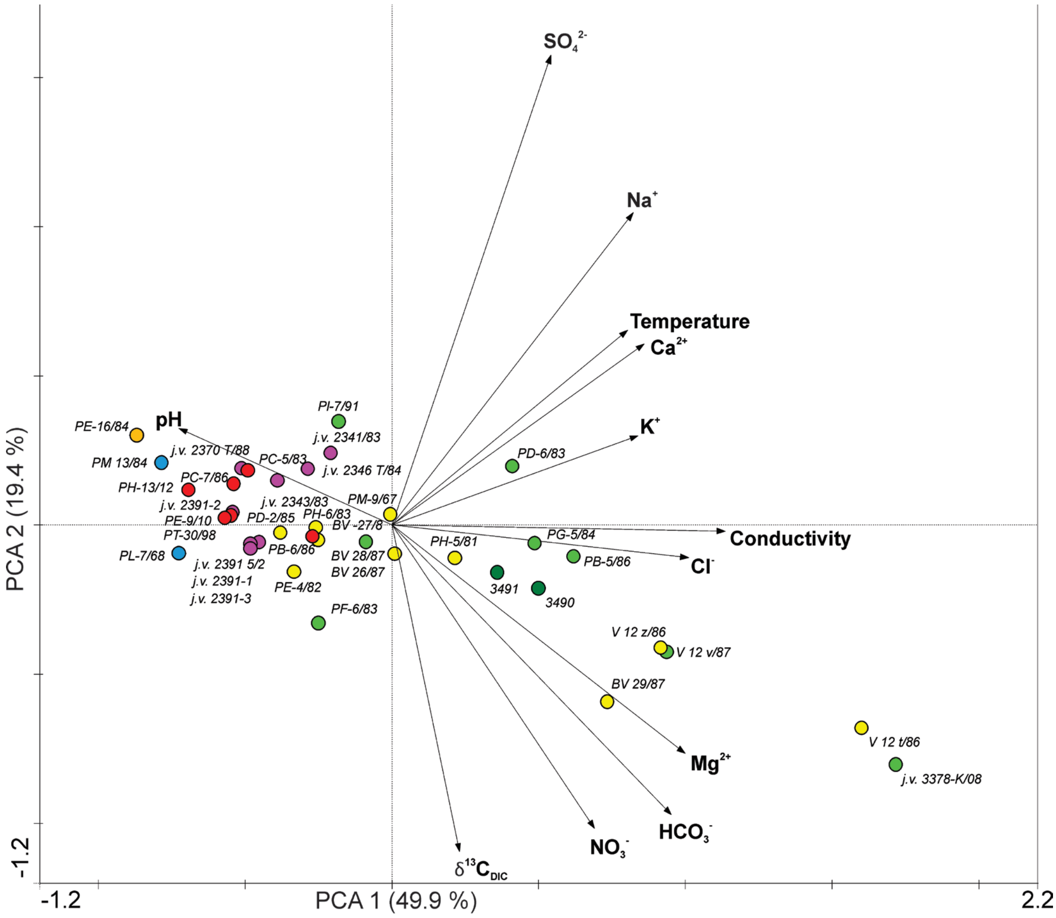
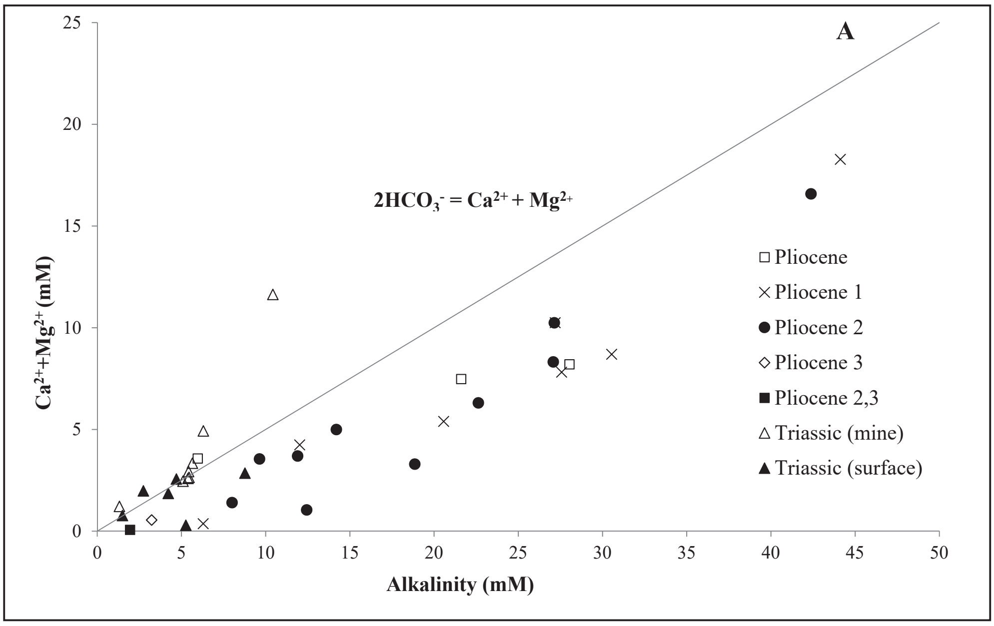


Fig. 4. PCA ordination diagram representing differences between groundwater samples taken during the years 2014-2015 (circles) and the gradients in environmental variables (arrows). Colors of the circles indicate the geology of the aquifer - for the legend see Fig. 2).

(44.12 mM = 2691.32 mg/l) was observed in well 3378-K/08 (Figs. 2, 3) and the lowest alkalinity of 1.32 mM (80.52 mg/l) at location j.v. 2370 T/88 (Figs. 2, 3). Na^+ concentrations range from 0.104 mM (2.38 mg/l) to 10.22 mM (234.0 mg/l), Mg^{2+} concentrations from 0.004 mM (0.097 mg/l) to 16.63 mM (4074. 1 mg/l), K^+ concentrations from 0.0001 mM (0.39 mg/l) to 0.51 mM (19.9 mg/l), and Ca^{2+} concentrations from 0.01 mM (0.401 mg/l) to 4.705 mM (188.5 mg/l) in Pliocene aquifers (Table 1). In groundwater from Triassic aquifer the following concentrations were obtained: Na^+ from 0.056 mM (1.28 mg/l) to 22.02 mM (504.3 mg/l), Mg^{2+} from 0.078 mM (1.89 mg/l) to 4.94 mM (120 mg/l), K^+ from 0.017 mM (0.66 mg/l) to 0.48 mM (18.7 mg/l) and Ca^{2+} from 0.21 mM (8.42 mg/l) to 6.69 mM (268.2 mg/l) mM (Table 1). SO_4^{2-} concentrations in groundwater from Pliocene aquifers are low due to reduction conditions in the aquifer (Kanduč et al., 2014) and range from 0.00078 mM (0.074 mg/l) to 0.50 mM (48 mg/l), NO_3^- concentrations range from 0.0002 mM (0.011 mg/l) to 0.11 mM (6.28 mg/l) mM in groundwater from Pliocene aquifers (Table 1). In addition, SO_4^{2-} and NO_3^- concentrations were low in the Pliocene aquifers (up to 0.5 mM (48 mg/l) and up to 0.11 mM (6.82 mg/l)) compared to groundwater from Triassic aquifer indicating sulfate and nitrate reduction (Kanduč et al., 2014), and consistent with microbial methanogenesis (Coetsiers & Walraevens 2009).

PCA analysis explained 49.9 % of all variability in data by the first, and an additional 19.4 % by the second axis (Fig. 4). Most of the samples are distributed along the first axis, described mostly as differences in pH and conductivity linked to chloride. Higher conductivity and chloride concentrations and lower pH were observed in the groundwater samples originating from Pliocene strata. The second axis represents mainly a gradient in sulfate and $\delta^{13}C_{DIC}$. Generally, the groundwater samples dewatering Triassic strata grouped together in the ordination diagram, while samples of groundwater dewatering Pliocene strata are scattered along both axes, indicating greater variation in measured variables. The outlier sample j.v. 3051/01 is from dewatering Triassic strata, having a high concentration of sulfate, 20.18 mM (1937 mg/l) (Table 1). The lowest $\delta^{13}C_{DIC}$ value of -19.3 ‰ in j.v. 3051/01 indicates greater soil CO_2 degradation in the groundwater. The other two outlier samples (V 12 t/86 and j.v. 3378-K/08) have high alkalinities and conductivities (Table 1).

Dissolution of calcite and dolomite produces groundwater with the molar ratio $(Ca^{2+}+Mg^{2+})$: HCO_3^- = 1:2. The weathering of dolomite in carbonate systems contributes the majority of the Mg^{2+}, in which Mg^{2+} : Ca^{2+} and Mg^{2+} : HCO_3^- molar ratios indicate the relative proportions of calcite and/or dolomite dissolution (Kanduč



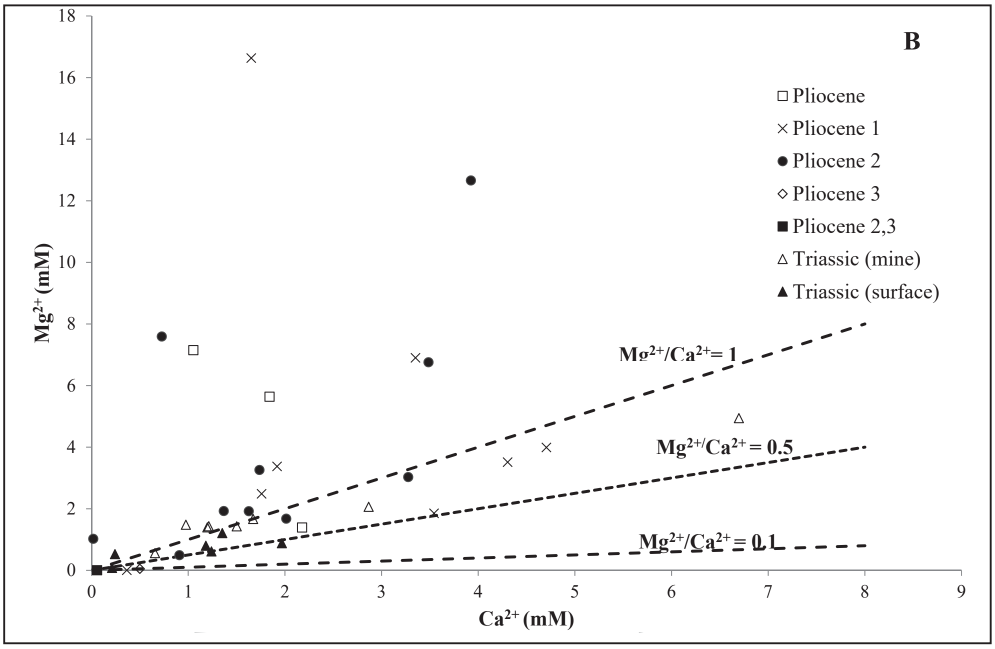


Fig. 5. A. Ca^{2+} + Mg^{2+} versus alkalinity concentrations. The line indicates the stoichiometry for weathering of carbonate minerals. B. Mg^{2+} versus Ca^{2+} concentrations in Velenje Basin groundwater.

et al., 2014). Groundwater dewatering Pliocene strata has higher alkalinity and deviates from the 2:1 groundwater line, while the groundwater in the Triassic aquifer falls along the 2:1 HCO_3^-: (Ca^{2+}+Mg^{2+}) line (Fig. 5A). Dissolution of calcite produces waters with a Mg^{2+} : Ca^{2+} molar ratio of less than 0.1, a ratio of 0.33 in the case of congruent dissolution of calcite and dolomite, and a ratio equal to 1 if only dolomite is dissolving (Szramek et al., 2011). Groundwater in the Triassic aquifer falls between lines 0.5 and 1, indicating weathering of dolomite (Fig. 5B), while groundwater in Pliocene aquifers deviates from the dolomite line (having a slope of 1) indicating that some other minerals (e.g. albite, plagioclase) contribute to alkalinity, already confirmed in previous studies by X-ray diffraction (Kanduč et al., 2014 and references therein).

Carbon cycling and strontium geochemistry of Velenje Basin groundwater

Partial pressures of CO_2 (pCO_2) in groundwater of Pliocene and Triassic aquifers ranged from 15.8 to 575,439.9 ppm and from 169.8 to 107,151.9 ppm, on average 80800 ppm, which is 202 times greater (supersaturated) than that of atmospheric CO_2 concentrations (400 ppm). $SI_{calcite}$ ranged from -0.8 to 1.48 and $SI_{dolomite}$ ranged from -0.32 to 2.93 in Pliocene aquifer. $SI_{calcite}$ ranged from -0.75 to 0.52 in groundwater dewatering Triassic aquifer and $SI_{dolomite}$ ranged from -1.54 to 1.06 in groundwater dewatering Triassic aquifer (Fig. 6). Groundwater samples from the Pliocene and Triassic aquifers therefore have calcite saturation indices ($SI_{calcite}$)

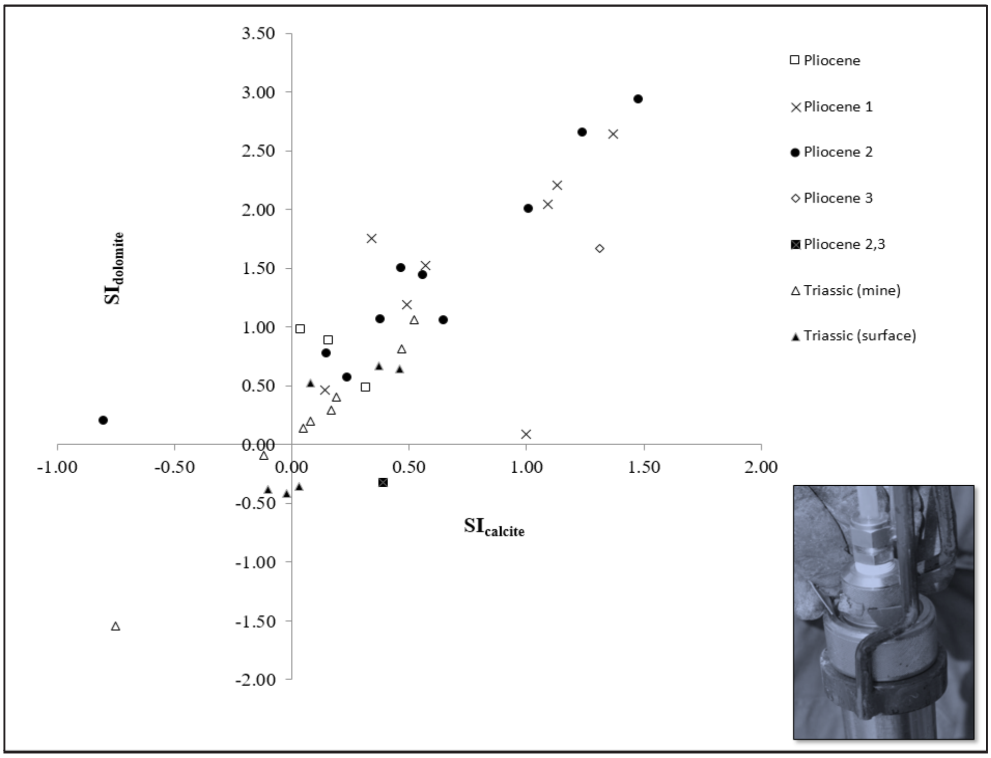


Fig. 6. Saturation index of calcite ($SI_{calcite}$) versus saturation index of dolomite ($SI_{dolomite}$) in the groundwater of the Velenje Basin. Photo on figure 6 represents precipitation of carbonates on a probe of "Solinst sampler".

generally well above the equilibrium ($SI_{calcite} = 0$), indicating that calcite is supersaturated and that precipitation is favored thermodynamically due to high alkalinities, especially in the Pliocene aquifer. Only two samples from mining wells and three samples that overflow dewatering Triassic strata are undersaturated with calcite and dolomite (Fig. 6). We also observed precipitates of dolomite/calcite as visible incrustations in some of the wells. Such incrustations have formed on the well casing, and were scratched from the casing walls when measuring with the Solinst Discrete Interval Probe (photo on Fig. 6).

Values of $\delta^{13}C_{DIC}$ for groundwater of dewatering Pliocene strata ranges from -14.4 to +4.6 ‰. Groundwater dewatering Triassic strata ranges from -19.3 to -2.8 ‰ (Table 1). Geochemical processes influencing the value of $\delta^{13}C_{DIC}$ in groundwater are presented on Figure 7. Groundwater samples from the Triassic aquifer have generally lower $\delta^{13}C_{DIC}$ and are similar to those investigated previously for surface waters (Kanduč et al., 2014). They fall approximately on the line of carbonate dissolution by carbonic acid produced from the soil zone with a $\delta^{13}C_{CO2}$ of -26.6 ‰ (Kanduč et al., 2007). Groundwater samples from the Pliocene aquifers have higher values of $\delta^{13}C_{DIC}$ (up to +4.6 ‰), which are attributed to microbial methanogenesis, causing enrichment in ^{13}C (Kanduč et al., 2012). Isotopic compositions of carbon in methane ($\delta^{13}C_{CH4}$) and of deuterium in methane (δD_{CH4}), analyzed directly from groundwater ranged from -77.7 to -51.4 ‰ and from -246.6 to -162.0 ‰, indicating bacterial gas (Kanduč et al., 2014; Kanduč et al., 2015b). Higher $\delta^{13}C_{DIC}$ values are due to methanogenesis within aquifer and are related to microbial methanogenesis associated with coal seam. We also found microbial gas collected from piezometers (as free gas) in previous studies and its $\delta^{13}C_{CH4}$ have values in the range of -70.5 to -34.2‰ (Kanduč et al., 2012; Kanduč et al., 2014).

Equilibration lines according to possible geochemical processes were calculated as follows:

- *Line 1.* Considering the isotopic composition of atmospheric CO_2 of -7.8 ‰ (Levin et al., 1987) and the equilibration fractionation with DIC of +9 ‰, DIC in equilibrium with the atmosphere should have a $\delta^{13}C_{DIC}$ about +1 ‰ (Fig. 7).
- *Line 2.* Given the average isotopic composition of carbonates ($\delta^{13}C_{CaCO3}$) with a value of -2 ‰ (Kanduč & Pezdič, 2005) and isotopic fractionation (and enrichment in ^{12}C) due to dissolution of carbonates, which is 1.0±0.2 ‰ (Romanek et al., 1992) (Fig. 7) would give a value of $\delta^{13}C_{DIC}$ of 1.0±0.2 ‰.
- *Line 3.* An average $\delta^{13}C$ value of particulate organic carbon (POC) of -26.6 ‰ was assumed to represent the isotopic composition of POC that was transferred to DIC by in stream respiration. Open system equilibration of DIC with CO_2 enriches DIC in ^{13}C by about 9 ‰ (MOOK et al., 1974), which corresponds to the value of -17.6 ‰ (Fig. 7).
- *Line 4.* This represents open system equilibration of DIC with soil CO_2 originating from degradation of organic matter with $\delta^{13}C_{CO2}$ of -26.6 ‰ (Fig. 7).

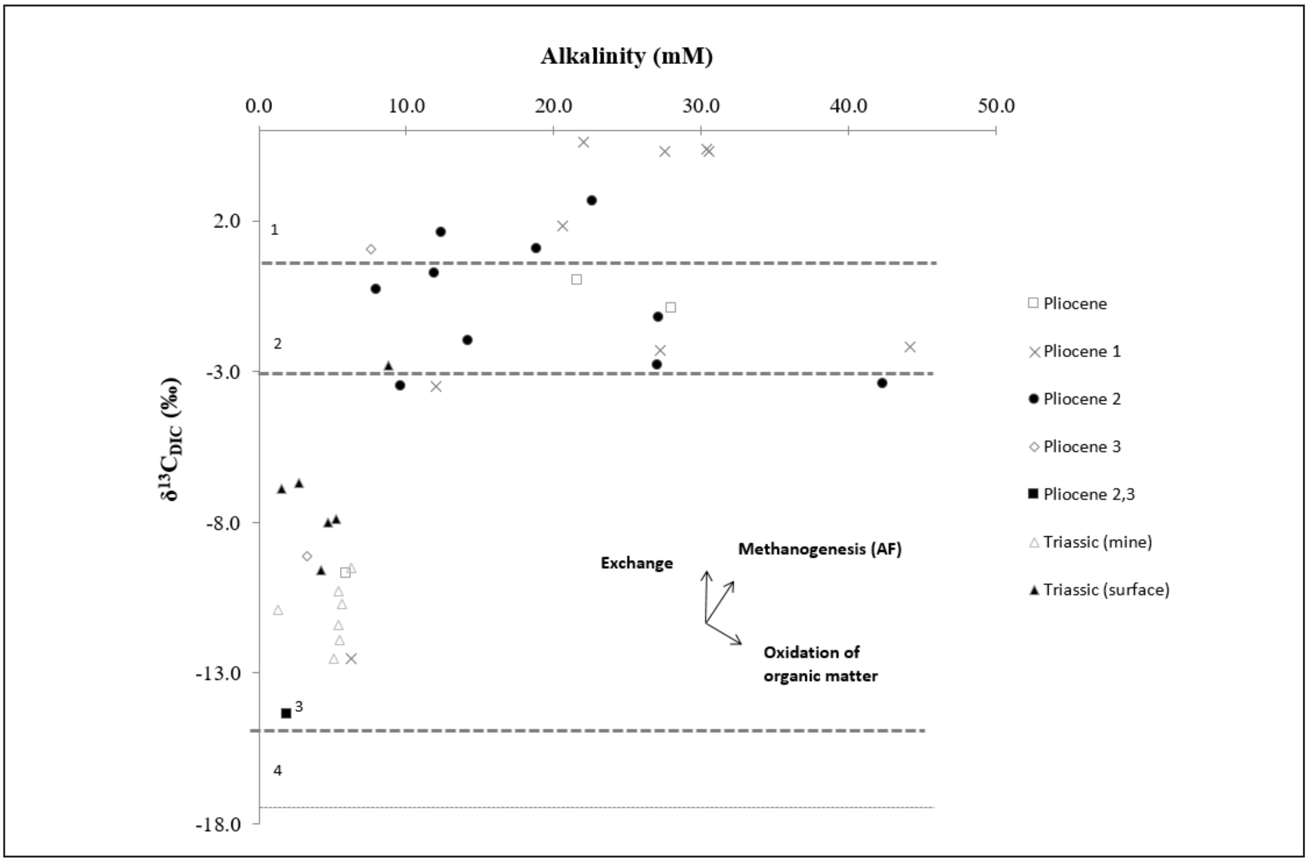


Fig. 7. $\delta^{13}C_{DIC}$ versus alkalinity in Velenje Basin groundwater. Variations in $\delta^{13}C_{DIC}$ values of groundwater samples compared to alkalinity concentrations, with lines indicating processes occurring in the Velenje Basin. Arrows show expected trends for a variety of processes. Lines indicate processes in aquifer as follows: 1: open system DIC equilibration with atmosphere (Exchange), 2: dissolution of carbonates with average $\delta^{13}C_{CaCO3}$ = -2 ‰, 3: nonequilibrium carbonate dissolution by carbonic acid produced from soil zone with a $\delta^{13}C_{CO2}$ of -26.6 ‰, 4: open system equilibration of DIC with soil CO_2 originating from degradation of organic matter with $\delta^{13}C_{CO2}$ of -26.6 ‰.

Groundwater in our study is considered as a closed system (Clark & Fritz, 1997), therefore any interactions with atmosphere are not possible.

It was found in previous studies that concentrations of dissolved organic carbon (DOC) in the Pliocene and Triassic aquifers in the Velenje basin are low, ranging from 1.54 to 14.69 mg/L (Kanduč et al., 2010), compared to groundwater associated with coalbeds in the Powder River Basin (Orem et al., 2010). In the latter, high DOC concentrations are related to methanogenesis and contact of groundwater with coal, but in Velenje Basin we can conclude that the methanogenesis (Fig. 7) in groundwater is probably related to the presence of low dissolved oxygen (DO), high alkalinity and high $\delta^{13}C_{DIC}$ values, occurring within the Pliocene aquifers (Kanduč et al., 2014).

The ratio $^{87}Sr/^{86}Sr$ ranges from 0.70820 to 0.71056 in groundwater dewatering Pliocene aquifers and from 0.70808 to 0.70910 in groundwater dewatering Triassic strata (Table 1). Figure 8 represents $^{87}Sr/^{86}Sr$ ratios and indicates characteristic values of $^{87}Sr/^{86}Sr$ isotopes in different environment with different geological composition e.g. marine limestone 0.711, while silicate fraction has higher $^{87}Sr/^{86}Sr$ ratio. The relations between $^{87}Sr/^{86}Sr$ ratios and $\delta^{13}C_{DIC}$ for groundwater in Pliocene and Triassic aquifers for Velenje Basin groundwater are presented on Figure 8. Based on the $^{87}Sr/^{86}Sr$ ratio in groundwater from both aquifers (Triassic and Pliocene), the carbonate fraction prevails (Fig. 8). The highest $^{87}Sr/^{86}Sr$ ratio was found in Pliocene 2, 3 strata, implying that more silicate fraction is leached in the aquifer. Generally, in Pliocene aquifers of Velenje Basin groundwater, higher $^{87}Sr/^{86}Sr$ ratios are observed than in Triassic aquifers (Table 1, Fig. 8). Given that carbonate dissolution rates are higher than those of silicates (Lasaga, 1984) as is the case for the Triassic and Pliocene aquifers of Velenje Basin carbonate dissolution may be important in controlling Sr isotope geochemistry (Harrington & Herzeg, 2003). However in the study of Murray Basin, Australia, $^{87}Sr/^{86}Sr$ ratios of groundwater lie between 0.71068 and 0.71905 (median = 0.71595), generally higher than values for potential carbonate sources (Cartwright et al., 2007). Trends in $^{87}Sr/^{86}Sr$ ratios versus $\delta^{13}C_{DIC}$ values for the mixing of groundwater from silicate and carbonate aquifers of Velenje Basin groundwater are shown schematically in Figure 8. Trends in $^{87}Sr/^{86}Sr$ ratios versus $\delta^{13}C_{DIC}$ values for the mixing of groundwater from silicate and carbonate aquifers or for the progressive dissolution of carbonates are shown in Figure 8. $^{87}Sr/^{86}Sr$ ratios of the silicate and carbonate fraction of aquifer

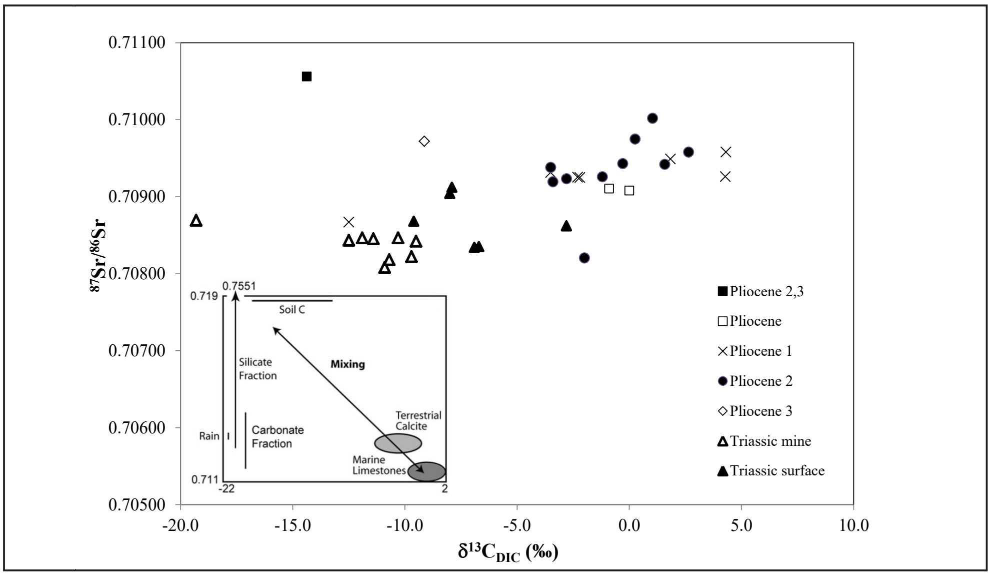


Fig. 8. $^{87}Sr/^{86}Sr$ versus $\delta^{13}C_{DIC}$ in Velenje Basin groundwater.

material in Velenje Basin groundwater, rainfall (Ullman & Collerson, 1994), typical $^{87}Sr/^{86}Sr$ ratios and $\delta^{13}C_{DIC}$ values of marine and terrestrial carbonates (Clark & Fritz, 1997; Faure, 1991), and typical $\delta^{13}C$ values of soil carbon (Clark & Fritz, 1997), are also shown.

Conclusions

Sampling in this study was performed only where possible due to the subsidence of the area, which destroyed some of the piezometers. New wells were sampled in the following three sampling campaigns during the period 2014–2015: a) overflow piezometers, b) groundwater and c) mine wells. Altogether, 38 wells were investigated for geochemical and isotopic analyses.

The major ion geochemistry and isotope geochemistry of the Velenje Basin groundwater are indicated in this study. The major ion geochemistry, isotopic composition of carbon and Sr ratios ($\delta^{13}C_{DIC}$, $^{87}Sr/^{86}Sr$) provides a new insight into geochemical processes (water - rock-interactions) in Velenje Basin groundwater.

The concentrations of dissolved ions and cations decreases in the order $HCO_3^- > Mg^{2+} > Na^+ > Ca^{2+}$ in the Pliocene aquifers and $HCO_3^- > Ca^{2+} > Mg^{2+}$ in the Triassic aquifer. Multivariate PCA analysis, based on "*in situ*" measured parameters (conductivity, pH, temperature), major geochemical parameters (Ca^{2+}, Mg^{2+}, K^+, Na^+, NO_3^-, Cl^-, SO_4^{2-}) and $\delta^{13}C_{DIC}$ revealed that groundwater samples dewatering Triassic strata were grouped together in the ordination diagram, while the samples of groundwater dewatering Pliocene strata were scattered along both axes due mainly to variations in pH, conductivity, chloride, sulphate and $\delta^{13}C_{DIC}$.

The values of $\delta^{13}C_{DIC}$ and $^{87}Sr/^{86}Sr$, together with major ion geochemistry help explain geochemical processes in Velenje Basin groundwater. $\delta^{13}C_{DIC}$ values of groundwater in Pliocene aquifers range from -14.4 to +4.6 ‰ and in groundwater of Triassic aquifer from -19.3 to -2.8 ‰. Alkalinities range from 1.95 to 44.12 mM in Pliocene aquifers and from 1.32 to 10.43 mM in Triassic aquifer. $\delta^{13}C_{DIC}$ of groundwater in the Triassic aquifer indicate carbonate dissolu-tion (dolostones and limestones) and organic matter degradation. In Pliocene aquifers, however methanogenesis (higher $\delta^{13}C_{DIC}$ values up to +4.6 ‰) is present in addition to degradation of organic matter and dissolution of carbonates, contributing to the very high alkalinity in these aquifers. Calculated value of pCO_2 in groundwater of Pliocene aquifers ranged from 15.8 to 575,439.9 ppm and in groundwater of Triassic aquifer from 169.8 to 107,151.9 ppm. Most groundwater in Pliocene and Triassic aquifers was oversaturated with calcite and dolomite. Pliocene groundwaters have much higher oversaturation values than the Triassic ones, also due to methanogenesis and high alkalinity.

The $^{87}Sr/^{86}Sr$ ratios in Pliocene aquifers range from 0.70820 to 0.71056 and, in groundwater of Triassic aquifer, from 0.70808 to 0.70912. $^{87}Sr/^{86}Sr$ isotopes in combination with $\delta^{13}C_{DIC}$, provide added value to the study in deciphering geochemical processes, water–rock interactions and silicate/carbonate weathering within the aquifers. The carbonate was found to have an $^{87}Sr/^{86}Sr$ ratio around 0.71120, the silicate fraction being in the range of 0.7120 to 0.7190. Groundwater from Pliocene aquifers has more positive $\delta^{13}C_{DIC}$ values and $^{87}Sr/^{86}Sr$ ratio, except for two samples located in the Pliocene 3 aquifer ($^{87}Sr/^{86}Sr$ ratio 0.70972, alkalinity 3.23 mM and $\delta^{13}C_{DIC}$ of -9.13 ‰, PM13/84) and Pliocene 2, 3 aquifer ($^{87}Sr/^{86}Sr$ ratio 0.71056 with low alkalinity of 1.95 mM and $\delta^{13}C_{DIC}$ of -14.37‰, PE 16/84 sample). Groundwater from Triassic aquifer has more negative $\delta^{13}C_{DIC}$ values and lower $^{87}Sr/^{86}Sr$.

From the hydrogeological (dewatering system) and geochemical (biogeochemical processes and age of groundwater) points of view it would be useful to investigate further the geochemical and hydrogeological relationships between shallow and deeper aquifers in different strata formations (Pliocene and Triassic). New observation objects (piezometers) will be drilled at northern part of the basin where mining activity is present.

As due to the mining activity, the basin is presently subsiding, a geochemical investigation in combination with hydrogeological studies is also necessary from the safety reasons and groundwater inrush into the mine.

Besides the groundwater investigations it would be useful to continue investigation of gases in groundwater and also geochemical characteristics of coalbed gases in coal matrix at active excavation fields. These investigations would be very useful for future development of CBM technology after the termination of mining activities in Velenje coal basin.

Acknowledgments

The study of "Hydrogeochemistry and isotope geochemistry of Velenje Basin groundwater" was performed in the framework of a broader research topic, supported financially by the Slovenian Research Agency (ARRS) research project L1-5451 entitled "Evaluating geological sequestration of CO_2 in low rank coals; Velenje Basin, Slovenia as a natural analogue" and the Velenje Coal Mine d.d. The authors are grateful to Mr. Igor Medved, Mr. Darian Božič and Mr. Stojan Žigon for technical support and assistance with field sampling and analytical help. Thanks to Prof. Roger Pain for linguistic corrections.

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GEOLOGIJA 59/1, 23-34, Ljubljana 2016

http://dx.doi.org/10.5474/geologija.2016.002

Anisian Strelovec Formation in the Robanov kot, Savinja Alps (Northern Slovenia)

Anizijska Strelovška formacija v Robanovem kotu, Savinjske Alpe (Severna Slovenija)

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Prejeto / Received 14. 3. 2016; Sprejeto / Accepted 30. 5. 2016; Objavljeno na spletu / Published online 11. 8. 2016

Key words: Middle Triassic, Illyrian, basin, anoxic, fine-grained turbidites, slumps, progradation
Ključne besede: srednji trias, ilirij, anoksični bazen, drobnozrnati turbiditi, zdrsi, progradacija

Abstract

A detailed sedimentological features of the Slatinski plaz section with a transition from the deep-water Anisian (Illyrian) Strelovec Formation to the Ladinian shallow-water Contrin Formation have been presented. The Strelovec Formation is divided into five different lithostratigraphic units that are characterised by dark hemipelagic and pelagic thin-bedded limestones and dolomitic mudstones that are frequently intercalated with deposits of gravity-mass flows, slump and slide to fine-grained low-density turbidity origin. The Strelovec Formation was deposited in a hydrodynamically quiet, pelagic deeper-water anoxic environment, most probably on a gentle platform slope. In the upper part of the formation, the presence of olistolith blocks of shallow-water limestones indicates the closing of the prograding shallow-water platform wedge. Massive dolostones of Unit 6 mark the complete filling of the basin and the beginning of the shallow-water sedimentation of the Contrin Formation in the Early Ladinian.

Izvleček

V članku predstavljamo detajlni sedimentološki profil Slatinski plaz, v katerem lahko opazujemo prehod iz anizijske (ilirske) globljevodne Strelovške formacije v ladinijsko plitvomorsko Contrinsko formacijo. Strelovško formacijo smo razdelili na pet litostratigrafskih enot, za katere je značilno menjavanje temnih hemipelagičnih tankoplastnatih apnencev in dolomitov (mudstone), med katerimi so pogosti sedimenti gravitacijskih tokov (od zdrsov do zdrobnozrnatih turbiditov). Strelovška formacija se je odlagala v hidrodinamsko mirnem, pelagičnem, globljevodnem anoksičnem okolju, najverjetneje na blagem pobočju. V zgornjem delu formacije se pojavijo olistolitni bloki plitvovodnih apnencev, ki nakazujejo približevanje progradacijskega klina napredujoče platforme. Šesta litostratigrafska enota vsebuje plivovodne kamnine zgodnjeladinijske Contrinske formacije, ki kažejo, da se je globljevodni bazen v tem času že popolnoma zasul.

Introduction

The Strelovec Formation is represented by Anisian bituminous thin-bedded limestone and dolomite deposits with intercalation of marls and clays that can be traced across the entire Kamik-Savinja Alps (Celarc, 2004a, Vičič, 2014). It was first defined by Celarc (2004a) and later investigated due to the rich macrofossil biota (Hitij et al. 2010; Hitij 2012; Žalohar & Hitij 2013). However, compared to younger Triassic rocks (Celarc, 2004a, 2004b; Celarc & Goričan, 2007; Celarc & Kolar Jurkovšek, 2008; Celarc et al., 2013, 2014; Rožič 2008, Rožič et al., 2009, 2013; Gale, 2010, 2012; Gale et al., 2013, 2014, 2015) it still remained insufficiently investigated.

In order to fill this gap, we present a first detailed sedimentological investigation of the Strelovec Formation from the almost perfectly exposed section (Slatinski plaz) in the Robanov kot valley (Kamnik-Savinja Alps, northern Slovenia). The aim of this study is to describe and determine different microfacies of the Strelovec Formation, to define sedimentation processes and environment and to interpret evolution of the Anisian basin in the studied area.

Geological setting

The investigated succession is located in the Kamnik-Savinja Alps in the SE part of the Robanov kot valley (Fig. 1), and structurally belongs to the eastern part of the Southern Alps (PLACER, 2008). During Middle Triassic times, the area was situated on the southwestern Neotethyan embayment /shelf of the opening Meliata-Maliac Ocean (e.g. STAMPFLI et al., 2002; SCHMIDT et al., 2008).

From the Late Permian onward, the eastern Southern Alps belonged to the Slovenian Carbonate Platform (BUSER, 1989). During the rifting phase in the middle Triassic, this platform was dissected into numerous small platforms bounded by relatively shallow basins, most of which were completely infilled in the early Late Triassic time (WINTERER & BOSELLINI, 1981; DOGLIONI, 1987; BUSER, 1989; BERTOTTI et al., 1993; OGORELEC & ROTHE, 1993). In the Robanov kot valley, Lower Triassic to

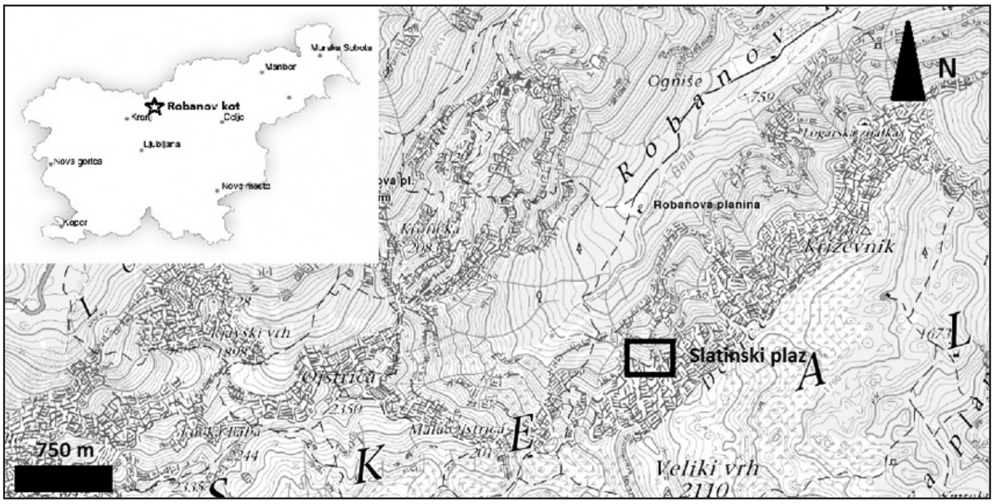


Fig. 1. Location of the studied section. A) Position of the Robanov kot valley. B) Position of the section (square).

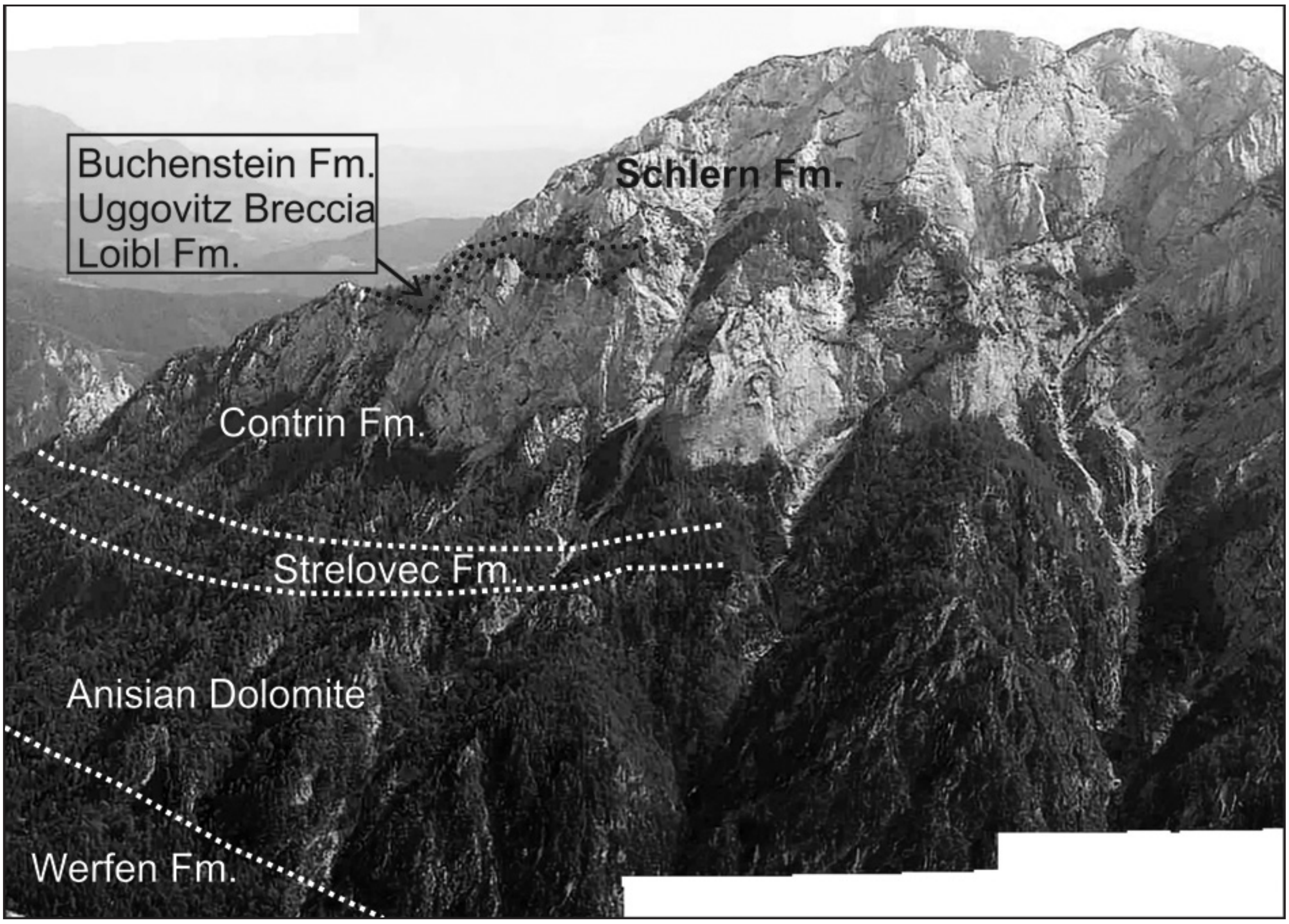


Fig. 2. Triassic formations cropping out in the Robanov kot Valley, below Križevnik Hill (modified after CELARC, 2004a).

lowermost Upper Triassic rocks crop out (Celarc, 2004a, Celarc et al., 2013, Fig. 2). The succession commence with a deposition of the Lower Triassic marls, and sandstones intercalated with of oolitic limestones and dolostone beds (Werfen Formation) continues with a deposition of Anisian bedded and massive dolostone. These rocks belong to the Slovenian Carbonate Platform (cf. Buser, 1987, 1989) that are conformably overlain by the deeper-water upper Anisian (Pelsonian to Illyrian) Strelovec Formation, composed of dark-coloured thin-bedded limestone. The Strelovec Formation is concordantly overlain with the shallow-water Anisian (Illyrian) Contrin Formation, characterised by bedded and massive limestones with rare intercalations of dolostones (Celarc et al., 2013). Middle Anisian to lower Ladinian strata are represented by the Loibl Formation, Uggowitz Breccia and Buchenstein Formation composed of thin-bedded limestones with cherts, tuffs, conglomerates, breccias, calcarenites and bedded and massive limestones representing renewed extensional tectonic activity and the formation of small basins. The youngest formation in the Robanov kot valley is Upper Anisian and Ladinian massive limestone and dolomite of the Schlern Formation, recording a progradation of the shallow-water platform over deposits of the deeper basin (Celarc et al., 2013).

The first workers to investigate Triassic strata in the Robanov kot area were Teller (1898) and Seidl (1907, 1908). The area was later mapped for the Basic Geological Map of Yugoslavia, at a scale of 1: 100 000 by Mioč et al., (1983). The Strelovec Formation was first defined and described by

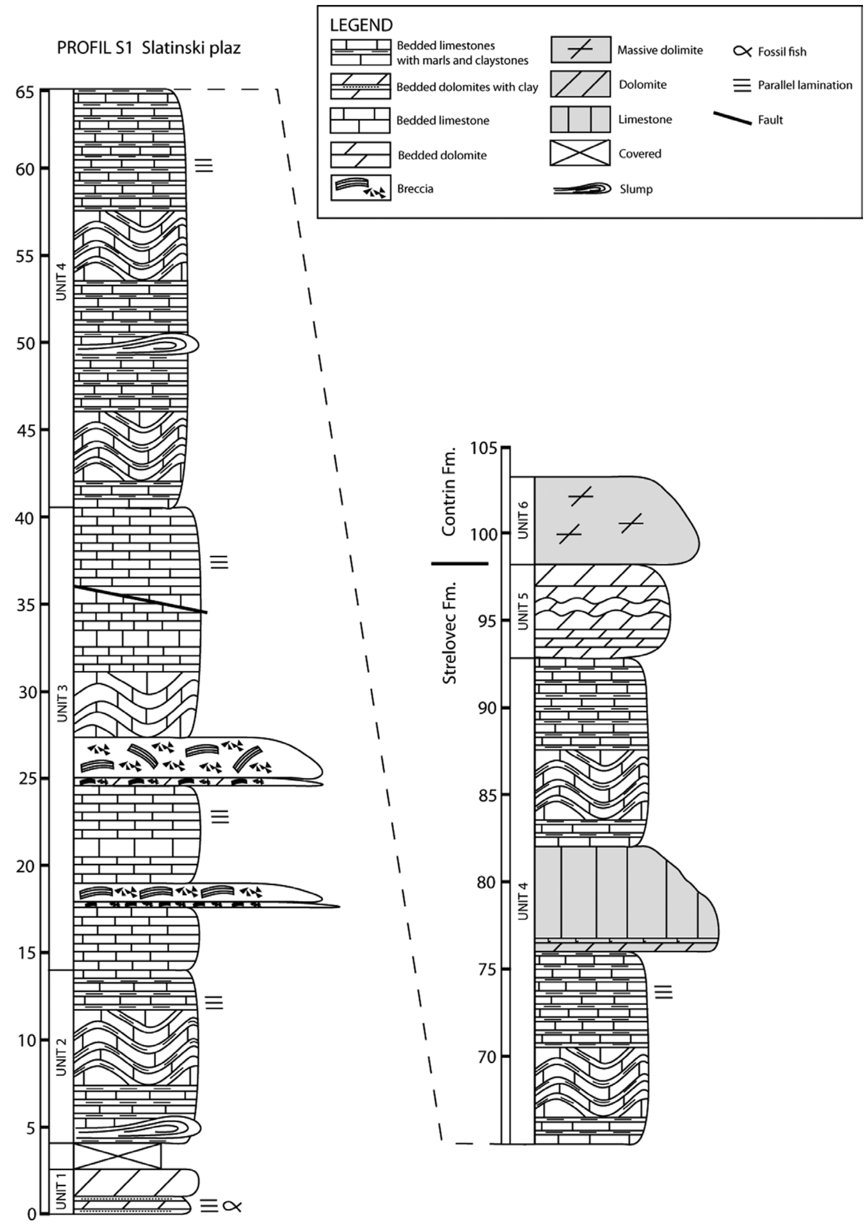


Fig. 3. Slatnikov Plaz section.

Celarc (2004a) who, on the basis of stratigraphic position, ascribed it to the upper Anisian to lower Ladinian age. The rich fossil fauna of the Strelovec Formation was described by Hitij et al. (2010), Hitij (2012), and Žalohar & Hitij (2013).

Materials and methods

The Anisian succession was recorded in the Slatnikov plaz section (lat. 46°21'55.76", lon. 14°39'29.23") by a standard sedimentological procedure (logging in scale 1:50). Total of twenty five thin sections were made for petrographical and sedimentological analysis that were conducted on a Zeiss Axioplan 2 microscope using plane and polarised light. The thin sections were photographed with a Zeiss AxioCam HRc camera. Limestones were classified according to Dunham's (1962) classification. The mineral composition of marls was determined for two samples by X-ray powder diffraction (XRD), using a Philips PW3710 X-ray diffractometer equipped with Cu–Kα radiation and a secondary graphite monochromator. Data were collected at 40 kV and a current of 30 mA in the range from 2–70° 2θ at a rate of 3° 2θ min^{-1}.

Additionally, composite conodont samples of 2.5–3 kg weight were collected aiming to determine the exact biostratigraphic position of the Strelovec Fm. The samples were crushed and treated with diluted acetic acid following standard procedures. Unfortunately, all analysed samples proved to be negative.

Slatinski plaz section

The Slatinski plaz section is 102 m long and exhibits a transition from the Strelovec to Contrin Formations (Fig. 3). The section is divided into six distinct lithostratigraphic units.

Lithostratigraphic Unit 1: *dark grey laminated thin-bedded dolostones with intercalated beds of greyish clays*

Unit 1 represents the base of the Slatinski plaz section and is composed of a 2.5 m-thick package of alternating dark grey, thin to thick bedded and horizontally laminated dolostones and thin beds of dark grey clays (Fig. 4). The contact with the underlying Anisian dolostones is not visible in the section.

Dolostones are thin-bedded or laminated (with the exception of one 1.5 m-thick bed in the middle of the unit). Lamination occur due to alternation of 180–1100 µm thick laminae of dark dolomicrite light crystalline dolomite with 350–2800 µm thick laminae of light crystalline dolomite. Horizontal laminae predominate; wavy laminae occur rarely (Pl. 1, fig. 1). In the dolostones mud rich types predominate with a grain to matrix ratio of 15:85. Grains are represented mainly by poorly sorted peloids, whereas grains of unknown origin occur rarely. Up to 20 µm large pyrite grains are also present. The microfacies also contains amorphous organic streaks and seams that occur parallel

Fig. 4. Grey thin-bedded dolostones of Lithostratigraphic Unit 1.

Fig. 5. Fish fossil (*Eosemionotus sp.*,-) discovered in Unit 1. Fish is 5 cm long.

Fig. 6. Alternation of black thin-bedded and laminated limestones with marls and claystones of lithostratigraphic Unit 2.

to lamination. The finest, muddy component is represented by homogenous dolomicrosparite and dolomicrite. The dolostones in rare cases contain extremely well preserved macrofossils of fish (*Eosemionotus* sp., Fig. 5), coprolites and brachiopods.

Lithostratigraphic Unit 2: *black laminated thin-bedded limestones with intercalated beds of dark grey marls and claystones*

Unit 2 conformably overlies Unit 1, however the contact is covered in the section. Unit 2 is 10 m thick and is represented by an alternation of black laminated and thin-bedded limestones and dark grey marls (Fig. 6).

Limestones are thin-bedded and horizontally laminated mudstones (Pl. 1, fig. 2) with a grain to matrix ratio of 10:90. Lamination are expressed as an alternation of thicker (up to 3 mm) micrite laminae with up to 0.5mm thick laminae of microsparite (Pl. 1, fig. 3). Grains are represented by recrystallised bioclasts, small pyrite grains and rare glauconite grains. The microfacies also contains amorphous organic matter disseminated in the matrix and /or streaks and seams parallel to the lamination.

The marl intercalations are up to 1 cm thick and are composed of illite/chlorite, dolomite, calcite, quartz and rare micas.

Lithostratigraphic Unit 3: *black laminated thin- to medium-bedded limestones with rare interbeds of breccias*

Unit 3 conformably overlies Unit 2. The contact is gradual but over a short distance. Unit 3 is 27 m thick and is characterised by black limestones (Fig. 7) with rare interbeds of breccias.

Fig. 7. Black, thin-bedded and laminated limestones of lithostratigraphic Unit 3.

Limestones are mainly thin- to medium-bedded; only a few thicker beds (up to 1 m) are present. Laminations are expressed as an alternation of 0.5–1 mm thick horizontal laminae of microsparite and micrite. In rare cases normal grading from micrite to microsparite occur (Pl. 1, fig. 4). Wispy and wavy discontinuous laminae are also present (Pl. 1, fig. 4). Mudstone lime types predominate while carbonate grains represented mainly by poorly sorted peloids, and recrystallised bioclasts are subordinate. Pyrite crystals are rare. Similar to the previously described microfacies, also amorphous organic component is common.

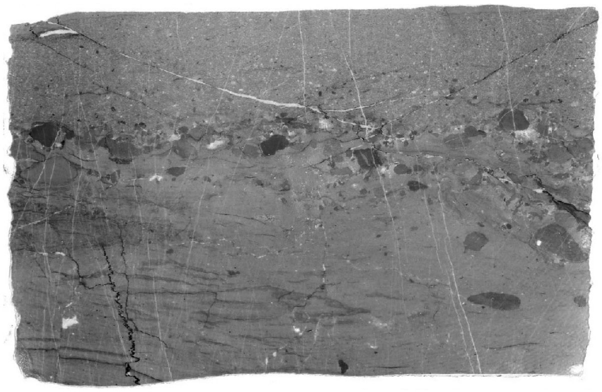


Fig. 8. Polished slab of intraclastic limestone. Lithostratigraphic Unit 3. Longer side of photo is 4 cm long.

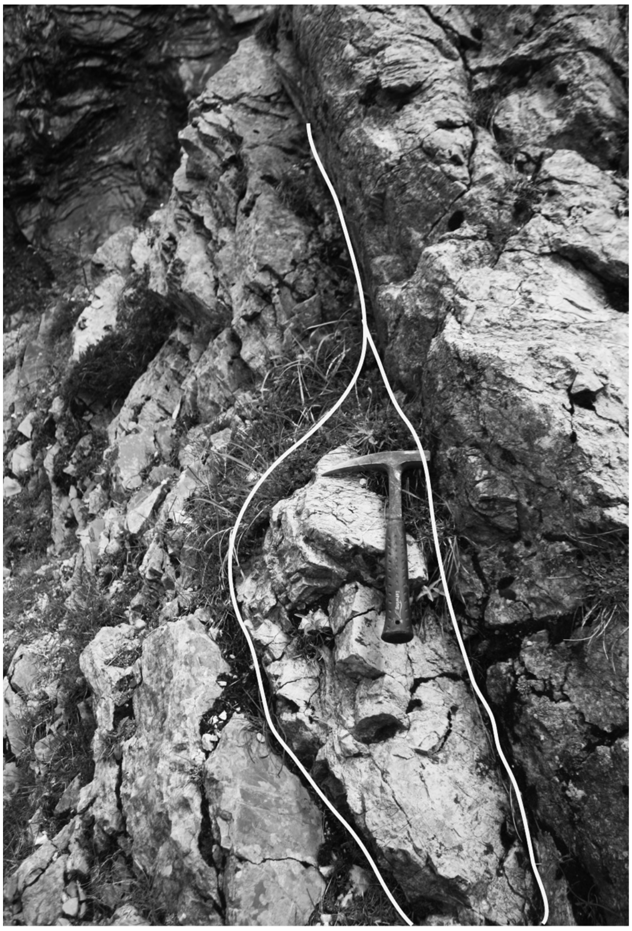


Fig. 9. Intercalated laterally discontinuous breccia bed. Lithostratigraphic Unit 3.

Rare thin-bedded intraclastic limestones are also present (Fig. 8). They are wackestones to packstones composed almost exclusively of small elongated, sub-rounded and rounded intraclasts of micritic limestones. Fragments of echinoderms are extremely rare. The matrix is micrite and rarely microsparite.

Matrix-supported breccias occur occasionally in the Unit 3. The beds are up to 2.6 m thick and in places represent laterally discontinuous beds (Fig. 9) perched into underlying lithologies. Clasts are up to 9 cm in diameter and are composed of microsparite. Occassionaly rip up clasts composed of laminated black limestone occurr (Fig. 10). Matrix of breccia is composed of rare peloids and some pyrite crystals embedded in microsparite and micrite.

Lithostratigraphic Unit 4: *black laminated and thin-bedded limestones with intercalated beds dark grey marls and claystones and large blocks of light grey limestone*

Unit 4 is 52 m thick and is composed of limestones and marls identical to those of Unit 2. In the upper part of the unit large megablocks of light grey limestone occur (Fig. 11). The most characteristic feature of the Unit 4 is numerous channels eroded into underlying beds, slumps and synsedimentary folds.

Fig. 10. Intraformational breccia with large clasts, composed of ripped-up and deformed beds of underlying limestones. Lithostratigraphic Unit 4.

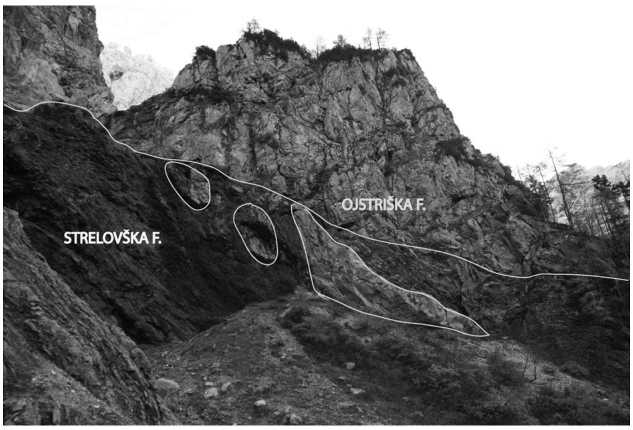


Fig. 11. Large olistolith blocks of shallow-water limestones in the upper part of lithostratigraphic Unit 4.

Fig. 12. Brown laminated, thin- to medium-bedded dolomites with erosional channels. Lithostratigraphic Unit 5.

Fig. 13. Conformable contact between Strelovec Formation (lower part of the photo) and Contrin Formation (upper right part of the photo).

Limestones are thin-bedded and horizontally laminated mudstones with only rare occurrence of wackestones (Pl. 1, fig. 5). Laminations are expressed as an alternation of micrite with microsparite laminae (Pl. 1, fig. 3). The grains are represented by recrystallised bioclasts, small pyrite grains and rare glauconite grains. Amorphous organic matter impregnates the matrix and also forms streaks and seams parallel to the lamination. The matrix in wackestones is microsparite and micrite.

Large blocks of light grey limestone are up 6.3 m in size and are composed of dolomitised medium to thick-bedded and massive limestones. Beds of black limestone underlying blocks are strongly deformed as slumps.

The dolomitised limestones from the lower part of the blocks are dark grey mudstones. The grain to matrix ratio is 10:90. The grains are rare echinoderm fragments and pyrite grains. Limestones from the upper part of the blocks are light grey wackestones to packstones. The grain to matrix ratio is 45:55. The grains are represented by bioclasts of echinoderms, shell fragments, fragmented microbialites, intraclasts and peloids (Pl. 1, fig. 6). Glauconite and small pyrite grains are rare. The matrix is mainly micrite, rarely microsparite.

Lithostratigraphic Unit 5: *brown laminated, thin- to medium-bedded dolostones*

Unit 5 represents the 5.5 m thick uppermost part of the Strelovec Formation. It is represented by thin- to medium -bedded laminated dolostones that contain clearly visible small channels eroded into underlying beds (Fig. 12).

Dolostones in the lower part of Unit 5 are laminated mudstones with micrite matrix and rare small pyrite grains. The matrix is micrite.

Lithostratigraphic Unit 6: *Contrin Formation: thick-bedded bioclastic dolostones*

Unit 6 conformably overlies Unit 5. The deposition started with one 60 cm thick bed of dolostone, followed by massive dolostone (Fig. 13).

The lowermost bed of Unit 6 is bindstone composed exclusively of microbialites with microsparite infill (Pl. 1, fig. 7).

Massive dolostones of Unit 6 are wackestones with a grain to matrix ratio of 30:70. The grains are represented by echinoderm fragments, foraminifera, and algal fragments, fragments of microbialites, intraclasts and peloids (Pl. 1, fig. 8). The grains are embedded in micrite and rarely sparite.

Age of Strelovec Formation

Based on stratigraphic position, Celarc et al. (2013) assigned the Strelovec Formation ranging from Pelsonian to Illyrian. Unfortunately, during our study, no age-relevant fossils were found in the Strelovec Formation.

Depositional environment of the Strelovec Formation

Microfacies in units differentiated in the Strelovec Formation share similar features. The predominance of fine-grained textures (mudstone), presence of organic matter, presence of horizontal lamination, thin bedding and absence of shallow-water elements (with the exception of rare peloids) suggest to hemipelagic and pelagic sedimentation in a hydrodynamically quiet deeper-water environment. According to Stow's (1986) classification of pelagic facies, these rocks correspond to the well-laminated and well-bedded organic rich facies.

Additionally, some beds exhibit normal grading and wispy and wavy discontinuous laminations and are also channelized into underlying beds (these features are especially evident in units 4 and 5, but not exclusive in Units 2 and 3). These features indicate deposition from low-density, fine-grained muddy turbidites (Piper & Stow, 1991).

Within hemipelagic limestones and fine-grained muddy turbidites slumps, synsedimentary folds and intraformational breccias were recognised as well. The nature of the clasts in breccias indicates redeposition within the sedimentary basin. In our opinion, these mass movement deposits represent a continuum of facies that evolved along slope environment. Facies include slides slumps that in some cases evolved into debris to mudflows and turbidites (cf. Coniglio & Dix, 1992; Whitham, 1993; Stow et al., 1998; Chough, 2001; Flügel, 2010). This interpretation is further proved by the fact that in some breccias, we could follow the deformation of indivudual beds: from initial folding, to breaking, and disintegration, resulting in the formation of the clasts that finally form breccias.

Common features of the Strelovec Formation are also fine lamination of limestones, a relatively high content of amorphous organic matter, the presence of pyrite and almost perfectly preserved fish skeletons (Hitij et al., 2010). All these features are indicative of sedimentation in a dysoxic or anoxic deeper-water environment with poor water circulation which allowed the preservation of organic matter, fish skeletons and also lack of bioturbation due to apparent absence of infounal biota. (e.g. Wignall, 1994).

In the lower (Units 1 and 2) and middle (Unit 4) part of the succession thin beds of marls and claystones are intercalated within limestones and dolostones. These beds indicate periods of intensified input of fine-grained clastic material into the basin.

In the upper part of the succession, large blocks of light grey shallow-water dolomitised limestones are embedded within pelagic deeper-water rocks. We interpret them as resedimented olistoliths transported from the edges of a prograding shallow-water platform (cf. Gale et al., 2015). Additionally they could represent the clasts from collapse of the platform edge. The emplacement of these large blocks caused the deformation of semilithified deeper-water sediments, as is clearly evident from the deformed and folded structures in the thin-bedded dolostones lying immediately below the blocks.

In the uppermost part of the succession, brown dolomitic bindstones and bioclastic wackestones are present. The presence of numerous shallow-water clasts and the absence of any indication of resedimentation processes indicate that these limestones were formed in a moderate to high-energy subtidal environment, most probably as a sand belt in a marginal part of a shallow-water carbonate platform (e.g. Flügel, 2010).

Sedimentary evolution of the present-day Robanov kot

In the Anisian, the shallow-water carbonate platform existed in the present-day area of Robanov kot, as evidenced by the Anisian Dolomite Formation (Celarc, 2004a). In the late Anisian (Illyrian), the platform drowned as a consequence of the rifting processes (e.g., Winterer & Bosellini, 1981; Doglioni, 1987; Buser, 1989; Bertotti et al. 1993; Ogorelec & Rothe, 1993; Celarc, 2004b). In the newly formed dysoxic basin in the distal part of the gentle platform slope below the storm wave base, the hemipelagic thin-bedded and laminated limestones of Lithostratigraphic Unit 1 deposited. During this time, there was also a significant input of clastic material into the basin. Lithostratigraphic Unit 2 represents a continuation of the hemipelagic sedimentation in the anoxic hemipelagic conditions. However, the increased occurrence of slides, slumps and fine-grained turbidites suggest sedimentation on the steeper slope compared to Unit 1 and/or increased tectonic activity that possibly triggered mass movements. Lithostratigraphic Unit 3 is similar to Unit 2; however it marks a decrease of the clastic input into the basin. A reduced input of clastics could be related to a drier climate or to Anisian-Ladinian sea-level fluctuations or formation of several dee-basins due to rifting (e.g., Razin et al., 1996). Clastic input was reestablished in Unit 4, while the olistolith blocks found in the upper part of Unit 4 indicating a shallowing of the environment and the reestablishing of the platform prograding wedge. The shallowing of the basin caused the oxygenation of the environment, as evidenced by the light colour and the absence of preserved organic matter in Unit 5. However, the sedimentation was still characterised by fine-grained turbidites and hemipelagites. Deposition of lithostratigraphic Unit 6 designate the complete infilling of the basin and beginning of shallow-water sedimentation of the Contrin Formation in the early Ladinian time.

Correlation with neighbouring areas

The Strelovec Formation was correlated with the Anisian deeper-water successions cropping out in the Dolomites, Julian Alps and Southern Karavanke areas (e.g. Krainer & Mostler, 1991, De Zanche et al., 1993; Gianolla et al., 1998). The Strelovec Formation is time equivalent of the Bivera (Pelsonian) and Ambata (Illyrian) Formations. The Bivera Formation is divided into five lithofacies, with predominant wavy-bedded limestones and clayey limestones and marls with frequent pyroclastic beds. Other facies include mass movement deposits, intra and extraformational breccias, condensed facies and hardgrounds (Metzeltin, 1973; Pisa, 1974; Assereto & Pisa, 1978; Jadoul & Nicora, 1979). The formation was deposited in the basin with complex sea-bottom topography. The Ambata Formation was also deposited in a deeper-water basin, and is divided into two lithofacies units. The first is characterised by bedded black limestones with intercalated marls and clayey limestones. The deposits are interpreted as fine-grained turbidites. The second facies are represented by thin-bedded and laminated marls with intercalation of nodular limestones, and some rare intercalated fine-grained turbidites. In the Southern Karavanke, the Kosiak Formation (Schafhauser, 1997) is also composed of the black, bituminous, platy limestones. Rihthofen Conglomerates in the Dolomites, and the Ugovizza Breccia 1 in the Italian part of the Julian Alps (Gianolla et al., 1998), could also reflect tectonism, related to the formation of the Pelsonian-Lower Illyrian basins.

PLATE 1

1 Lithostratigraphic Unit 1: In the microphotograph of laminated mudstone alternation of thinner micritic and thicker microsparitic laminae is visible. A clast composed of organic matter is present in the centre of the photograph (Sample S2 2, 3).

2 Lithostratigraphic Unit 2: mudstone composed of microsparite and a glauconite grain (centre) (sample S1 89, 25).

3 Lithostratigraphic Unit 2: Microphotograph of the laminated mudstone. In the darker laminae, the recrystallised grains show orientation parallel to the lamination. Organic matter is visible as dark streaks and seams in the middle and lowermost parts of the photograph (Sample 58, 63).

4 Lithostratigraphic Unit 3: laminated mudstone with visible wispy and wavy discontinuous laminae of mudstone in the microsparitic matrix (sample S1 64, 39).

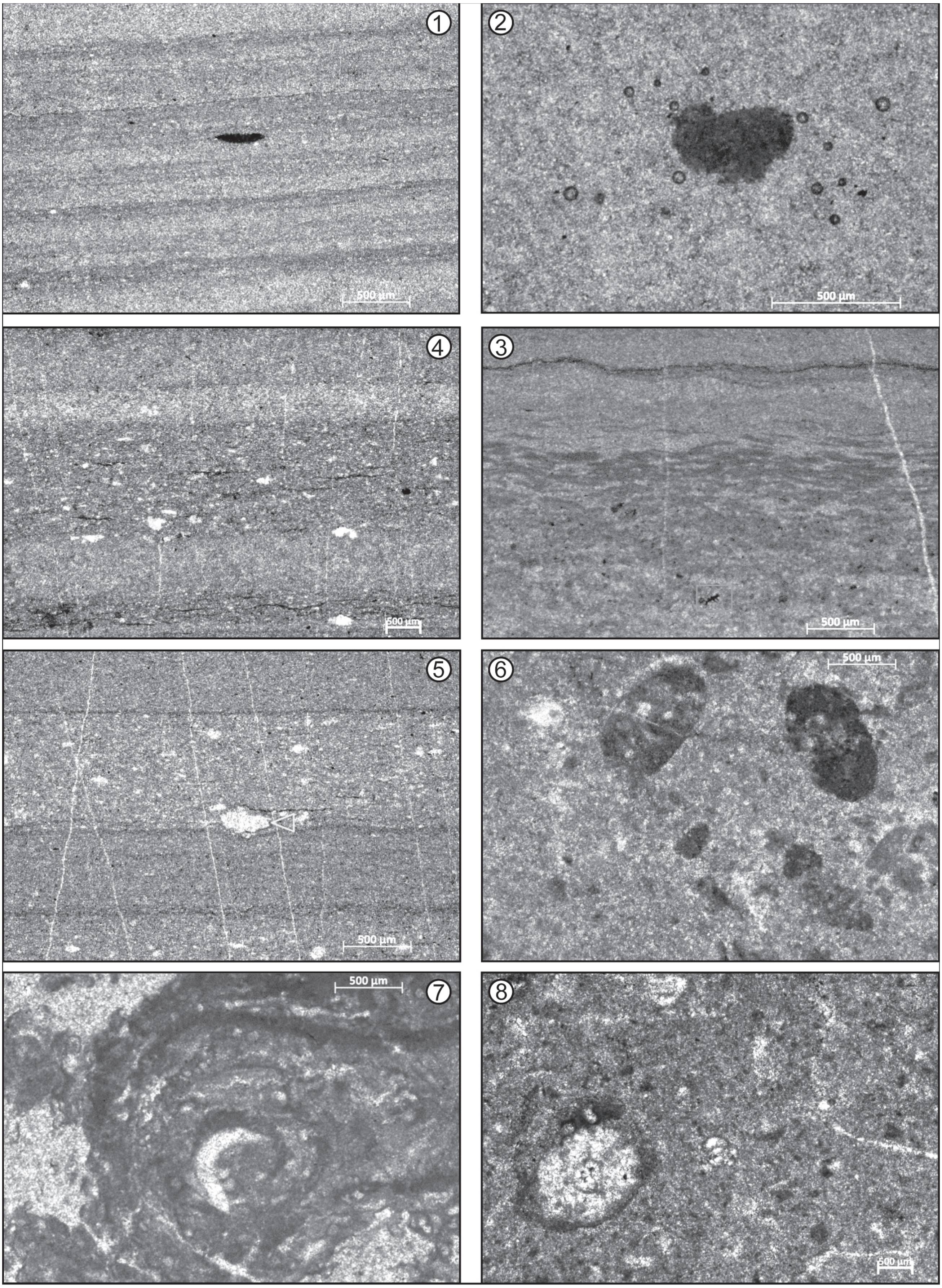
5 Lithostratigraphic Unit 4: Microphotograph of the laminated mudstones with recrystallised grains in the middle part of the photo. The larger grain (marked with the arrow) is impressed into the lower lamina (sample S1 58, 63).

6 Lithostratigraphic Unit 4, sample from megablock: wackestone with intraclastic sand-sized peloids (sample S1 22, 45).

7 Lithostratigraphic Unit 6. Microphotograph of the brown dolomitic, bindstone of microbial origin and some microsparitic infill (sample S1 5, 1).

8 Lithostratigraphic Unit 6: Microphotograph of homogenous dolomitic wackestone texture with small foraminifers and algae (sample S1 4, 7)

PLATE 1



Conclusions

The Anisian (Illirian) Strelovec Formation can be traced across the entire Kamik-Savinja Alps and is characterised by dark thin-bedded limestones and dolostones with intercalated marls and clays. Here, the 102 m-thick Slatnikov plaz section in the Robanov kot area was investigated. The section exhibits a transition from the Strelovec to the Contrin Formations and is divided into six different lithostratigraphic units. Laminated limestone and dolostones with clay-marl interbeds predominates. Intraclastic breccias are common in the lower half of the section. Slumps and synsedimentary folds are also common. Massive dolomite is the uppermost exposed unit. Sedimentary features of the Strelovec Formation indicate hemipelagic and pelagic sedimentation in a hydrodynamically quiet, deeper-water anoxic environment. Pelagic and hemipelagic sedimentation was frequently interrupted by various gravity mass movements ranging from slumps and slides to fine-grained low-density turbidites. Presence of the gravity flow deposits indicate deposition on the slope. In the upper part of the succession, large olistolith blocks of shallow-water limestones embedded within pelagic deeper-water rocks, indicate steepening of the platform wedge and transport of megablocks/ olistolith or possibly a collapse of platform edges. Massive bioclastic dolostone marks complete infilling of the basin and the reestablishing of shallow-water sedimentation of the Contrin Formation in the early Ladinian.

Acknowledgments

The authors would like to thank Dr. Tea Kolar-Jurkovšek for inspection of conodont samples and to Tomaž Hiti and Jure Žalohar for help in determination of the macrofossils. We would also like to thank two anonymous reviewers for thorough and constructive review that improve the original version of the manuscript.

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GEOLOGIJA 59/1, 35-54, Ljubljana 2016

http://dx.doi.org/10.5474/geologija.2016.003

Provenance analysis of Roman stone artefacts from sedimentary rocks from the archaeological site near Mošnje, NW Slovenia

Določanje izvora rimskih kamnitih artefaktov iz sedimentnih kamnin z arheološkega najdišča pri Mošnjah, SZ Slovenija

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Prejeto / Received 18. 3. 2016; Sprejeto / Accepted 31. 5. 2016; Objavljeno na spletu / Published online 11. 8. 2016

Key words: Roman stone artefacts, clastic sedimentary rocks, limestones, microfacies, provenance, Mošnje, Slovenia

Ključne besede: rimske kamnite najdbe, klastične sedimentne kamnine, apnenci, mikrofacies, izvor, Mošnje, Slovenija

Abstract

This study deals with the macroscopic and microfacies characterisation of Roman stone artefacts excavated in 2006 from a Roman villa rustica near Mošnje (NW Slovenia) with the aim of defining their provenance. A total of 28 representative finds (querns, mortars, whetstones, tooled and rounded stones, a fragment of stone slab, mosaic tesserae and two architectural elements - one with a relief) made of clastic and carbonate sedimentary rocks were examined. Comparison was made with rock samples taken from quarries and gravel bars close to the archaeological site, as well as from larger distance to the site. The majority of artefact sampled is composed of Upper Palaeozoic quartz sandstones, which are found as pebbles in gravel bars close to the archaeological site; while 2 samples were from Quaternary coarse grained clastic rocks which can be found in local glacio-fluvial sediments. Other finds were made of four different Mesozoic shallow-water limestones which outcrop in different areas of Central and SW Slovenia. The nearest Lower Jurassic biopelmicritic limestones are found at the western periphery of Ljubljana in Podutik. Cretaceous miliolid limestones and biocalcarenitic limestones with rudists are common in the successions of the Dinaric Carbonate Platform in SW Slovenia (for example, on the Trieste-Komen Plateau), NE Italy and SW Croatia. This indicates that the limestones for architectural elements, stone mortars and tesserae were brought to Mošnje from distant locations. Smaller stone tools are likely to have been made at the location of the archaeological site from material gathered locally, mostly pebbles from clastic rocks, which were accessible and suitable for tooling.

Izvleček

Raziskava obravnava makroskopsko in mikrofaciesno karakterizacijo kamnitih rimskih artefaktov, izkopanih leta 2006 v rimski podeželski vili pri Mošnjah (SZ Slovenija), z namenom določitve njihovega izvora. Pregledali smo 28 reprezentativnih najdb (žrmlje, možnarji, brusi, obdelani in okrogli kamni, odlomek kamnite plošče, mozaične kocke in dva arhitekturna elementa - eden z reliefom) iz klastičnih in karbonatnih sedimentnih kamnin. Kamnite najdbe smo primerjali z vzorci kamnin iz kamnolomov in prodišč v ožji in širši okolici arheološkega najdišča. Večina vzorcev artefaktov je iz zgornjepaleozojskih kremenovih peščenjakov, ki smo jih našli tudi v prodnikih na prodiščih v okolici Mošenj, medtem ko sta dva vzorca iz kvartarnh debelozrnatih klastičnih kamnin, ki se nahajajo v lokalnih ledeniško-rečnih nanosih. Ostale najdbe so izdelane iz štirih različnih mezozojskih plitvovodnih apnencev, ki se pojavljajo na različnih območjih v osrednji in jugozahodni Sloveniji. Spodnjejurske biopelmikritne apnence najdemo najbližje na zahodnem obrobju Ljubljane v Podutiku. Kredni miliolidi apnenci in biokalkarenitni apnenci z rudisti so pogosti v horizontih Dinarske karbonatne platforme na JZ Slovenije (npr. na Tržaško-Komenski planoti), SV Italije in JZ Hrvaške. Domnevamo, da so apnence za izdelavo arhitekturnih elementov, možnarjev ter mozaičnih kock v Mošnje pripeljali z oddaljenih lokacij. Manjša kamnita orodja so verjetno izdelovali na lokaciji najdišča in so uporabili dosegljivi material iz okolice, večinoma prodnike klastičnih kamnin, primernih za obdelavo.

Introduction

During construction of a section of motorway (Vrba–Peračica) in the Gorenjska region NW Slovenia near the village of Mošnje, a Roman *villa rustica* was discovered (Fig. 1). The villa was built in the first half, respectively no later than the middle of the 1st century A.D., and had been used until the end of the 2nd century (Lux & Sagadin, 2012). The *villa rustica* consisted of five masonry buildings built on the support wall. The largest and best preserved was the easternmost building that contained a residential area with baths. More than six thousand individual artefacts were collected, consisting of tools, jewellery, coins, pottery and other finds; most dating from the period between the 1st and the 4th centuries A.D. (Lux, 2008). Among numerous stone finds are the querns, whetstones, mortars, two architectural elements – one with a relief and one similar to altar, black and white mosaic and other functional and decorative objects.Despite various archaeological finds of Roman stone artefacts within Slovenia there has been only a small number of publications regarding the provenance of the archaeological stone materials. Kramar (2009) published a short review of the stone material from this archaeological site, Košir (2011) analysed pyroclastic rocks finds from the Mošnje site, while similar analysis from other parts of Slovenia include stone material from Emona (Brecelj et al., 1989; Ramovš, 1990; Šašel Kos, 1990; Ramovš, 2002; Rižnar, 2010), studies of querns from Central and Coastal Slovenia (Horvat & Župančič, 1987) and NE Slovenia (Djurič et al., 2005; Djurič & Müller, 2009; Kramar & Dolenec, 2013).

The aims of the present study were:

- to define and describe the sedimentary rocks used for various artefacts and stone articles found at the *villa rustica* near Mošnje,
- to compare the stone materials with the samples from quarries and gravel bars close to and further away from the archaeological site in order to determine their provenance.

Geological setting

The archaeological site near Mošnje is located in an intramontane basin known as the Gorenjska Basin (Vrabec & Fodor, 2006). Tectonically the basin is located in the northeastern corner of the Adria-Europe convergent margin, situated at the contact between Southern Alps (northern margin) and External Dinarids (southern margin). The geological basement of the basin and its margins is quite complex; composed of mainly clastic Carboniferous-Permian strata, Mesozoic carbonate rocks and Oligocene to Miocene clastic and volcanoclastic rocks (Grad & Ferjančič 1974; Grad & Ferjančič, 1976; Buser & Cajhen 1978; Buser, 1980). The basin itself is filled with Quaternary alluvial and fluvial deposits from the Sava River and its tributaries. Pebbles found in these deposits are mainly composed of Permian Val Gardena sandstones, Lower Triassic conglomerates, Middle Triassic limestones with cherts and sandstones, Upper Triassic Dachstein limestones and Upper Cretaceous reddish marls (Jurkovšek, 1986; Buser, 2004; Županec & Herlec, 2004).

Materials and methods

A total of 28 stone finds were sampled for petrographic analysis (Table 1). Eighteen of these samples were also microscopically examined (Tables 2, 3). Among sampled finds were querns, whetstones, tooled and rounded stones, stone mortars, a fragment of stone slab, two architectural elements – one with relief, the other similar to altar and black and white mosaic tesserae.

Fig. 1. Aerial photograph of the archaeological site near Mošnje (Source: author Jože Hanc, archived by the Institute for the Protection of Cultural Heritage of Slovenia in Kranj)

Table 1. List of analysed archaeological samples.

SAMPLE	ARCHAEOLOGICAL FIND	TYPE OF STONE MATERIAL
ANM 159	*quern*	*laminated grey lithic coarse grained quartz sandstone*
ANM 161	*quern*	*laminated grey medium grained mica-quartz sandstone*
ANM 163	*quern*	*yellow limonitsed grained lithic-quartz sandstone*
ANM 164	*quern*	*limonitsed yellow-brownish coarse grained lithic-quartz sandstone with transition to fine grained quartz conglomerate*
ANM 165	*quern*	*beige pebbly medium grained feldspar-lithic sandstone*
ANM 167	*quern*	*laminated light grey pebbly medium grained lithic-quartz sandstone to medium grained quartz coglomerate*
ANM 174	*tooled stone*	*limonitsed yellowish brown medium grained lithic-quartz sandstone*
ANM 179	*quern*	*limonitsed laminated grey medium grained mica-feldspar-quartz sandstone*
ANM 187	*quern*	*grey pebbly coarse grained quartz sandstone to medium grained conglomerate*
ANM 189	*fragment of stone slab*	*limonitsed yellowish brown fine to medium grained lithic-quartz sandstone*
PN 779	*quern*	*limonitsed green greyish fine to medium grained quartz sandstone*
PN 1341	*rounded stone*	*medium grey medium grained mica-quartz sandstone*
PN 1465	*rounded stone*	*medium grey medium grained mica-quartz sandstone*
PN 1514	*whetstone*	*limonitsed grey medium grained quartz sandstone*
PN 2734	*rounded stone*	*limonitsed grey medium grained quartz sandstone*
PN 2740	*rounded stone*	*limonitsed yellowish brown coarse grained quartz sandstone*
PN 4051	*whetstone*	*limonitsed light grey medium grained quartz sandstone*
PN 6476	*whetstone*	*limonitsed grey medium grained quartz sandstone*
PN 6497	*whetstone*	*limonitsed yellowish brown fine to medium grained mica-quartz sandstone*
PN 6569	*tooled stone*	*greenish grey medium grained quartz sandstone*
ANM 177	*tooled stone*	*grey medium grained quartz-calcareous conglomerate*
ANM 186	*quern*	*dark grey fine grained mica-quartz breccia*
ANM 160	*stone mortar*	*medium grey biopelmicritic limestone*
ANM 170	*architectural element*	*dark grey pelbiomicritic limestone*
ANM 185	*stone mortar*	*white to light grey biocalcarenitic limestone*
PN 6178	*architectural element with relief*	*white to light grey biocalcarenitic limestone*
ANM 133	*white tessera*	*yellowish white to light grey biomicritic limestone*
ANM 133	*black tessera*	*laminated dark grey to black bituminous micritic limestone*

In addition, 21 comparative samples, taken from identified potential source areas in vicinity and more distant localities to Mošnje (Tables 4, 5), were used for comparison (Table 6). These potential source areas were determined on the basis of the rock type and the characteristics of the stone artefacts, a detailed review of existing literature on provenance of the Roman stone materials and a review of the geology of the research area (Jurkovšek, 1986; Brecelj et al., 1989; Ramovš, 1990; Ramovš, 2002; Buser, 2004; Županec & Herlec, 2004; Bavec, 2008; Jurkovšek, 2010; Rižnar, 2010).

Potential provenance areas included following localities (Fig. 2, Tables 4, 5):

- in vicinity to the archaeological site pebbles of clastic rocks were taken from the gravel bars of the Sava River near Lancovo (Fig. 2: loc. 1), along with 13 samples of carbonate rocks from the quarries at Brezovica (Fig. 2: loc. 2), Stara Hleva (Fig. 2: loc. 3), and the exploration area Kodrasti vrh (Fig. 2: loc. 4).
- more distant localities included a limestone quarry in Podutik (Fig. 2: loc. 5) near Ljubljana (3 samples) and an Italian limestone quarry Cava Romana (Fig. 2: loc. 6) near Aurisina/Nabrežina, Italy (15 samples).

For all comparative rock samples thin sections were made and the selected carbonate rocks were coloured with the Alizarin-red S dye. Samples were analysed under an optical microscope - Nikon Eclipse E200 in transmitted light. Digital images were taken with a Nikon Coolpix digital camera. Clastic rocks were classified according to Wentworth (1922) and Pettijohn (1973), while carbonate rocks were classified according to Folk (1962) and Dunham (1962) classifications.

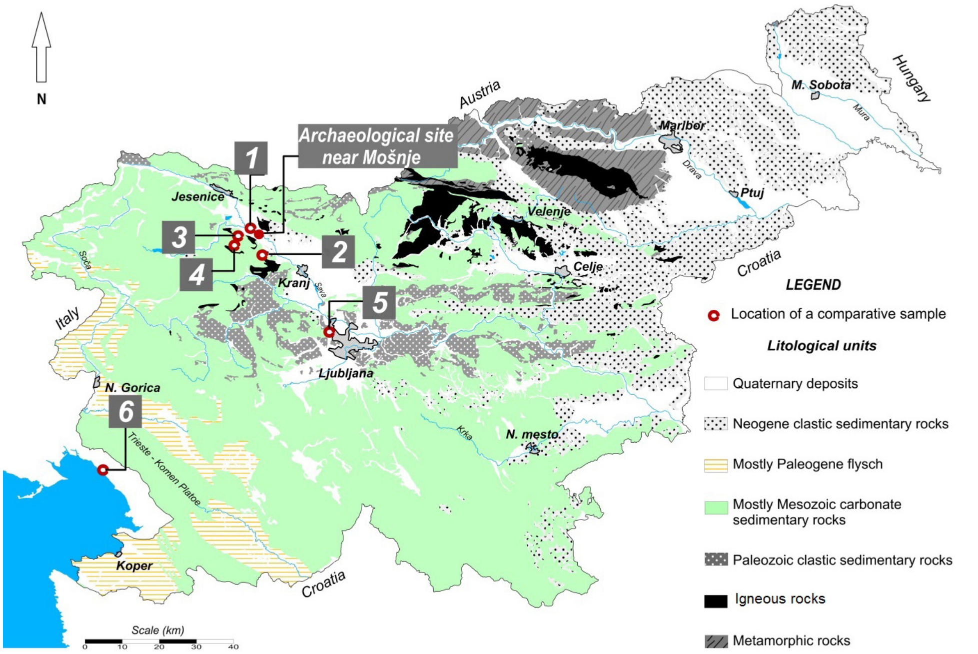


Fig. 2. Locations of comparative samples: 1–Gravel bar Lancovo in Sava River; 2–Brezovica quarry; 3–Kodrasti vrh; 4–Stara Hleva quarry; 5–Podutik quarry; 6–Cava Romana quarry near Aurisina (Geological map after: Šajn, 1998).

Results and discussion

Archaeological samples

The results of analyses of samples indicate the use of a diverse variety of rock material. Two major groups were identified: smaller tools, such are querns and whetstones, mostly made of various medium to coarse-grained quartz sandstones, and mosaic tesserae and larger items, such as architectural elements, made of different limestones (Plate 1, figs. 1–8; Plate 2, figs. 9–16; Plate 3, figs. 17–18).

GROUP 1. Clastic sedimentary rocks (Table 2)

Facies 1.A. Medium to coarse grained quartz sandstones: 20 samples (analysed only macroscopically: PN 779 (quern), PN 1341 (rounded stone), PN 1465 (rounded stone), PN 1514 (whetstone), PN 2734 (rounded stone), PN 2740 (tooled stone), PN 4051 (whetstone), PN 476 (whetstone), PN 6497 (whetstone) and PN 6569 (tooled stone). Microscopically analysed: ANM 159 (quern), ANM 161 (quern), ANM 163 (quern), ANM 164 (quern), ANM 165 (quern), ANM 167 (quern), ANM 174 (tooled stone), ANM 179 (quern), ANM 187 (quern) and ANM 189 (fragment of stone slab)).

Macroscopic description—common characteristics: Rock samples are grey to yellowish brown, medium to coarse grained, in places laminated quartz sandstones. Some also contain larger (1–5 mm) grains. Usually these rocks are strongly weathered exhibiting grey-greenish weathered surfaces.

Microscopic description: The rocks structure is mostly heterogeneous, usually composed of 80 % grains and 20 % of matrix. Some are laminated (ANM 159, ANM 161, ANM 167). Grain sizes range from 0.05 to 0.8 mm, only rarely larger grains (2.5–25 mm) are present (ANM 163, ANM 164, ANM 165, ANM 167, ANM 187). They are poorly sorted, sub-angular to angular and elongated to isometric, and show no visible orientation. Often are coated with red haematite. Contacts between the grains are long and concavo-convex. Grains are represented mainly by mono and polycrystalline quartz grains (45–60 % of all), with irregular edges and undulose extinction. Others are lithic grains (25–45 % of all) mostly of igneous rocks, but also grains of slates, siltstones, limestones, sandstones, and cherts are present. These are rare and present only in some samples: micas (10–30 % of all) in ANM 161, ANM 164, ANM 179, ANM 189, feldspars (5–20 % of all) in ANM 161, ANM 165, ANM 179, ANM 187, Fe minerals in ANM 159, ANM 161, ANM 174, ANM 179, ANM 187, and carbonates in ANM 163, ANM 164, ANM 189. The grains are usually bounded by sericite and quartz-sericite matrix or cemented by quartz and/or carbonate. In some samples (ANM 163, ANM 164, ANM 189) the matrix is strongly limonitised. Clay matrix occurs only rarely (ANM 164, ANM 179, ANM 189).

These sandstones are most likely of Upper Palaeozoic age (Plate 1, figs. 1–8; Plate 2, figs. 9–10).

Facies 1.B. Grey medium grained quartz-calcareous conglomerate: (ANM 177 (tooled stone))

Macroscopic description: Grey conglomerate, clast-supported, composed of well-rounded grains of various compositions up to 3 cm in size. Grains are cemented by highly weathered carbonate cement.

Microscopic description: The rock has a grain supported, heterogeneous structure and consists of 80 % of grains and 20 % of partly weathered carbonate (mostly calcite) cement. The grains

Table 2. Petrographic characteristics of microscopically analysed archaeological samples-clastic sedimentary rocks.

FACIES	SAMPLE MARK	ARCH. FIND	NAME OF ROCK	MINERAL COMPOSITION (GRAINS)				MATRIX OR CEMENT	MATRIX OR CEMENT /GRAINS RATIO	GRAIN SIZE (mm)
				QUARTZ %	LITHIC GRAINS %	MICA %	OTHER %			
1.A Medium to coarse grained quartz sandstones	ANM 159	*quern*	*laminated grey coarse grained lithic-quartz sandstone*	60	30	/	*Fe minerals 10*	*carbonates*	25/75	0.07-1.05 (0.7)
	ANM 161	*quern*	*laminated grey medium grained mica-quartz sandstone*	60	15	20	*feldspars 3, Fe minerals 2*	*sericite, quartz*	20/80	0.05-0.45 (0.25)
	ANM 163	*quern*	*limonitised yellow coarse grained lithic-quartz sandstone*	45	45	/	*calcite 5, plagioclase 5*	*carbonates (limonitisation)*	15/85	0.05-0.9 (0.6), *pebbles up to 2.5*
	ANM 164	*quern*	*limonitised yellow-brownish coarse grained lithic-quartz sandstone, transition to fine grained quartz conglomerate*	45	40	10	*carbonates 5*	*calcite, clay (limonitisation)*	20/80	0.19-0.5 (0.1), *pebbles up to 5*
	ANM 165	*quern*	*beige pebbly medium grained feldspar-lithic sandstone*	60	25	/	*feldspars 15*	*sericite, quartz*	20/80	0.07-0.7 (0.4). *pebbles up to 5*
	ANM 167	*quern*	*laminated light grey pebbly medium grained lithic-quartz sandstone to medium grained quartz conglomerate*	60	40	/	/	*quartz sericite*	25/75	0.05-0.45 (0.25), *pebbles 10*
	ANM 174	*tooled stone*	*limonitised yellowish brown medium grained lithic-quartz sandstone*	50	45	*in lithic grains*	*Fe minerals < 5*	*carbonates*	15/85	0.07-1 (0.3)
	ANM 179	*quern*	*limonitised laminated grey medium grained mica-feldspar-quartz sandstone*	50	15	10	*feldspars 20, pyrite 5*	*sericite – muscovite, clays*	15/85	0.04-0.8 (0.5)
	ANM 187	*quern*	*grey pebbly coarse grained quartz sandstone to medium grained conglomerate*	60	25	*in lithic grains*	*Fe minerals < 10, feldspars 5*	*sericite, quartz, Fe minerals*	25/75	0.07-2.5 (0.8), *pebbles up to 25*
	ANM 189	*fragment of stone slab*	*limonitised yellowish brown fine to medium grained lithic-quartz sandstone*	45	40	10	*carbonates 5*	*calcite, clay (limonitisation)*	20/80	0.04-0.6 (0.25)
1.B Grey medium grained quartz-calcareous conglomerate	ANM 177	*tooled stone*	*grey medium grained quartz-calcareous conglomerate*	15	83	*in lithic grains*	*feldspars, plagioclase, Fe minerals < 2*	*carbonates*	20/80	0.05-30 (5)
1.C Dark grey fine grained mica-quartz breccia	ANM 186	*quern*	*dark grey fine grained mica-quartz breccia*	60	/	35	*feldspars 5*	*sericite, quartz*	85/15	0.12-0.8 (0.35), *rubble 5*

Table 3. Petrographic characteristics of microscopically analysed archaeological samples—carbonate sedimentary rocks.

FACIES	SAMPLE MARK	ARCH. FIND	NAME OF ROCK	BIOCLASTS %	INTRACLASTS %	PELOIDS %	OOIDS %	OTHER	MATRIX OR CEMENT %	MATRIX OR CEMENT /GRAINS RATIO	GRAIN SIZE (mm)
2.A Grey biopelmicritic limestones	*ANM 160*	*stone mortar*	*grey biopelmicritic limestone*	*35*	*5*	*60*	*indeter-minable*	*geopetal structures, rounded sparry grains, pyrite*	*micrite - sparite*	35/65 (avg.)	0.03 - 0.45
	ANM 170	*architectural element*	*dark grey pelbiomicritic limestone*	*20*	*< 10*	*15*	*indeter-minable*	*rounded sparry grains 55 %, pyrite*	*micrite*	70/30 (avg.)	0.03 - 0.15 (0.7)
2.B White to light grey biocalcarenitic limestone	*ANM 185*	*stone mortar*	*white to light grey biocalcarenitic limestone*	*30*	*60*	*10*	/	/	*micrite, sparite 60/40*	60/40	0.04 - 1 (0.1)
	PN 6178	*architectural element with relief*	*white to light grey biocalcarenitic limestone*	*30*	*60*	*10*	/	/	*micrite, sparite 60/40*	60/40	0.04 - 1 (0.1)
2.C Yellowish white to light grey biomicritic limestone	*ANM 133*	*white tessera*	*yellowish white to light grey biomicritic limestone*	*90*	*some*	*10*	/	/	*micrite 70, microsparite 20, sparite 10*	70/30	0.1 - 0.9 (0.2)
2.D Laminated dark grey to black limestone	*ANM 133*	*black tessera*	*laminated dark grey to black bituminous micritic limestone*	*80*	/	/	/	*organic matter 10 %, pyrite 10 %*	*microsparite 90, micrite 10*	90/10	0.02 - 0.15

Table 4. Petrographic characteristics of microscopically analysed comparative samples—clastic sedimentary rocks.

PROVENANCE	SAMPLING LOCATION	SAMPLE MARK	NAME OF ROCK	MINERAL COMPOSITION (GRAINS)				MATRIX OR CEMENT %	MATRIX OR CEMENT /GRAINS RATIO	GRAIN SIZE (MM)
				QUARTZ %	LITHIC GRAINS %	MICA %	OTHER %			
Local	*Gravel bar Lancovo (Sava River)*	P-1	*laminated dark green very fine to fine grained mica-quartz sandstone*	70	/	30	/	*sericite 75, clay 20, carbonates 5*	15/85	0.03 - 0.13 (0.07)
		P-2	*reddish brown fine grained mica-feldspar-quartz sandstone*	60	/	15	*feldspars 25*	*sericite, clay*	15/85	0.03 - 0.2 (0.14)
		P-3	*grey medium grained feldspar-quartz sandstone*	55	< 10	10	*feldspars 25*	*sericite - clay 75, Q 25, traces of carbonates*	15/85	0.06 - 0.4 (0.25)

Table 5. Petrographic characteristics of microscopically analysed comparative samples-carbonate sedimentary rocks.

PROVENANCE	SAMPLING LOCATION	SAMPLE MARK	NAME OF ROCK	BIOCLASTS %	INTRACLASTS %	PELOIDS %	OOIDS %	OTHER	MATRIX OR CEMENT %	MATRIX OR CEMENT /GRAINS RATIO	GRAIN SIZE (mm)
Local	*Brezovica quarry*	Br-1	*light grey recrystallised slightly dolomitic pelbiosparite*	70	*some*	20	*recrystallised 10*	*anhydritisation, dolomitisation*	*sparite 70, microsparite 20, micrite 10, traces of dolomites*	70/30	0.02 -0.7
		B-1	*light grey recrystallised slightly dolomitic pelbiosparite to pelbiomicrite*	70	*some*	20	*recrystallised 10*	*weak dolomitisation*	*sparite to micrite, traces of dolomites*	70/30	0.02 -0.7
		B-2	*light grey recrystallised dolomitic pelbiosparite*	70	*some*	20	*recrystallised 10*	*bioturbations*	*sparite 70, microsparite 20, micrite 10*	70/30	0.02 -0.7
	Kodrasti vrh	KV-1	*whitish and reddish recrystallised intrasparitic limestone*	/	20	/	/	*calcite grains 80 %, stylolites, carstification*	*sparite 70, micrite 30*	80/20	*variable, up to 0.5*
	Stara Hleva	SH-1	*light grey medium grained calcareous dolomite*	/	/	/	/	*dolomite and calcite grains*	/	0/100	*variable*
Distant	*Quarry in Podutik*	P-19	*dark grey biopelmicritic limestone*	10	< 10	*highly variable*	*indeterminable*	*rounded sparry grains 30 %, pyrite*	*micrite, fields of sparite*	70/30	0.5 - 9
		P-26	*grey biopelmicritic limestone*	20	< 10	65	10	*rounded sparry grains 5 %, pyrite*	*micrite, partly recrystalisation (sparite)*	40/60	0.02 – 0.2
		P-28	*dark grey biopelmicritic limestone*	10 - 20	< 10	*highly variable*	*indeterminable*	*rounded sparry grain 10 %*	*micrite, sparite*	70/30	0.5 - 9
	Cava Romana (Aurisina)	CR-1	*white to light grey biocalcarenitic limestone*	30	60	10	/	*bituminous substance, pyrite*	*micrite, sparite*	60/40	0.02 – 3 (1)

Table 6. Overview of analysed stone material from the archaeological site near Mošnje and their related rock type and provenance

GROUP OF ROCKS	FACIES	SAMPLE MARK	ARCH. FIND	NAME OF ROCK	GEOL. AGE	PROVENANCE
1. Clastic sedimentary rocks	*1.A Medium to coarse grained quartz sandstones*	ANM 159	*quern*	*laminated grey lithic coarse grained quartz sandstone*	P	*gravel bars*
		ANM 161	*quern*	*laminated grey medium grained mica-quartz sandstone*	C	*gravel bars*
		ANM 163	*quern*	*yellow coarse grained lithic-quartz sandstone*	C	*gravel bars*
		ANM 164	*quern*	*limonitised yellow-brownish coarse grained lithic-quartz sandstone with transition to fine grained quartz conglomerate*	P	*gravel bars*
		ANM 165	*quern*	*beige pebbly medium grained feldspar-lithic sandstone*	P	*gravel bars*
		ANM 167	*quern*	*laminated light grey pebbly medium grained lithic-quartz sandstone to medium grained quartz conglomerate*	P	*Sava River terrace*
		ANM 174	*tooled stone*	*limonitised yellowish brown medium grained lithic-quartz sandstone*	P	*gravel bars*
		ANM 179	*quern*	*limonitised laminated grey medium grained mica-feldspar-quartz sandstone*	C	*Quaternary deposits*
		ANM 187	*quern*	*grey pebbly coarse grained quartz sandstone to medium grained conglomerate*	P	*gravel bars*
		ANM 189	*fragment of stone slab*	*limonitised yellowish brown fine to medium grained lithic-quartz sandstone*	P	*gravel bars or Sava River terrace*
		PN 779	*quern*	*limonitised green greyish fine to medium grained quartz sandstone*	C	*gravel bars or Sava River terrace*
		PN 1341	*rounded stone*	*grey medium grained mica-quartz sandstone*	C	*gravel bars*
		PN 1465	*rounded stone*	*grey medium grained mica-quartz sandstone*	C	*gravel bars*
		PN 1514	*whetstone*	*limonitised grey medium grained quartz sandstone*	C	*gravel bars or surrounding deposits*
		PN 2734	*rounded stone*	*limonitised grey medium grained quartz sandstone*	C	*gravel bars*
		PN 2740	*tooled stone*	*limonitised yellowish brown coarse grained quartz sandstone*	C	*gravel bars*
		PN 4051	*whetstone*	*limonitised light grey medium grained quartz sandstone*	C	*gravel bars or surrounding deposits*
		PN 6476	*whetstone*	*limonitised grey medium grained quartz sandstone*	C	*gravel bars or surrounding deposits*
		PN 6497	*whetstone*	*limonitised yellowish brown fine to medium grained mica-quartz sandstone*	P	*gravel bars or surrounding deposits*
		PN 6569	*tooled stone*	*greenish grey medium grained quartz sandstone*	C	*gravel bars*
	1.B Grey medium grained quartz-calcareous conglomerate	ANM 177	*tooled stone*	*grey medium grained quartz-calcareous conglomerate*	Q	*Sava River terrace*
	1.C Dark grey fine grained mica-quartz breccia	ANM 186	*quern*	*dark grey fine grained mica-quartz breccia*	*Upper Pz*	*Quaternary deposits*
2. Carbonate sedimentary rocks	*2.A Grey pelbiomicritic limestones*	ANM 160	*stone mortar*	*grey biopelmicritic limestone*	J1	*probably Podutik*
		ANM 170	*architectural element*	*dark grey pelbiomicritic limestone*	J1	*probably Podutik*
	2.B White to light grey biocalcarenitic limestone	ANM 185	*stone mortar*	*white to light grey biocalcarenitic limestone*	K2	*the Trieste - Komen Plateau*
		PN 6178	*architectural element with relief*	*white to light grey biocalcarenitic limestone*	K2	*the Trieste - Komen Plateau*
	2.C Yellowish white to light grey biomicritic limestone	ANM 133	*white tessera*	*yellowish white to light grey biomicritic limestone*	K2	*probably the Trieste - Komen Plateau*
	2.D Laminated dark grey to black limestone	ANM 133	*black tessera*	*laminated dark grey to black bituminous micritic limestone*	Mz (K2?)	*not local*

are poorly sorted, size ranging from 0.05 mm to 10 mm. They are rounded to well rounded, with isometric to elongated forms. Contacts between the grains are point to concavo-convex. Pores comprise approx. 10 % of the rock. Most grains (85 % of all) are comprised of various lithic grains (fossiliferous Mesozoic and Paleogene limestones, Ladinian or Oligocene tuffs, quartz sandstones and other types of rocks). The remaining 15 % is comprised of individual grains of quartz. The rock is partly cemented by coarse grained mostly carbonate (calcite) cement.

Grey medium grained quartz-calcareous conglomerate, probably of Quaternary age (Plate 2, fig. 11).

<u>Facies 1.C.</u> Dark grey fine grained mica-quartz breccia (ANM 186 (quern))

Macroscopic description: Fine-grained dark grey matrix-supported breccia with up to 5 mm large quartz clasts, embedded in the dark matrix with mica flakes.

Microscopic description: Breccia is homogeneous, consisting of 85 % matrix and 15 % of grains. The grains range in size from 0.12 to 0.80 mm, are very well sorted, angular to sub-angular and of different shapes. Quartz grains dominate (60 %), while muscovite and weathered feldspars are subordinate. Matrix is of sericite (75 %) and fine-grained quartz (25 %).

Fine grained mica-quartz breccia, probably of Upper Palaeozoic age (Plate 2, fig. 12).

GROUP 2. Carbonate sedimentary rocks (Table 3)

<u>Facies 2.A.</u> Grey to dark grey biopelmicritic limestones: 2 samples (ANM 160 (stone mortar), ANM 170 (architectural element))

Macroscopic description: The rock is a grey bioclastic micritic limestone, in places cut by calcite veins.

Microscopic description: Sample ANM 160 is heterogeneous wackestone to packstone. Grain to matrix ratio is very variable, but on average 65/35. Grains are up to 0.6 mm in size and composed mainly of peloids (around 60 %) and bioclasts (35 %) with some pyrite crystals while intraclasts occur rarely. Bioclasts are of biserial foraminifera and other small foraminifera (Glomospira?), algae (Thaumathoporella?), mollusc shells and ostracoda. Some are unidentifiable. Also, small rounded sparitic grains are present; some of these are probably ooids. Sample ANM 170 shows similar composition, with average grain to matrix ratio 30/70, however here ostracods (50 %) dominate over other bioclasts, small peloidal grains and micritic intraclasts. The matrix in ANM 170 is micrite, while in ANM 160 micrite and microsparite, in places sparry calcite cement is present.

The observed characteristics indicate shallow-water depositional environment. Absence of age-diagnostic fossils prevents stratigraphic determination of this facies, however, based solely on the microfacies characteristic (cf. Ogorelec, 2011) the rock is tentatively attributed to the Lower Jurassic.

<u>Facies 2.B.</u> White to light grey biocalcarenitic limestone: 2 samples (ANM 185 (stone mortar), PN 6178 (architectural element with relief))

Macroscopic description: White to light grey fine-grained calcarenitic limestone exhibiting shell fragments.

Microscopic description: Limestone is homogeneous packstone to grainstone. Grains are bioclasts of small spherical and biserial foraminifera, sparite-filled rudist shell fragments and echinoderms fragments. They are bounded by micrite to microsparite and in places also by sparite.

Based on the presence of the rudist shells we assigned this limestone to a shallow-water environment of Upper Cretaceous age (Plate 2, figs. 15 & 16).

<u>Facies 2.C.</u> Yellowish white to light grey biomicritic limestone: 1 sample (ANM 133 (white tessera))

Macroscopic description: Yellowish white to light grey homogeneous limestone.

Microscopic description: Limestone is heterogeneous wackestone, composed of 70 % matrix and of 30 % grains. Grains are randomly distributed, without preferred orientation and up to 0.9 mm in size. The majority of grains are miliolid and other foraminifera. Shells, algae fragments and peloids occur rarely. Matrix is micritic and rarely microsparitic. Sparitic infilling of foraminifera moulds is present.

Based on the abundance of miliolids and other shallow-water grains we believe that the limestone was deposited in a shallow water environment and is probably Cretaceous in age (Plate 3, fig. 18).

<u>Facies 2.D.</u> Laminated dark grey to black bituminous limestone: 1 sample (ANM 133 (black tessera))

Macroscopic description: Laminated black to dark grey micritic limestone with transition to homogeneous dark brown micritic limestone. The rock is intersected by 1 mm thick white calcite veins.

Microscopic description: The limestone is homogeneous bioturbated and laminated mudstone. The proportion of matrix approaches 90 %. Lamination is expressed as alternating bands of 3 mm thick laminae of clear microsparite with 5 mm thick laminae with higher content of organic matter. In some places we noted traces of bioturbation, oriented perpendicular to lamination. Grains are represented by ostracod fragments and rare particles of amorphous organic matter. Small particles of autogenous pyrite are also present. Amorphous organic matter is common and forms streaks and seams roughly parallel to the lamination.

Abundant presence of fine-grained matrix, lamination and high content of preserved organic matter points to the sedimentation in a hydrodynamically quiet anoxic environment. These conditions are typical for sedimentation in restricted lagoonal or deeper-water environments (Plate 3, fig. 17).

Comparative samples

A total of 21 samples with macroscopic petrographic characteristics potentially comparable with artefacts were taken for further examination. Petrographic analyses have shown that 12 of the comparative samples (Plate 3, figs. 19–24, Plate 4, figs. 25–30) from 6 locations (Fig. 2) have certain similarities with the investigated archaeological materials. The results of microscopic analysis of these samples are shown in Table 4 and Table 5, while their significant characteristics are given within the results of comparative analysis in the next subchapter.

GROUP 1. Clastic sedimentary rocks (Table 4)

Samples of local provenance:
Pebbles of quartz sandstone (3 selected samples from the Sava River gravel bars in Lancovo: P-1, P-2, P-3) (Plate 3, figs. 19–21): P-1 is a laminated dark grey to dark reddish brown medium grained sandstone. P-2 is reddish brown homogeneous fine grained sandstone. P-3 is a homogeneous grey to dark greenish grey medium grained sandstone with light grains of quartz, feldspars and micas. The rocks are of Upper Palaeozoic age.

GROUP 2. Carbonate sedimentary rocks (Table 5)

Samples of local provenance:
Light grey recrystallised limestone (3 selected samples from the quarry Brezovica pri Kropi: BR-1, B-1, B-2) (Plate 3, figs. 22–24) is heterogeneous with carbonate grains of different sizes and numerous parallel calcitic veins, up to 0.5 cm thick. The limestone is a pelbiosparite i.e. wackestone of Upper Triassic age.

Whitish and reddish recrystallised limestone (1 representative sample from the exploration area Kodrasti vrh: KV-1) (Plate 4, fig. 25) with thick white (Note 3) calcitic veins is recrystallised intrasparite i.e. wackestone of Upper Triassic age.

Light grey calcareous dolomite (1 representative sample from the abandoned quarry Stara Hleva: SH-1) (Plate 4, fig. 26) is recrystallised and fractured, with anhedral crystals, cut by thin white veins, with a gradual transition to dolomitic limestone of Triassic age.

Samples of distant provenance:
Grey micritic limestones (3 selected samples from an abandoned quarry in Podutik: P-19, P-26 and P-28) (Plate 4, figs. 27 - 29) of varying lighter and darker shades with thin calcitic veins, showing individual fossils, with an average size of 3 mm. The rocks are biopelmicrites i.e. grainstones of Lower Jurassic age.

Light grey biocalcarenitic limestone (1 selected sample from the Roman quarry Cava Romana in Aurisina/Nabrežina: Cr-1) (Plate 4, fig. 30) homogeneous in nature with darker fragmented fossils varying from 1 to 3 mm in size in a lighter coarse grained recrystallised carbonate matrix. The rock is a biointrasparite to biointramicrite i.e. packstone to grainstone of Upper Cretaceous age.

PLATE 1

1 ANM 159: limonitised, grey, coarse grained lithic-quartz sandstone: subangular quartz grains connected with fine grained carbonate cement (+A).

2 ANM 161: laminated, grey, medium grained mica-quartz sandstone: jagged contacts between quartz and lithic grains in quartz-sericite matrix (+A).

3 ANM 163: limonitised, yellow, coarse grained lithic-quartz sandstone: angular lithic and quartz grains are surrounded by limonitised calcitic cement (+A).

4 ANM 164: limonitised, yellowish, coarse grained lithic-quartz sandstone with transition to fine grained quartz conglomerate: quartz grains of different sizes bonded with calcitic cement (+A).

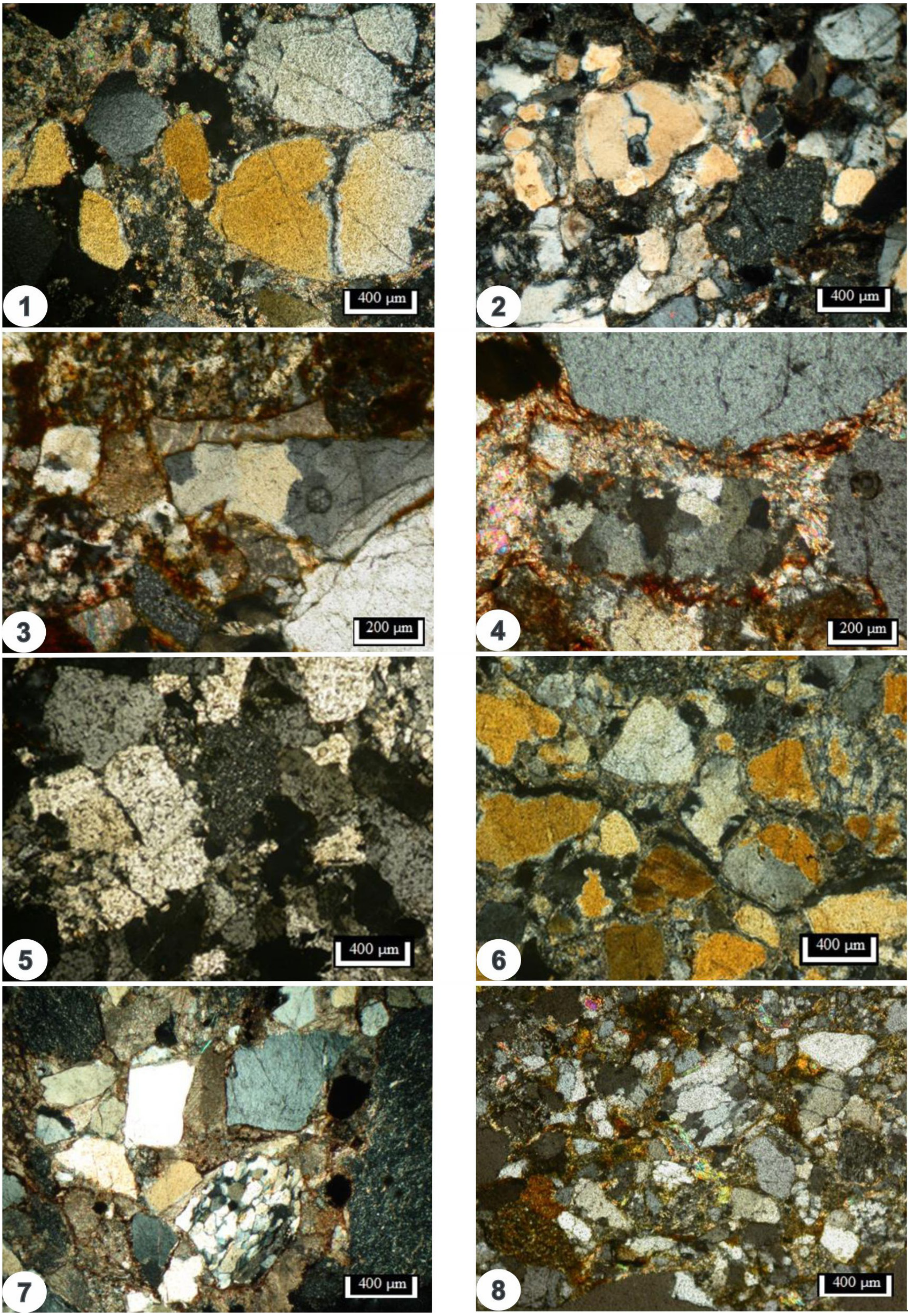
5 ANM 165: beige, pebbly, medium grained feldspar-lithic sandstone: irregular contacts between quartz and different lithic grains in quartz-sericite matrix (+A).

6 ANM 167: laminated, light grey, pebbly, medium grained lithic-quartz sandstone with transition to medium grained quartz conglomerate: quartz and lithic grains with fine grained sericite quartz matrix between them (+A).

7 ANM 174: limonitised, yellowish brown, medium grained lithic-quartz sandstone: quartz and lithic grains of different size (+A).

8 ANM 179: limonitised, laminated, medium grey mica-feldspar-quartz sandstone: different angular grains in sericite matrix (+A).

PLATE 1



Comparison of archaeological and comparative samples

GROUP 1. Clastic sedimentary rocks

Facies 1.A. Medium to coarse grained quartz sandstones

Finer-grained clastic rocks, from which querns, whetstones, tooled and rounded stones were made (ANM 159, ANM 161, ANM 163, ANM 164, ANM 165, ANM 167, ANM 174, ANM 179, ANM 187, ANM 189, PN 779, PN 1341, PN 1465, PN 4051, PN 4676, PN 1514, PN 2734, PN 2740, PN 6497, PN 6569), show similarity to the Upper Carboniferous—Lower Permian clastic rocks and the Middle Permian Val Gardena formation. Upper Carboniferous and Lower Permian rocks consist of grey siltstones, grey lithic-quartz sandstones and grey quartz sandstones (Pleničar et al., 2009), while the Val Gardena formation includes red and grey sandstones, shale and conglomerates (Skaberne, 1995; Buser, 2009). These rocks are found at several locations in NW Slovenia in the Gorenjska region, especially in the South Karavanke and at the hills around Škofja Loka (Grad & Ferjančič, 1976; Buser, 1980). Comparison of the archaeological samples with pebbles collected from gravel bars showed relative similarity in macroscopic characteristics and mineral composition, but they differ in the amount of feldspars (P-2, P-3) and lithic grains. However, due to the rounded shape of some artefacts (Fig. 3) and the presence of even large boulders (of several decimetres in size) of similar sandstones in the surrounding Quaternary fluvial and glacial deposits, we assume that the material for their production was brought from these deposits, located in the close vicinity of the archaeological site. The differences in the composition of the sandstones used to produce the artefacts are considerable and exceed the lateral and vertical facies variations expected in any one quarry, we presume that the material was obtained as pebbles from the gravel bars.

Facies 1.B and 1.C. Medium grained quartz calcareous conglomerate and fine grained quartz breccia

Fig. 3. Quern - medium grained quartz sandstone (ANM 161) (Source: author Aleš Ogorelec, archived by the Institute for the Protection of Cultural Heritage of Slovenia in Kranj)

The sample of conglomerate (ANM 177, tooled stone) contains clasts of limestones with fossils from the Mesozoic and Paleogene, Ladinian or Oligocene tuff and other rocks of different ages. The variety of centimetre-sized clasts in the partly cemented conglomerate clearly indicates post Oligocene erosion and glacio-fluvial transportation. All of the recognised clast lithologies in the conglomerate occur in the catchment area of the Sava River, so the rock most probably originates from Quaternary glacial and fluvial deposits in the vicinity of Mošnje. Fine grained mica-quartz breccia, from which one quern is made (ANM 186), is presumably of Carboniferous age and such cobbles and boulders can be found in the Quaternary fluvial deposits in the vicinity of the archaeological site as well.

GROUP 2. Carbonate sedimentary rocks

Facies 2. A. Grey pelbiomicritic limestones

The samples of darker grey stone mortar (ANM 160) and architectural element, similar to altar (ANM 170) (Fig. 4), are made of pelbiomicritic limestones. Microscopic analysis showed that these microfacies belong to the subtidal shallow-water environment located on a carbonate platform.

PLATE 2

9 ANM 187: grey, pebbly, coarse grained quartz sandstone to medium grained conglomerate: irregular contacts between quartz grains (+A).

10 ANM 189: limonitised, yellowish brown, fine to medium grained lithic-quartz sandstone: quartz and lithic grains in limonitised carbonate cement, which replaces sericite matrix (+A).

11 ANM 177: grey, medium grained quartz calcareous conglomerate: a rounded lithic grain of biomicritic limestone (+A).

12 ANM 186: dark grey, fine grained mica-quartz breccia: smaller quartz grains in fine grained quartz-sericite matrix (+A).

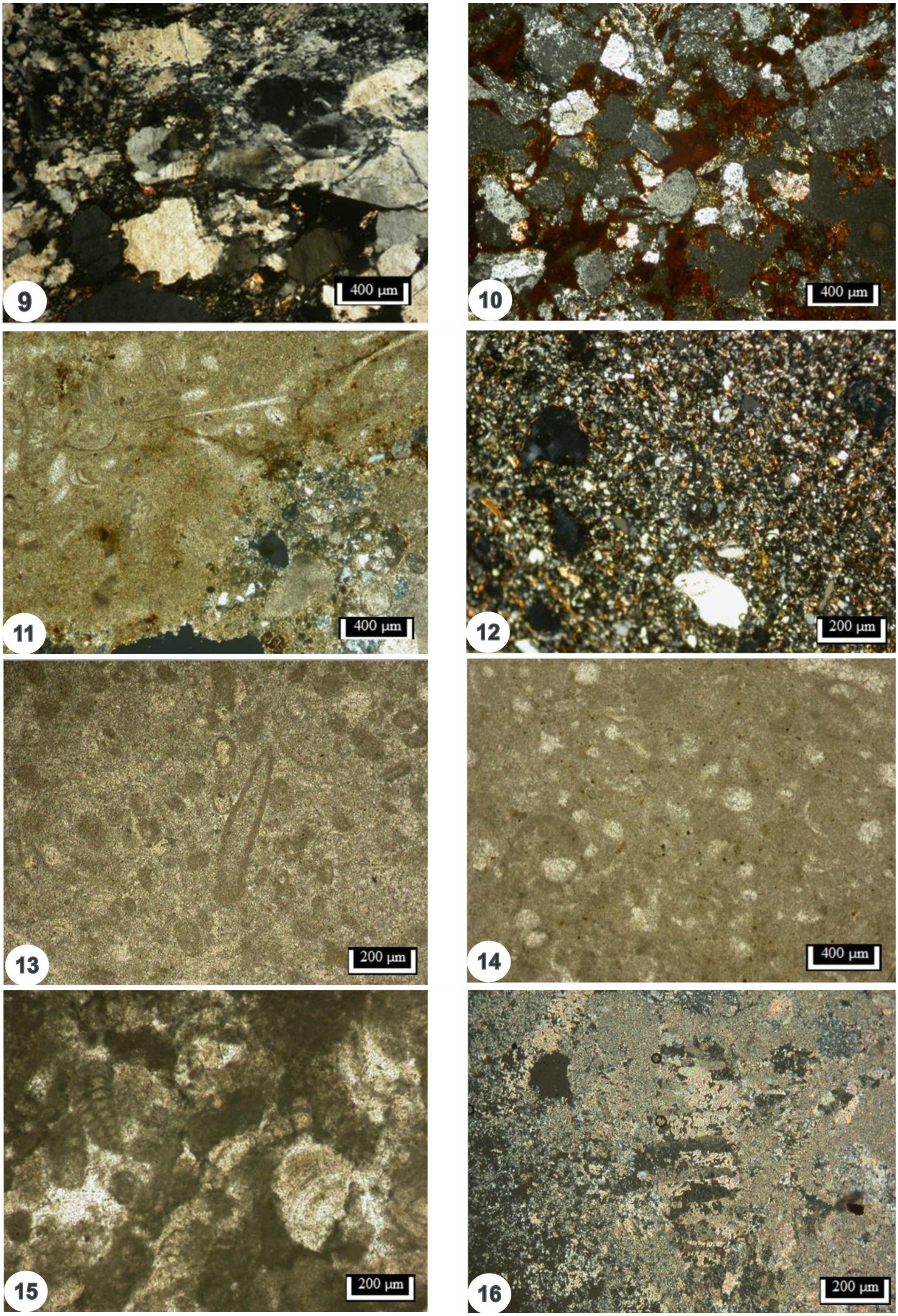
13 ANM 160: grey biopelmicritic limestone: peloids and bioclasts (–A)

14 ANM 170: dark grey pelbiomicritic limestone: unrecognised bioclasts and small rounded sparitic grains with peloids in micritic matrix (–A).

15 ANM 185: white to light grey biocalcarenitic limestone: bioclasts, intraclasts and peloids in micritic-microsparitic matrix (–A).

16 PN 6178: white to light grey biocalcarenitic limestone: a shell fragment in micritic matrix (+A).

PLATE 2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According to the geological map of Kranj (Grad & Ferjančič, 1976), shallow–water Upper Triassic and Lower Jurassic limestones exist on the Jelovica Plateau (in the vicinity of the sampling sites of the comparison samples from Kodrasti vrh (KV-1) and Stara Hleva (SH-1)). However they lack any similarity with the investigated artefacts. Furthermore, macroscopic and microscopic characteristics of samples ANM 160 and ANM 170 are in conformance with the samples P-19, P-26 and P-28. The latter were sampled in the vicinity of Podutik near Ljubljana from different Lower Jurassic rock beds, for which such sedimentary depositional environment is proven (Novak, 2003). In addition, Müllner (1879) and after him Ramovš (1990) were supposing the existence of ancient quarries and stone masonry workshops at this location.

Facies 2.B. White to light grey biocalcarenitic limestones

The material of the lighter grey stone mortar (ANM 185) and architectural element with relief (PN 6178) is biocalcarenitic limestone containing recrystallised small foraminifera, fragments of rudist shells and echinoderms. The presence of the rudist shells indicates an Upper Cretaceous shallow-water environment of the Dinaric Carbonate Platform. These limestones outcrop in SW Slovenia, NE Italy and SE Croatia. In Aurisina/Nabrežina, near Trieste in Italy, four types of Upper Cretaceous shallow-water limestone from the Dinaric Carbonate Platform are quarried, just as they were in Roman times (Brecelj et al., 1989; Cucchi & Gerdol, 1986). The most similar to the Mošnje samples is a variety called *fiorito,* which is also found in the Cava Romana quarry. Similar horizons are found in Slovenia as well, in the Lipica formation (Jurkovšek et al., 1996; Ramovš, 2002).

Facies 2.C. Yellowish white to light grey biomicritic limestones

The white mosaic tessera (ANM 133) is made of yellowish to greyish white micritic limestone with miliolid and other benthic foraminifera and algae.

Fig. 4. Architectural element - dark grey pelbiomicritic limestone (ANM 170) (Source: author Aleš Ogorelec, archived by the Institute for the Protection of Cultural Heritage of Slovenia in Kranj)

PLATE 3

17 ANM 133 (a black tessera): laminated, dark grey to black, bituminous, micritic limestone: lamination almost parallel with a vein, filled with sparite (+A)

18 ANM 133 (a white tessera): yellowish white to light grey biomicritic limestone: miliolids in micritic matrix (+A)

19 P-1: laminated, dark green, very fine to fine grained mica-quartz sandstone: small quartz grains and mica flakes (+A)

20 P-2: reddish brown, fine grained mica-feldspar-quartz sandstone: angular grains of quartz and feldspar with mica flakes (+A)

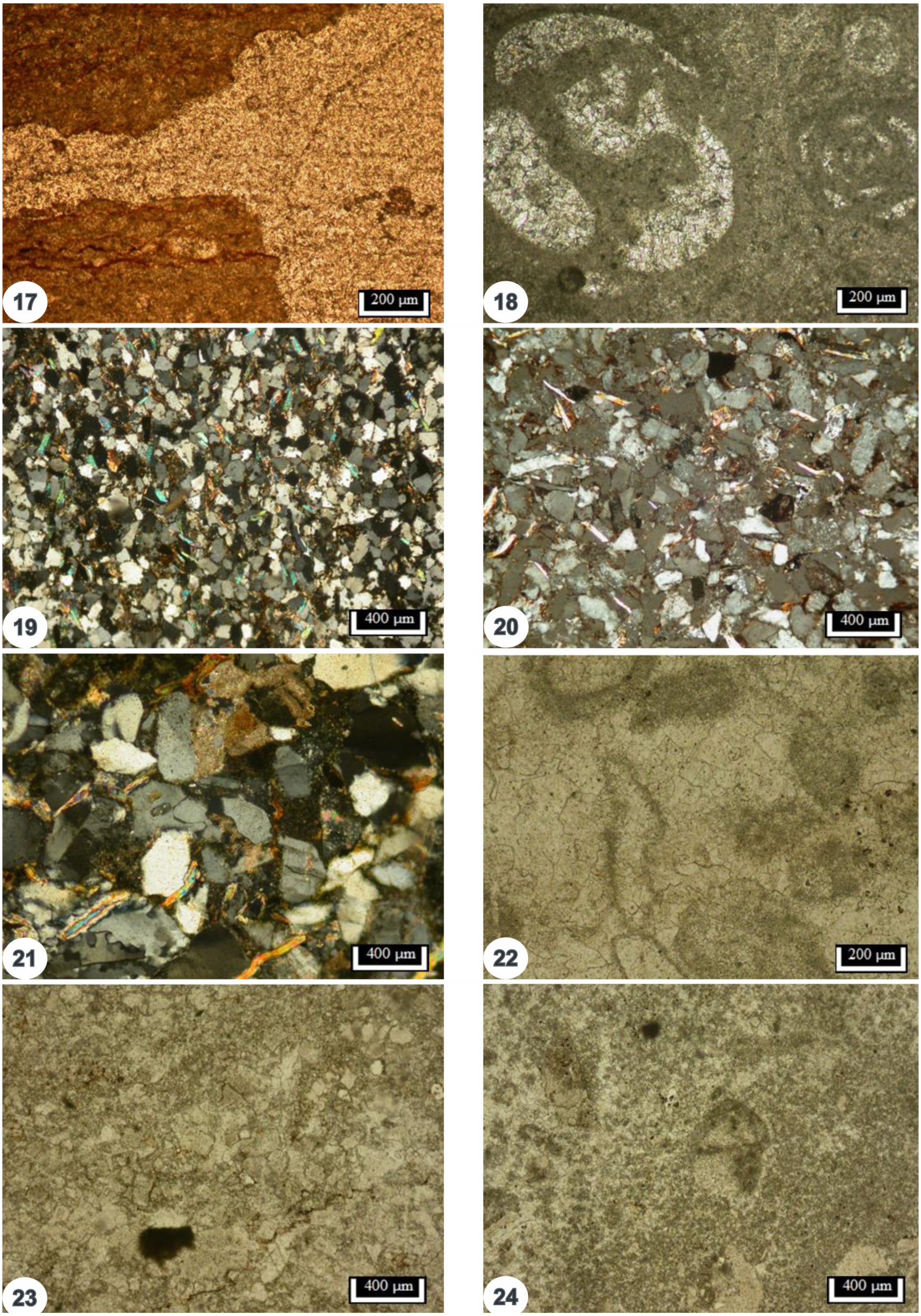
21 P-3: grey, medium grained feldspar-quartz sandstone: different angular grains of quartz and feldspar with mica flakes in fine grained matrix (+A)

22 B-2: light grey, recrystallised dolomitic pelbiosparite: fossil fragments and peloids (–A)

23 Br-1: light grey, recrystallised slightly dolomitic pelbiosparite: calcitic crystaIs and cavities filled with surrounding carbonate material (–A)

24 B-1: light grey, recrystallised very slightly dolomitic pelbiosparite to pelbiomicrite: recrystallised limestone with bioclasts and remains of micrite (–A)

PLATE 3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Their abundance and the presence of other benthic shallow-water organisms indicate a shallow-water subtidal environment on a carbonate platform (Flügel, 2004). Miliolids occur over a wide stratigraphic range; however they show highest abundance in Cretaceous shallow-water limestones of the Dinaric Carbonate Platform. These limestones today outcrop in the External Dinarides of Northeastern Italy, Southern Slovenia and Southwestern Croatia.

Facies 2.D. Laminated dark grey to black bituminous limestones

The black mosaic tessera (ANM 133) is of laminated dark grey to black bituminous micritic limestone. Such limestone usually formed in an anoxic–deep or shallow water environment. In the immediate vicinity of the archaeological site we did not find any such rocks. Larger quantities suitable for extraction can be found in the Kras region where shallow-water carbonates containing beds of laminated bituminous limestones with cherts are present within the various Cretaceous formations of Cenomanian–Campanian age (Jurkovšek, 2010). Šribar (1995) has shown that the sedimentary environment for the formation of bituminous limestones in Southwestern Slovenia could also exist in areas of «upwelling» and intertidal coastal areas. However, it must be emphasized that similar sedimentation conditions, optimal for development of the laminated bituminous limestones, existed elsewhere at differing times during the Mesozoic. This wide potential area could be reduced in further research by combining geological with archaeological aspects which assume arrival of a mosaist to Mošnje from the area of today's Italy bringing tesserae with himself.

Conclusions

The Roman villa near Mošnje in NW Slovenia was discovered during the construction of a section of motorway (Vrba–Peračica). The numerous stone finds from this archaeological site are comprised of differing stone materials. By microfacies analysis of selected samples, we determined the rock type and attempted to establish the provenance of these materials.

The studied stone artefacts can be divided in to two groups dependent on sedimentary rock type: clastic or carbonate.

Small stone artefacts, such as querns, whetstones and tooled stones, including pebbles with tool marks, are made of clastic sedimentary rocks (Facies 1.A to 1.C). The rocks are mainly quartz sandstones, most likely of Upper Palaeozoic age, although there are also coarse grained materials like conglomerates and breccias from local Quaternary deposits of the Sava River. Fieldwork and data from the Basic Geological Map (Grad & Ferjančič, 1976), clearly shows that similar rocks are present in the Sava gravel bars and terraces, located in immediate vicinity of the archaeological site. Therefore we propose that these small artefacts were most probably produced locally.

Artefacts made of carbonate rocks tell us a different story. Microscopic analysis and comparison with the carbonate samples, taken local to the archaeological site, and with samples from further afield, indicate that the investigated limestone Roman artefacts were not produced locally. The architectural element and grey stone mortar are made of dark grey pelbiomicritic limestone (Facies 2.A), which is tentatively correlated with Lower Jurassic limestones from the vicinity of Podutik near Ljubljana.

The light grey stone mortar and the architectural element with relief are made of white to light grey Upper Cretaceous biocalcarenitic limestone with rudist shells (Facies 2.B). Similar limestones are characteristic for the Upper Cretaceous successions of the Dinaric Carbonate Platform outcropping in the SW Slovenia, NE Italy and SE Croatia. These limestones were quarried in Roman times near Aurisina/Nabrežina in Italy, and are still quarried today. Similar limestones are also typical for the Lipica formation on the Karst in Slovenia. We presume that the two architectural elements were imported to Mošnje from one of these areas, even though an archaeological aspect based on current knowledge favours the Italian extraction site.

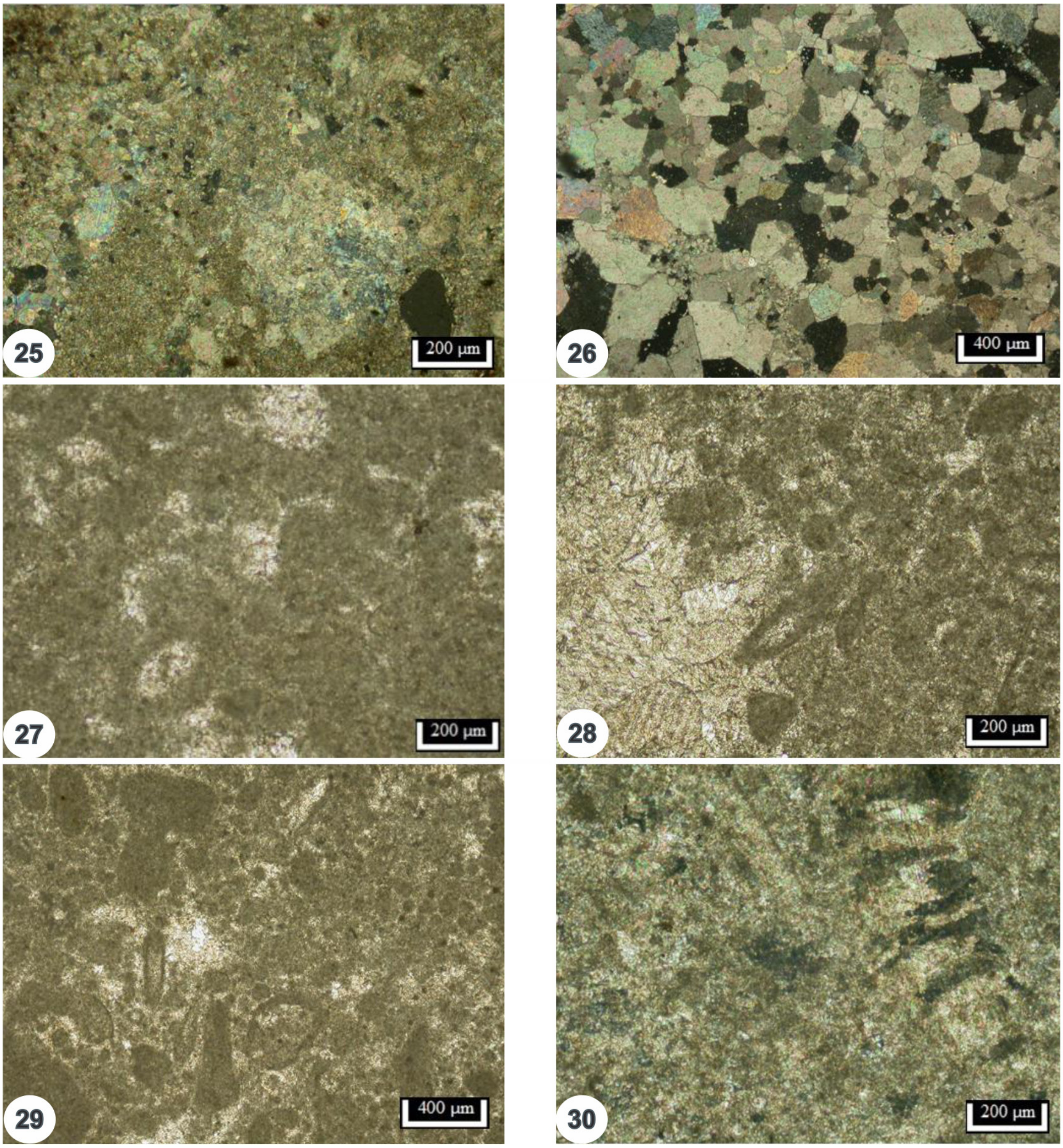
The white and black mosaic tesserae composed of Cretaceous miliolid limestone (Facies 2.C) and dark organic-rich laminated limestone (Facies 2.D), respectively might originate from different horizons of the Cretaceous succession typical for the Dinaric Carbonate Platform. These rocks outcrop on the Trieste–Komen Plateau, but also in some other areas in Slovenia, therefore we cannot unequivocally determine their provenance.

The presented study indicates that in the Roman archaeological site near Mošnje smaller and useful consumable items, such as querns and whetstones, were made from locally sourced materials, easily picked from the ground. Conversely, larger items such as stone mortars, and more prestigious such as architectural elements and tesserae, were obtained by quarrying and imported.

Acknowledgements

For assistance in analysis of the samples we express our gratitude to dr. Dragomir Skaberne, dr. Bogdan Jurkovšek and dr. Matevž Novak. Their opinions, comments and advices were greatly appreciated. For preparation of thin sections and technical assistance we would like to thank the technical staff of the Department of Geology, Faculty of Natural Sciences at University of Ljubljana and to Ivan Mesič from the INA d.d. in Zagreb.

PLATE 4



25 KV-1: whitish and reddish, recrystallised intrasparitic limestone with transition to limestone breccia: calcitic crystals of different size in recrystallised limestone (+A)

26 SH-1: light grey, medium grained calcareous dolomite: xenotopic and hipidiotopic structure of the dolomite (+A)

27 P-19: dark grey biopelmicritic limestone: small rounded sparitic grains in micritic matrix (–A)

28 P-28: dark grey biopelmicritic limestone: microfacies modification, variable amount of peloids (–A)

29 P-26: grey to dark grey biopelmicritic limestone: bioclasts, intraclasts and peloids (–A)

30 Cr-1: white to light grey biocalcarenitic limestone: a shell fragment and intraclasts (+A)

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GEOLOGIJA *59/1*, 55-66, Ljubljana 2016

http://dx.doi.org/10.5474/geologija.2016.005

New reports of decapod *Portunus monspeliensis* A. Milne Edwards, 1860 from Miocene beds of eastern Slovenia with notes on palaeoecology and palaeobiogeography

Nove najdbe rakovice *Portunus monspeliensis* A. Milne Edwards, 1860 iz miocenskih plasti vzhodne Slovenije z opisom paleookolja in njihove paleogeografske razširjenosti

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Prejeto / Received 2. 5. 2016; Sprejeto / Accepted 1. 6. 2016; Objavljeno na spletu / Published online 11. 8. 2016

Key words: Portunus monspeliensis, Decapoda, Miocene, Badenian, Central Paratethys, Palaeogeography, Palaeoecology, Slovenia
Ključne besede: Portunus monspeliensis, deseteronožci, miocen, badenij, Centralna Paratetida, paleogeografija, paleoekologija, Slovenija

Abstract

In the present paper we report on several new occurrences of decapod *Portunus monspeliensis* A. Milne Edwards, 1860 from Miocene beds of eastern Slovenia, *i. e.* from the already known locality Šentilj in the northeastern Štajerska region and additional new localities in the Kozjansko and Dolenjska regions. These new reported occurrences of *P. monspeliensis* from the Middle Miocene (Badenian) strata of eastern Slovenia improve our knowledge of this otherwise widespread decapod crustacean. Additionally, we also re-evaluate the environmental preferences of the species and its wider palaeobiogeographical distribution during the Miocene in the Mediterranean, Atlantic and Paratethys Seas.

Izvleček

V pričujočem članku poročamo o novih primerkih rakovic vrste *Portunus monspeliensis* A. Milne Edwards, 1860 iz miocenskih plasti v vzhodni Sloveniji, in sicer iz že znanega najdišča pri Šentilju v severovzhodnem delu Štajerske in iz novih nahajališč iz območja Kozjanskega in Dolenjske. Nove najdbe iz miocenskih plasti vzhodne Slovenije dopolnjujejo naše poznavanje vrste *P. monspeliensis*. Med drugim v članku na novo opredeljujemo okoljske preference te vrste in njeno širšo paleobiogeografsko razširjenost v obdobju miocena na območju Sredozemskega morja, Atlantskega oceana in Paratetide.

Introduction

The portunid crab *Portunus monspeliensis* A. Milne Edwards, 1860 has a widespread distribution during the Miocene period. The species has been reported from the Mediterranean, the Paratethys as well as from Atlantic coastal waters. It is known from Miocene sediments of Austria, France, Hungary, Italy, Malta, Portugal, Spain, Slovenia, Egypt and the Sinai Peninsula (Milne Edwards, 1860; Ristori, 1888; Glaessner, 1928, 1933; Lörenthey & Beurlen, 1929; Via, 1932; Müller, 1979, 1984, 1993; Mikuž, 2003; Gatt, 2006). The remains of *P. monspeliensis* are one of the most abundant Miocene crabs and almost always represent the dominant decapod species in the strata where they occur. They are almost exclusively found in siliciclastic sediments such as sandstones and calcarenites, and their state of preservation is mostly not good. Due to their size, they are usually compressed, fractured and lacking exocuticle. Only recently illustrated specimens from the marly limestone of the middle Miocene Sardinia (Marangon & De Angeli, 2009) are exceptionally well preserved and provide better insight on the species morphology of the dorsal carapace.

Despite the widespread distribution and common occurrence, this fossil portunid species has not received relevant scientific attention in the last decades. In the 19th and in the beginning of the 20th century several authors (Via, 1923; Veiga Ferreira, 1954; Philippe & Secretan, 1971) have reported the European specimens under different, synonymous, names: *Lupa hastata* Linnaeus, 1767; *Neptunus convexus* Ristori, 1888; and *Neptunus granulatus* A. Milne Edwards,, 1860. Beside these recognized synonyms of *P. monspeliensis*, there are currently over 40 valid fossil species of genus *Portunus* Weber, 1795 (Karasawa et al., 2008), and many of them were described only from single poorly preserved specimens or chelae. Although even a superficial investigation of the fossil representatives of the genus shows great morphological variations, descriptions of fossil species usually illustrate carapaces lacking cuticle, severally fragmented specimens, and descriptions of isolated chelipeds. As it has already been pointed out by Karasawa and co-authors (2008) a re-evaluation and revision of all fossil species of *Portunus* would be welcome, but that is out of the scope of the present paper.

The only know occurrence of fossil remains of *P. monspeliensis* from the Miocene strata of Slovenia so far is the report of 27 fragments of this decapod (five carapaces) from Badenian sandstones of Šentilj (Mikuž, 2003). Interestingly, Križnar (2014) also presents a historical report of donations of a fossil crab specimen to the Nature History Museum in Vienna in 1850. The original report of this donation was published in the Leibacher Zeitung newspaper on the 21st of February 1853 and details the donations done in 1850 as: *"Der hochwertige Herr Primus Remiz, Cooperator in Grossdolina, welcher Herrn Freyer bei seinen geognostischen Wanderungen ein Paar Tage zu begleiten die Gefälligkeit hatte, verehrte dem Museum eine fossile Krabbe, welche er in Tschatesch am nördlichen Bügel nächst der Strasse ob der Post gefunden hat. Eine ausgezeichnete Stelle und reiche Fundgrube zur Zussammlung von fossilen Muscheln, Schneckenschalen usw... Herr Vincenz Kollar, Kustos der vereinigten k. k. Hof-Naturalien-Cabinete, wirkl Mitglied der Kaiserliche Academie der Wissenschaften zu Wien, hatte die Gewogenheit, oberwähnten Krebsen zu bestimmen, mit den Worten: "Dieser Krebs gehört zu der recenten Gattung Lupa, stimmt in Größe und den Verhältnissen der einzelnen Theile mit Lupa dicantha Latreille und Milne Edwards überein, und scheint zunächst mit Lupa spinimana Milne Edwards verwandt. Auf jeden Fall nähert sich diese Art den Formen, welche an den amerikanischen Küsten vorkommen".*

The cited passage in German, illustrates the finding of a fossil crab by Mr. Primož Remic in today's town Čatež (on the hill north of the Post) in eastern Slovenia, who sent it to the curator Mr. Vincenz Kollar from the Nature History Museum in Vienna. Mr. Kollar determined it as belonging to the genus *Lupa* (junior objective synonym of *Portunus*) and closely resembling extant species *Lupa dicantha* or *Lupa spinimana*. This historical specimen can no longer be located, but likely represents the first documented find of the crab *Portunus monspeliensis* and the first recognized find of a fossil decapod crustacean in Slovenia.

Geology and stratigraphy of the localities

The newly presented specimens originate from various localities of the former Central Paratethys Sea that covered the eastern part of Slovenia in the Miocene period (Fig. 1). The following localities yielded new material of this widespread decapod crustacean:

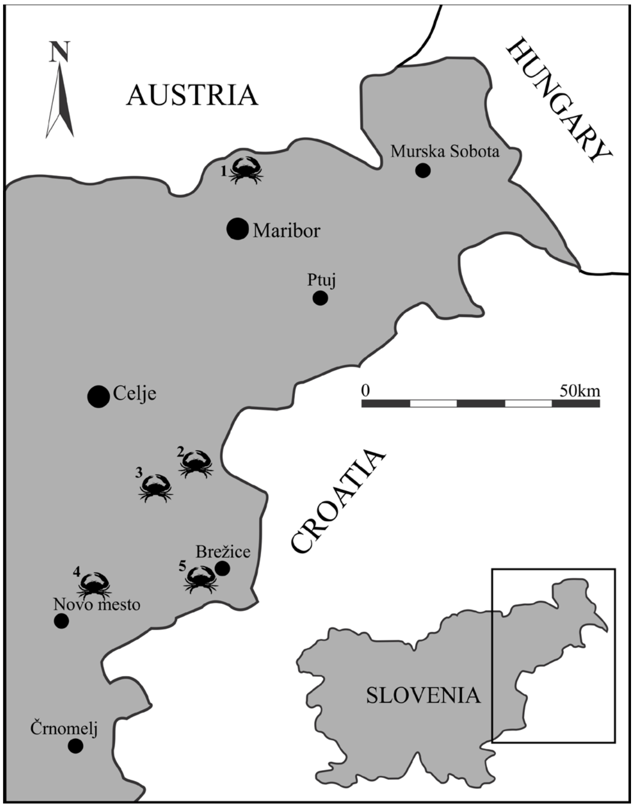


Fig. 1. Simplified geographical map of East Slovenia showing all known occurrences of decapod *Portunus monspeliensis* A. Milne Edwards, 1860. 1 – Štrihovec / Šentilj, 2 – Gruška / Kozje, 3 – Trebče / Bistrica ob Sotli, 4 – Dolnja Stara vas, 5 – Šentvid / Čatež.)

1. Štrihovec / Šentilj

Štrihovec was until recently the only known locality with fossil remains of *P. monspeliensis* from the Slovenian territory (Mikuž, 2003). Štrihovec is situated near Šentilj, a town in northeast Slovenia, bordering on Austria. The fossil bearing layers were accessible in the years 1995/1996, when middle Miocene (Badenian) sandstone, marl, and lithothamnium limestone were exposed during construction works for the new highway.

A rich association of macrofossils was collected by amateur collectors and described in the following years (Mikuž 1997, 1998, 2003, 2008; Mikuž & Mitrović-Petrovič, 2001). The represented fossil taxons include brachiopods, pectinid bivalve fauna, clypeasteroid echinoderms, octocorals, nautiloids, and crabs.

2. Gruška / Kozje

One decapod crab specimen was recovered from the Gruška jama locality near the town of Kozje in eastern Slovenia, close to border of Croatia. The Middle Miocene (Badenian) strata exposed here are comprised of sandstone and lithothamnium limestone (Aničić & Juriša, 1985), where macrofossils are rare. Sporadic finds from this locality comprise mostly poorly preserved bivalves with dissolved shells and rare echinoderms (Mikuž, 2010).

3. Trebče / Bistrica ob Sotli

This specimen was retrieved from a road cut on local road from Trebče towards Podsreda in eastern Slovenia, in the Kozjansko region. The crab was collected in yellowish calcareous sandstone of Middle Miocene (Badenian) age. There is also an outcrop of coarser clastic rocks, i. e. conglomerates with rhodoid spheres located close by (Aničić et al., 2002).

4. Dolnja Stara vas

A construction site behind the gasoline station in Dolnja Stara vas near Škocjan na Dolenjskem was opened in the early 2000s, which exposed a long outcrop of Middle Miocene (Badenian) strata (Mikuž & Horvat, 1998). The lithologies at outcrop vary from breccia, sandstone, biocalcarenites and lithothamnium limestone. A rich macro fauna, comprising mostly of bivalve species with rare gastropods and cirripeds was described from the sandstones and calcarenites (Mikuž & Petrič, 2008), from which we also collected a specimen of the *P. monspeliensis*.

5. Šentvid / Čatež

Grey to yellowish sandstones and calcarenites interbedded with grey siltstone are exposed along the slopes of hill St. Vid, south of Brežice in eastern Slovenia. Similarly to the wider surrounding area this lithology is part of the middle Miocene (Badenian) Čatež formation sequence (Rižnar et al., 2002). So far only sporadic finds of echinoderm fragments and indeterminable bivalves are reported from these beds. The crab specimens are surprisingly common in the yellowish calcarenites in this locality.

Material and methods

We describe 25 new specimens of *Portunus monspeliensis* that were not yet presented. One articulated specimen in the collection of Mr. Damjan Zupančič (Inv. No. DZ3135) from the locality Štrihovec, a single carapace from the locality Gruška (Inv. No. RGA/SMNH 1988), a complete carapace from the locality Trebče (Inv. No. RGA/SMNH 0586), one partial carapace from the locality Dolnja Stara vas (Inv. No. RGA/SMNH 1885) and 21 specimens from the collection of Mrs. Natalija Grdovič from the locality Šentvid near Čatež. These later include seven well-preserved, almost complete carapace (Inv. Nos.: NG118, 123,

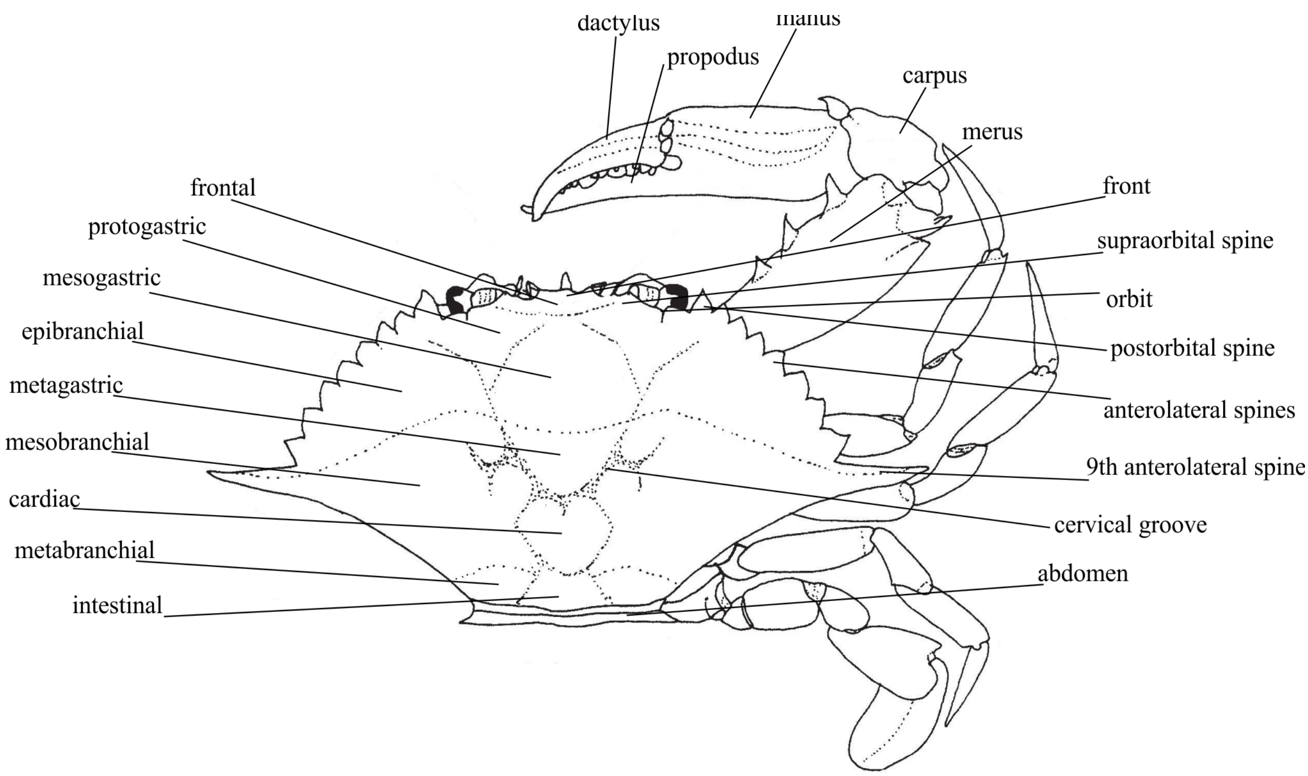


Fig. 2. Descriptive terminology used in the text showing dorsal morphology of portunid crab (modified after Lai et al., 2010).

124, 132, 133, 137, 138), thirteen partial carapace remains (Inv. Nos.: NG94, 117, 119, 120, 121, 122, 125, 127, 129, 130, 136, 141, 147), and one specimen of left propodus (Inv. No. NG128). All specimens were analysed and compared to other remains of the species *Portunus monspeliensis* from Štrihovec, Slovenia (Inv. No.: SMNH 1939, 1940, 1941, 1942, 1943, 1962), Austria (Inv. No.: RGA/SMNH 0837, 0838, 0963, 1031, 1036, 1037, 1109, 1123, 1339, 1340, 1341, 1344, 1345, 1438, 1477, 1479, 1480, 1484, 1911), and from Catalonia and Portugal (AO collection, Inv. No.: C-040/1, C-040/2, C-040/3, C-040/3, C-040/4, C-040/5, C-040/6). Specimens from the Mediterranean of Italy and France were analysed using data from references. All specimens were photographed, measured and studied using computer graphic programmes (CorelDRAW X5, Adobe Photoshop CC). Photographs were taken with digital camera Nikon Coolpix P340.

Abbreviations: SMNH - Slovenian Museum of Natural History, Ljubljana, Slovenia; RGA/SMNH - Slovenian Museum of Natural History, Ljubljana, Slovenia (R. Gašparič Collection); AO - Àlex Ossó fossil crab collection, Tarragona, Catalonia; DZ – Damjan Zupančič private collection, Maribor, Slovenia; NG – Natalija Grdovič private collection, Brežice, Slovenia.

Systematic description

The systematics used herein follows Karasawa et al., 2008.

Subsection Heterotremata Guinot, 1977
Superfamily Portunoidea Rafinesque, 1815
Family Portunidae Rafinesque, 1815
Subfamily Portuninae Rafinesque, 1815

Genus ***Portunus*** Weber, 1795

Type species. *Cancer pelagicus* Linnaeus, 1758.

Diagnosis: Carapace much wider than long; carapace regions moderately developed; six frontal spines including inner-orbital spines which are usually present; orbit with two closed supraorbital fissures; nine anterolateral spines including outer-orbital spine; chelae keeled; male abdomen triangular with somites 3–5 fused. (after Schweitzer et al, 2006)

Portunus monspeliensis (A. Milne Edwards, 1860)
(Plate 1. A–G, Plate 2. A–G)

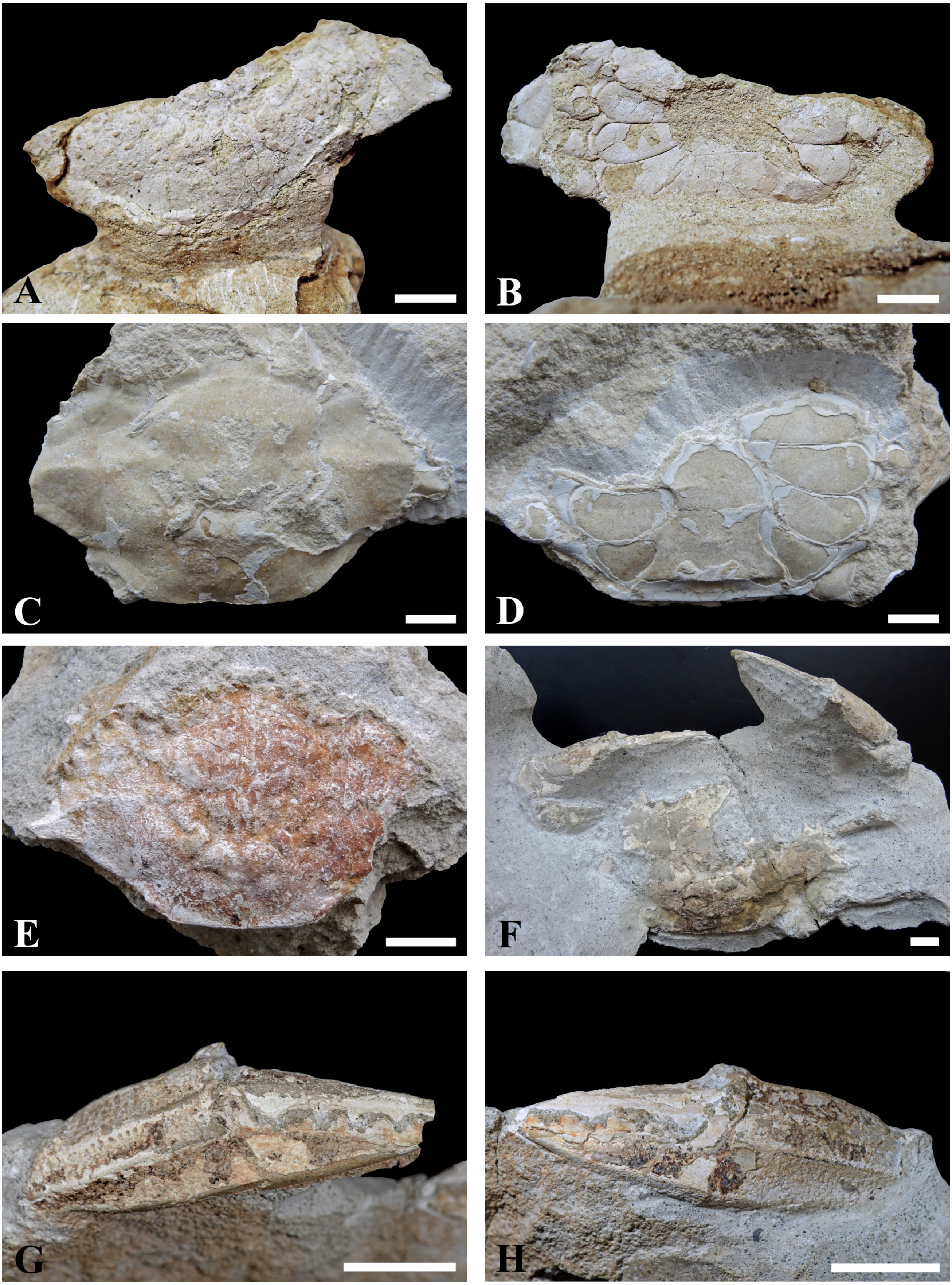
1860 *Neptunus monspeliensis* A. Milne Edwards; p. 232
1860 *Neptunus monspeliensis* A. Milne Edwards; Pl. 4 (fig. 1), Pl. 5 (fig. 1)
1860 *Neptunus granulatus* A. Milne Edwards; p 241, Pl. 3 (fig. 1), Pl. 7 (fig. 2)
1888 *Neptunus granulatus* A. Milne Edwards - Ristori; p. 215, Pl. 4 (figs. 5–11)
1893 *Neptunus cfr. granulatus* A. Milne Edwards - Bittner; p. 11
1897 *Neptunus cfr. granulatus* A. Milne Edwards - Lörenthey; p. 159
1898 *Neptunus cfr. granulatus* A. Milne Edwards - Lörenthey; p. 110, 153, Pl. 9 (figs. 2, 3)
1909 *Neptunus granulatus* A. Milne Edwards - Lörenthey; p. 242, Pl. 2 (figs. 1, 2)
1929 *Neptunus granulatus* A. Milne Edwards -Lörenthey & Beurlen; p. 188, Pl. 13 (figs. 3, 4), Pl. 14 (figs. 1, 4)
1950 *Neptunus granulatus* A. Milne Edwards - Comaschi Caria; p. 324, Pl. 1
1956 *Neptunus granulatus* A. Milne Edwards - Comaschi Caria; p. 284, 288, P. 1 (figs. 1–7), Pl 2 (figs 1–6), Pl. 3 (figs. 1, 2)
1968 *Neptunus granulatus* A. Milne Edwards - Stancu & Andreescu; p. 466, Pl. 7 (fig. 85)
1979 *Portunus granulatus* A. Milne Edwards - Förster; p. 94
1979 *Portunus monspeliensis* (A. Milne Edwards) - Müller; p. 274, 280, 288, Pl. 18
1984 *Portunus monspeliensis* (A. Milne Edwards) - Müller; p. 79, Pl. 62 (figs. 1, 2)
1991 *Portunus monspeliensis* (A. Milne Edwards) - Marras & Ventura; p. 108, Pl. 1 (figs. 1–4), Pl. 2 (figs. 1, 4), Pl. 3 (figs. 1–3)
1992 *Portunus granulatus* A. Milne Edwards - De Angeli & Marangon; p. 176
1993 *Portunus monspeliensis* (A. Milne Edwards) - Müller; p. 14–15, Pl. 6 (fig. G), Pl. 7 (fig. A)
2003 *Portunus monspeliensis* (A. Milne Edwards) - Mikuž; p. 187–199, Pl. 1 (figs. 1-5), Pl. 2 (figs. 1–8)
2007 *Portunus monspeliensis* (A. Milne Edwards) - Marangon & De Angeli; p. 70–72, Pl. 1 (figs. A–H)

PLATE 1

Portunus monspeliensis A. Milne Edwards, 1860.
A – RGA/SMNH 1885, partial dorsal carapace;
B – RGA/SMNH 1885, partial ventral side with abdomen (male);
C – RGA/SMNH 0586, dorsal carapace;
D – RGA/SMNH 0586, partial ventral side with abdomen (male);
E – RGA/SMNH 1988, dorsal carapace;
F – DZ3135, fragmented dorsal carapace with an associated chelipeds;
G – DZ3135, right cheliped;
H – DZ3135, left cheliped.

All scale bars are 10 mm.

PLATE 1



Description: The specimens have a medium sized hexagonal carapace, significantly wider than long (width/length ratio is about 1.75, greater in bigger individuals, up to 1.85); greatest width at the last (ninth) anterolateral spine (Tab. 1). The carapace is slightly convex in the cross section and its dorsal surface is densely covered by small granules. The front is protruding and slightly downturned, approx. 20 % of maximum carapace width, with axial notch; two forward directed short spines on either side and followed by a distinctive sharp, outward pointing, inner orbital spine. Fronto-orbital margin about 50 % of maximum carapace width. Orbits wider than front, forward directed; supraorbital margin sinuous, incised by two closed fissures, one medially and other near the outer orbital tooth. Anterolateral margin long and slightly convex with nine anterolateral spines, first spine (outer orbital) directed forward and strong, with subsequent seven subtrigonal spines each somewhat smaller and outwards directed; ninth anterolateral spine prominent, the largest and laterally directed at almost a right angle to the vertical axis; in younger specimens steeper angle with regards to anterior margin. Posterolateral margin straight with concave depression (re-entrant of fifth pereiopod) in the last third of its length. Posterior margin slightly concave and rimmed, broad, width approx. 75 % of the fronto-orbital margin width.

Carapace regions faintly defined; protogastric region semi-circular lobes with transverse ridge; mesogastric and metagastric regions are trapezoid shaped and separated by faint transverse ridge; mesogastric process long, ending behind frontal axial notch. Cardiac region well-defined, pentagonal, anterior borders straight, posterior borders concave, whole region somewhat swollen with longitudinally running central depression. Intestinal region faint and circular. Hepatic region flat and triangular. Epibranchial region wide, forming arcuate transverse ridge from largest anterolateral spine to mesogastric region, separating the epibranchial and mesobranchial regions. Cervical groove distinct. Branchiocardiac grooves well marked, along sides of cardiac region.

Thoracic sternum broad, oval, widening posteriorly, widest at 6 thoracic sternite, with straight to slightly concave sutures between sternites. Thoracic sternites 1–2 not preserved, sternites 3–4 fused in a trapezoidal plate, axial sulcus reaching the anterior margin of sternite 3, transverse ridge in sternite 4 medially interrupted; sternites 5–7 transversely elongated, distally rounded; sternite 6 the longest; sternite 7 shorter than sternite 6; sternite 8 reduced, subtrigonal; sternites 5–7 form laterally expanded episternites. Suture 2 complete; suture 3/4 distinct; sutures 4/5 to 7/8 laterally complete.

Male abdomen subtriangular with straight converging margins, abdominal somite 1 and 2 narrow and wide, only somite 2 is observable from the ventral side with a concave notch on the distal end where it interlocks with thoracic sternite 8; abdominal somites 3–5 fused in a wide, subtrapezoidal plate with slightly concave lateral margins, somite 3 widest, transversely keeled; somite 6 trapezoidal, longer than somites 3–5 with convex lateral margins; male telson subtriangular approximately as high as wide. Female abdomen much wider, about half the carapace width, semi-circular; somites 1 and 2 narrow and wide; somites 3–5 rectangular in shape with convex lateral margins; somite 6 wider posteriorly, with sinuous lateral margin, posteriorly convex and anteriorly concave, telson roundly triangular.

Merus of the third maxillipeds subrectangular and elongated. Chelipeds subequal with elongated merus; carpus short, palm rectangular and elongated, with three longitudinal ridges on outer surface. Fixed finger is triangular and elongated, as long as palm. Occlusal margin of chelae heterodontic with a clear knobstick molariform tooth in the right chela, followed by a series of tuberous teeth.

Table 1. Comparison of dimensions of new specimens of *Portunus monspeliensis* A. Milne Edwards, 1860.

Species	Specimen No.	Carapace width (in mm)	Front width (in mm)	Fronto-orbital width (in mm)	Posterior width (in mm)	Carapace length (in mm)
Portunus monspeliensis	RGA/SMNH0586	87.0	16.0	45.5	34.0	50.5
Portunus monspeliensis	RGA/SMNH1988	60.2	12.7	28.0	21.4	32.9
Portunus monspeliensis	DZ3135	99.0	17.4	49.6	40.2	53.5
Portunus monspeliensis	NG118	77.4	14.6	40.9	34.4	42.2
Portunus monspeliensis	NG123	33.4	7.2	18.4	12.1	19.2
Portunus monspeliensis	NG124	50.8	10.5	28.9	18.2	29.6
Portunus monspeliensis	NG132	66.1	11.6	33.3	23.2	36.1
Portunus monspeliensis	NG133	74.8	14.5	40.2	29.2	41.8
Portunus monspeliensis	NG137	76.7	14.4	38.2	33.2	43.5
Portunus monspeliensis	NG138	32.1	6.8	17.4	12.5	19.0

Palaeoecology and environment

As indicated in the geological setting of most of the aforementioned works and personal observations of the authors, specimens of *Portunus monspeliensis* are recovered from typical Miocene siliciclastic sediments. *Portunus monspeliensis* is almost exclusively collected from sandstone and sandy limestone that is interbedded with marl. These lithologies represent a variety of sublittoral facies comprising from inshore to offshore waters (Comaschi Caria, 1956; Marangon & De Angeli, 2009), or from estuarine and even lagoon or brackish environments with a sandy, muddy, or sea grass bottom (Nichols, 2009).

Portunus monspeliensis may be considered a euryhalin species given the high salinity fluctuation existent in the different observed ecosystems it inhabits (Müller, 1993). Many of the extant portunids, such as *Portunus pelagicus*, are found in the Indo-Pacific waters and even in the oriental margin of the Mediterranean Sea and share similar ecological preferences and habitats as well as clear morphological similarities with species *P. monspeliensis* (Lai et al., 2010). From this it can be inferred that other aspects of their biology and ecology, such as predation or swimming capacities, may be similar as well. Both species have similar nearly homochelic claws with a clear knobstick molariform tooth in the right chela and followed by tuberous teeth or a series of conical teeth (Pl. 1,F) which indicate the capacity of chelae for crushing and cutting its prey (Spiridonov et al., 2014). Accordingly, *P. monspeliensis* must have been, similarly as *Portunus pelagicus*, an opportunistic predator and scavenger, depending on the availability of prey. The majority of its diet would consist of teleost fish, molluscs, crustaceans, polychaetes, and substrate debris (Kunsook et al., 2014). Judging by the shared paddle-like form of the fifth pereiopod in *Portunus monspeliensis*, it is supposed that the species was an active swimmer, remaining buried in the sediment during inactivity, analogous to the extant *P. pelagicus*.

When evaluating the depositional settings that bear fossils of *Portunus monspeliensis*, it can be concluded from comparison with extant *P. pelagicus* and fossil bearing lithologies, that they inhabited a wide range of habitats, but preferred sublittoral algal and sea grass meadows on both sandy and muddy substrata (Kunsook et al., 2014; Chande & Mgaya, 2003). The choice of habitat, ranging from shallow inshore waters to deeper offshore waters, would most likely also vary with age, sex, and season (Svane & Hooper, 2004). In addition to the above mentioned similarities with the extant *Portunus pelagicus* which may share its habitat with genus *Scylla* De Haan, 1833 and

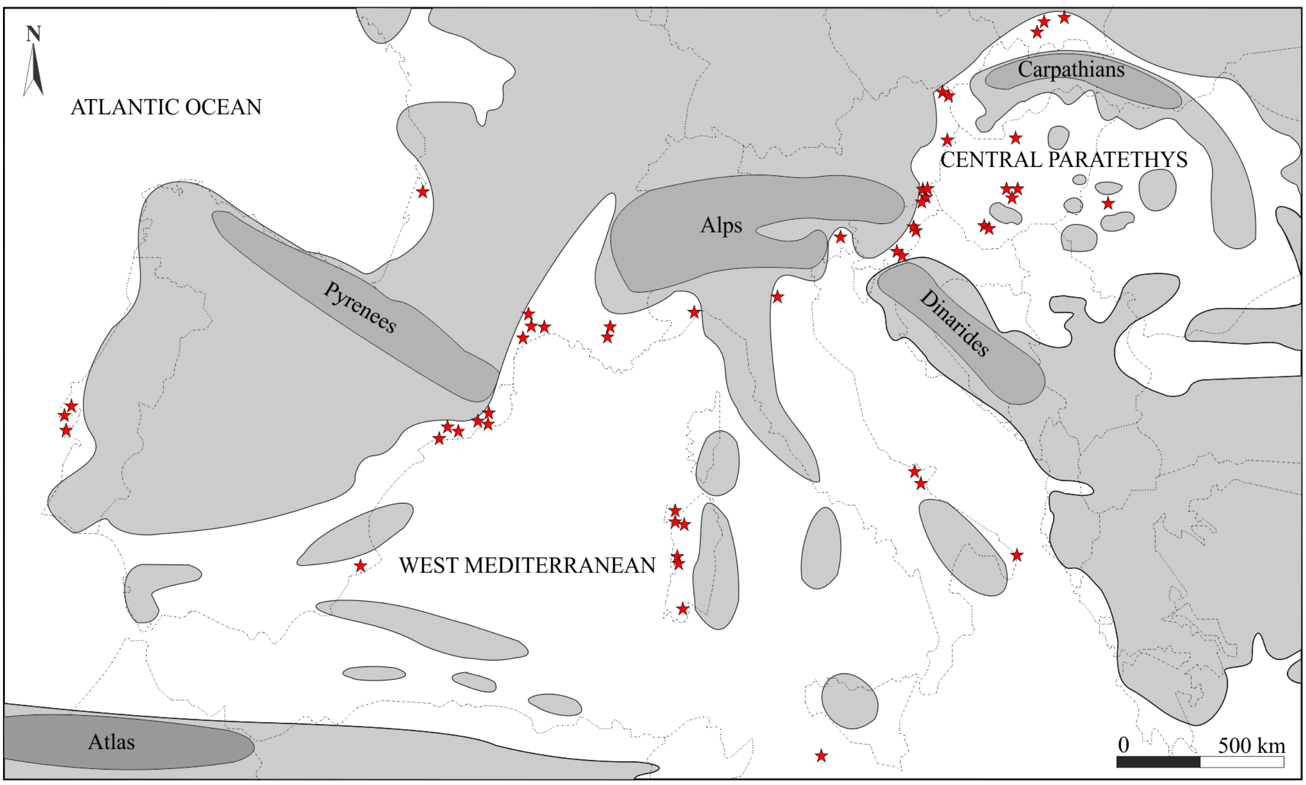


Fig. 3. Distribution of *Portunus monspeliensis* A. Milne Edwards, 1860 in the Central Paratethys, Mediterranean and Atlantic Ocean, during the middle Miocene, projected onto the Recent geographical map of Europe (modified after Popov et al., 2004). White areas represent respective Miocene basins, grey areas represent land masses, stars represent known localities of *Portunus monspeliensis*.

with other portunids (Chande & Mgaya, 2003), *P. monspeliensis* species frequently occurs with less common Miocene portunids such as *Scylla* and *Necronectes* Milne-Edwards, 1881 (Via, 1932; Veiga Ferreira, 1954; Müller, 1993 and AO pers. obs.).

Palaeobiogeography

True portunids first appeared in the Middle-Late Eocene period according to the present fossil record (Ossó, 2016). The *Portunus monspeliensis* species appears to be a derived taxon from the robust stock of true portunids that dwelt in the western margin of the Tethys during the Middle-Late Eocene and Oligocene, and inhabited coasts with siliciclastic sediments that originated from the Alpine Orogeny and filled the Mediterranean and Central Paratethys basins during the Miocene period. Strikingly, we have no fossil records of *P. monspeliensis* from the Miocene of the Balearic Islands (J. Juárez, pers. comm.) nor in the extensive Miocene deposits of the Betic Strait (I. Bajo, pers. comm.), which would seem a natural migration path from the Mediterranean to the Atlantic coast in Portugal during the middle Miocene.

Portunus monspeliensis was widely distributed along the Paratethys, the Mediterranean and the southern Atlantic coast of the Iberian Peninsula during the Miocene. Interestingly the reported distribution of *P. monspeliensis* in Paratethys is heavily dominated in the Central and Western Paratethys (Fig. 3), near the hypothetical Slovenian Corridor, connecting the Central Paratethys and the Mediterranean (Bartol et al., 2014). Further fossil species of *Portunus* were present either eastward in the Indo-Pacific waters or westward in the Caribbean waters. Different species of *Portunus* have so far been reported in Miocene outcrops in Iran (Glaessner, 1928; Heidari et al., 2012; Yazdi et al., 2013), India (Ralte et al., 2009; Tiwari & Vega, 2014), Pakistan and Burma (Satsangi & Parida, 1980), Malaysia (Collins et al., 2003), Indonesia (van Straelen, 1924), Taiwan (Hu, 1984), and Fiji (Rathbun, 1945). The genus was first recorded in Japan only from strata that date to the Pliocene period (Karasawa & Nobuhara, 2008).

Concurrently, the genus *Portunus* is also present westward during the Miocene, *i. e.* in the Caribbean and in the Central and South America waters, for example in Cuba (Schweitzer et al., 2006), Haiti and Dominican Republic (Rathbun, 1919; 1920 & 1923), in the southeast of the US of America (Rathbun, 1935; Portell, 2004), Mexico (Vega et al., 1999; 2009), Costa Rica and Panama (Todd & Collins, 2005; Collins et al., 2009), and Brazil (Brito, 1972; Martins Neto, 2001).

Conclusions

In the present paper, we described 25 new specimens of *Portunus monspeliensis* A. Milne Edwards, 1860 from Middle Miocene beds of eastern Slovenia from four new localities. The newly presented diversity and richness of *P. monspeliensis* in sublittoral siliciclastic lithologies of eastern Slovenia confirms the presence of Middle Miocene Slovenian Corridor, connecting the Central Paratethys and the Mediterranean Sea.

Considering the near shore facies and lithologies of new localities from eastern Slovenia *P. monspeliensis* must have been a euryhalin species, similar to some extant portunids. This widespread decapod crustacean usually has a dominant role in the ecosystems it shares with less common portunids such as *Scylla* and *Necronectes*.

The described material shows that the fossil record of *P. monspeliensis* in Slovenia is much more robust than previously thought. New localities in eastern Slovenia are important data points on palaeobiogeographical map of Middle Miocene, which illustrate the possible seaway connection between Paratethys and Mediterranean.

Acknowledgements

We wish to thank José Juárez (Binissalem, Spain), Ildefonso Bajo (Alcalá de Guadaira, Spain), Damjan Zupančič (Maribor, Slovenia) and Natalija Grdovič (Brežice, Slovenia) for access to the relevant fossil material, Matija Križnar for providing important literature data and Andreja Žibrat Gašparič for thoroughly proofreading our manuscript.

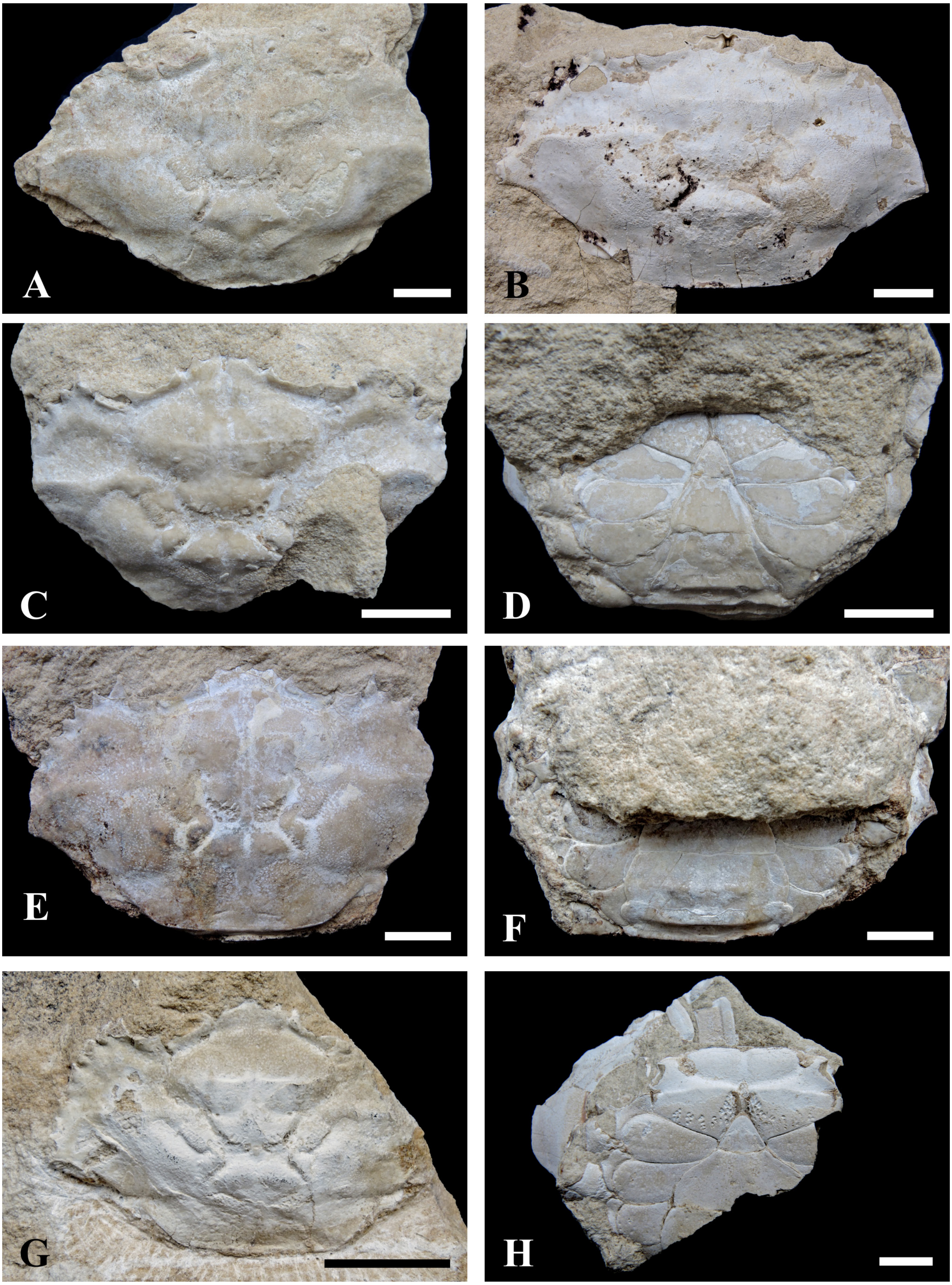
PLATE 2

Portunus monspeliensis A. Milne Edwards, 1860.

A – NG137, dorsal carapace;
B – NG133, dorsal carapace;
C – NG124, dorsal carapace;
D – NG124, ventral side with abdomen (male);
E – NG132, dorsal carapace;
F – NG132, ventral side with abdomen (female);
G – NG123, dorsal carapace;
H – NG141, partial ventral side with abdomen (female).

All scale bars are 10 mm.

PLATE 2



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GEOLOGIJA 59/1, 67-84, Ljubljana 2016

http://dx.doi.org/10.5474/geologija.2016.004

Slovenian Network of Isotopes in Precipitation (SLONIP) – a review of activities in the period 1981–2015

Slovenska mreža opazovanj izotopske sestave padavin (SLONIP) – pregled aktivnosti v obdobju 1981–2015

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Prejeto / Received 5. 5. 2016; Sprejeto / Accepted 9. 6. 2016; Objavljeno na spletu / Published online 11. 8. 2016

Key words: precipitation, isotopes, oxygen, hydrogen, tritium, GNIP, SLONIP, Slovenia

Ključne besede: padavine, izotopi, kisik, vodik, tritij, GNIP, SLONIP, Slovenija

Abstract

The first investigations of oxygen and hydrogen isotope composition ($\delta^{18}O$ and $\delta^{2}H$) and the tritium activity (^{3}H) in precipitation over Slovenia were performed in the frame of tracer experiments conducted in the period 1972–1975 in the Ljubljanica River drainage basin. The first regular and systematic monitoring of isotope composition of precipitation only began in 1981 in Ljubljana but has been extended during the last 35 years to 30 different locations countrywide. Herein, we present a review of research performed during the period 1981–2015. We collected information about sampling, analytical methods, available data and their evaluation including calculations of local meteoric water lines. Based on the data, we identify gaps in the research and make recommendations for future monitoring in the frame of the Slovenian Network of Isotopes in Precipitation (SLONIP).

Izvleček

Prve raziskave izotopske sestave kisika in vodika ($\delta^{18}O$ in $\delta^{2}H$) ter aktivnosti tritija (^{3}H) v padavinah na območju Slovenije so potekale v okviru sledilnih poskusov, ki so se v obdobju 1972–1975 izvajali na območju reke Ljubljanice. Prvo redno in sistematično spremljanje izotopske sestave padavin se je pričelo leta 1981 v Ljubljani in bilo zadnjih 35 let izvajano na 30 različnih lokacijah. V prispevku podajamo pregled raziskav, ki so bile v Sloveniji opravljene v obdobju 1981–2015. Zbrali smo podatke o vzorčenju, uporabljenih analiznih postopkih, dostopnih rezultatih in obdelavah podatkov vključno z izračuni lokalnih meteornih premic. Na osnovi zbranih informacij smo identificirali pomanjkljivosti predhodnih raziskav in izdelali priporočila za bodoče raziskave v okviru Slovenske mreže opazovanj izotopske sestave padavin (SLONIP).

Introduction

The importance of systematically collecting data on the water isotope composition of precipitation, i.e. stable isotopes of oxygen (expressed as $\delta^{18}O$) and hydrogen (expressed as $\delta^{2}H$) and the radioactive hydrogen isotope tritium (^{3}H), in the frame of the Global Network of Isotopes in Precipitation (GNIP) has been steadily increasing since it was initiated by the International Atomic Energy Agency (IAEA) and the World Meteorological Organisation (WMO) in 1958 (Internet 1). Initially, the GNIP was focused on monitoring atmospheric thermonuclear test fallout through levels of radioactive tritium and, after 1970, became an observation network of stable hydrogen and oxygen isotope data for hydrologic investigations of water resources. The GNIP provides also an important database for verifying and improving atmospheric circulation models, studying regional, global and temporal climates, studying the interactions between water in the atmosphere and the biosphere, providing baseline information for the authentication of commodities, tracking migratory species and for forensic purposes. Particularly in the last decade has the demand for accurate spatial and temporal predictions of point, regional, and continental-scale δ^{18}O and δ^{2}H values in precipitation been increasing (Terzer et al., 2013). This is especially the case for those regions where little or no GNIP data exist. In Slovenia water isotopes in precipitation have been systematically monitored since 1981 only in Ljubljana (Pezdič, 1999). In 2000, the need for a much more refined understanding of isotope variations was identified due to geographical diversity, which influences the climate and also the water cycle in Slovenia considerably. Therefore, a programme of collecting new data at a higher spatial density and temporal frequency in different parts of the country has been initiated and was extended several times during the last 15 years. Consequently, the number of sampling locations has grown to a Slovenian Network of Isotopes in Precipitation (SLONIP). Unfortunately, the network is still not a part of a national monitoring programme, such as that operating in European countries, for example, in Switzerland (Schürch et al., 2003) and Germany (Stumpp et al., 2014).

In the past 35 years, water isotopes in precipitation were monitored in Slovenia by different institutions mostly in the frame of short-term research projects and many isotope data were collected but only partly evaluated and published. The data were used in many hydrological and hydrogeological investigations, as well as in investigations of precipitation, moisture recycling in Alpine regions, identification and characterisation of nitrate pollution sources, in evaluations of GNIP data, investigations of bottled waters (e.g. Brenčič et al., 2015; Mezga, 2014; Vreča et al., 2014, 2015a and references therein) and other studies related to food authentication (Bizjak Bat et al., 2012).

A growing need for water isotope data and the establishment of the SLONIP database, which could be used in other applications, particularly in water resources research and food authentication, stimulated the authors to review the activities performed in Slovenia in the period 1981–2015. The main aims of this paper are the following: 1) to review the history of isotope in precipitation investigations performed in Slovenia in the period 1981–2015, 2) to summarize the main information about sampling, analytical methods used and basic isotope data for a particular sampling location, 3) to identify the main gaps in the research, and 4) to present general recommendations for future work in the frame of SLONIP.

Materials and methods

We collected available publications: national and international journals, conference papers, PhD theses, and Master theses, reporting data on isotope composition of oxygen and hydrogen in precipitation over Slovenia during the period 1981–2015. We also searched the following databases: Google, Google Scholar, Co-operative Online Bibliographic System and Service – COBISS along with unpublished material including internal reports available at the Jožef Stefan Institute (JSI). The following information were collected:

1. sampling data including location - coordinates, type of sampling station, sampling period, sampling collector, sample treatment including filtration and type of storage bottle.
2. analytical methods used for determining stable oxygen (δ^{18}O) and hydrogen (δ^{2}H) isotope composition.
3. analytical methods used for determining tritium activity (^{3}H) if available together with stable isotope data.
4. reported isotope data, mean isotope values and local meteoric water lines (LMWLs).

Publications in which isotope composition of precipitation was mentioned but it was not clear where, when or how sampling was performed, which analytical methods were used and reporting limited or no numerical data, were used to prepare a list of the main gaps and general guidelines for future work in the frame of SLONIP.

Results and discussion

History of isotopes in precipitation investigations performed in Slovenia in the period 1981–2015

Water isotopes were applied in Slovenia for the first time in investigations in the frame of extensive underground water tracing performed in the period 1972–1975 in the Ljubljanica River drainage basin by the international Association of Tracer Hydrology (Gospodarič & Habič, 1976). Samples of precipitation were collected at the Šmarata, Postojna and Logatec meteorological stations. Stable isotopes of oxygen and hydrogen were determined in Munich, Germany and tritium activity in Vienna, Austria. Later, in the early 1980s, isotope ratio mass spectrometer (IRMS) techniques for determining stable oxygen and hydrogen isotope composition in water samples were implemented for the first time also in Slovenia at the JSI. The first systematic monitoring of isotopes in precipitation started in 1981 at the synoptic station Ljubljana–Bežigrad located at the Hydrometeorological Survey of Slovenia (today Slovenian Environment Agency – ARSO; Fig. 1, Tab. 1, Pezdič, 1999; Vreča et al. 2008). In 1993, the collection of precipitation was moved to the JSI (station Ljubljana–IJS) and finally, in September 2000 to the Reactor Centre of the JSI (station Ljubljana–Reaktor) in the vicinity of Ljubljana (Fig. 1, Tab. 1, Vreča et al., 2008). The stable isotope composition of monthly precipitation samples was determined at the JSI and tritium activity was measured at the Ruđer Bošković Institute (RBI) in Zagreb, Croatia (Krajcar Bronić et al., 1998; Pezdič, 1999; Vreča et al., 2008). Data have been regularly reported to the IAEA and published until 1994 in the IAEA Technical Reports Series (IAEA 1986, 1990, 1994), and afterwards on the internet (Internet 2). Later, in 2008, a review of all data collected in the period 1981–2006 was performed and sampling history recorded (Vreča et al., 2008). New data and corrections were submitted to the IAEA GNIP database (Internet 2). Data collected in the period 2007–2010 were reported and evaluated by Vreča et al. (2014) and the whole 1981–2010 dataset was used for the first time to study the relation between isotope composition of precipitation and atmospheric circulation patterns (Brenčič et al., 2015).

Monitoring of water isotopes in precipitation was carried out continuously and systematically by the JSI until 2000 only in Ljubljana (Tab. 1, Vreča et al., 2008). A short-term monthly stable isotope monitoring was performed in 1999 and 2000 also at the ARSO precipitation station in Sela na Krasu (Fig. 1, Tab. 1, Doctor, 2002) and at Sinji vrh (Tab. 1, Trček, 2003). Due to the geographical diversity, which influences the climate of Slovenia considerably (Pučnik, 1980) and the large karstic aquifers important for the water supply of SW Slovenia, sampling was extended to two stations, namely to the ARSO synoptic station Portorož airport and the ARSO precipitation station Kozina in October 2000 (Fig. 1, Tab. 1). At both stations stable and radioactive water isotopes were monitored on a monthly basis (Vreča et al., 2005–2007, 2009, 2011, 2015a). Unfortunately, since 2004, due to the lack of financial support monitoring has been continued only at the Portorož airport. First monitoring of stable water isotopes in precipitation in eastern Slovenia started in 2001 in Selniška Dobrava (Fig. 1, Tab. 1, Mali, 2006), and was performed by the staff of the Geological Survey of Slovenia (GeoZS). Afterwards, in 2009 two additional locations were selected by the JSI for monitoring stable oxygen and hydrogen isotope composition in SW and SE Slovenia, one at the

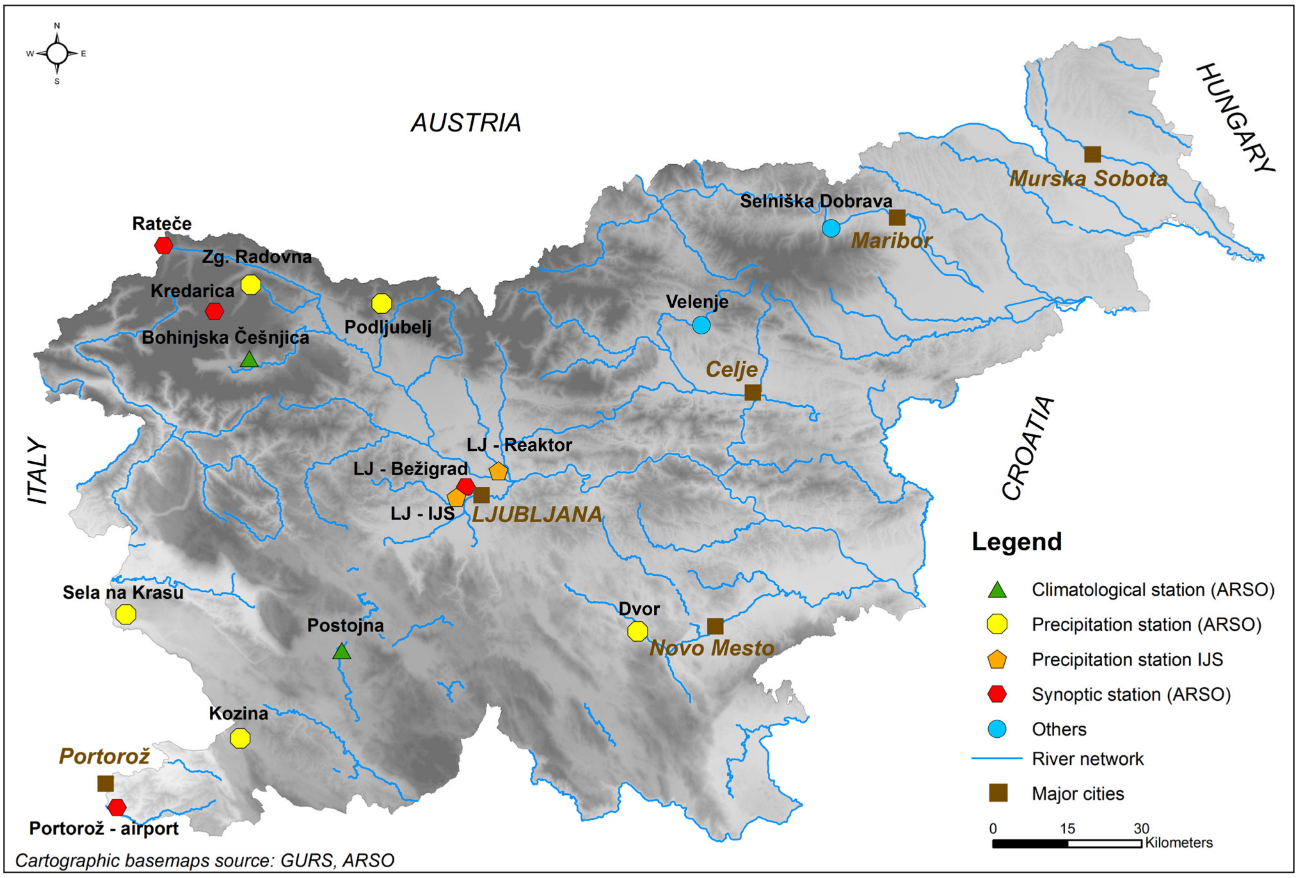

Fig. 1. Slovenian Network of Isotopes in Precipitation (SLONIP) according to sampling station type.

Table 1. Sampling locations and types of sampling station within SLONIP (1 – synoptic station ARSO; 2 – climatological station ARSO; 3 – precipitation station ARSO; 4 – precipitation station at JSI; 5 – others), GNIP code, coordinates and altitude of the sampling station, as well as period of sampling (n.r. – not reported).

Location[x] (x … type of station)		GNIP code	Coordinates		Altitude (m a.s.l.)	Sampling period
			N	E		
1a	Ljubljana–Bežigrad[1]	1401500	46º03'56"	14º30'45"	299	1981–1992
1b	Ljubljana–IJS[4]	1401500	46º02'31"	14º29'16"	292	1993–08/2000
1c	Ljubljana–Reaktor[4]	1401500	46º05'41"	14º35'50"	282	09/2000–
2	Portorož airport[1]	1410501	45º28'31"	13º36'58"	2	10/2000–
3	Kozina[3]	1411001	45º36'15"	13º55'54"	486	10/2000–12/2003
4	Dvor[3]	1411801	45º48'12"	14º57'41"	195	2009–2012
5	Postojna[2]	1411200	45º45'58"	14º11'34"	533	2009–
6	Kredarica[1]	1400800	46º22'45"	13º50'57"	2514	03/2010–
7	Rateče[1]	1400700	46º29'50"	13°42'47"	864	03/2010–
8	Bohinjska Češnjica[2]	1400601	46º17'39"	13º56'32"	595	03/2010–06/2014
9	Zgornja Radovna[3]	1400801	46º25'42"	13º56'36"	750	04/2010–
10	Podljubelj[3]	1401001	46º23'48"	14º17'17"	740	03/2010–06/2014
11	Velenje[5]	-	46º21'36"	15º07'43"	433	09/2012–05/2015
12	Murska Sobota[1]	-	46º39'08"	16º11'29"	189	2015–
13	Kleče[5]	-	n.r.	n.r.	n.r.	1997–1998
14	Blatnik[5]	-	n.r.	n.r.	n.r.	1998–1999
15	Ponikve[5]	-	n.r.	n.r.	n.r.	1998–1999
16	Sinji vrh[5]	-	n.r.	n.r.	n.r.	1999–2000
17	Sela na Krasu[3]	-	45º49'15"	13º37'38"	270	08/1999–10/2000
18	Selniška Dobrava[5]	-	46º32'	15º28'	295	1/2001–10/2005
19	Union brewery, Ljubljana[5]	-	n.r.	n.r.	n.r.	07/2003–06/2005
20	Postojna cave[5]	-	n.r.	n.r.	n.r.	2004–2005
21	Rogaška Slatina[5]	-	n.r.	n.r.	n.r.	2008–2010
22	Postojna Karst Research Institute[5]	-	n.r.	n.r.	n.r.	03/2010–02/2011
23	Ilirska Bistrica[5]	-	n.r.	n.r.	1043	03/2011–02/2012
24	Snežnik[5]	-	n.r.	n.r.	1300	03/2011–03/2012

ARSO climatological station Postojna (Fig. 1, Tab. 1, Lojen, personal communication) and the second at the ARSO precipitation station Dvor (Fig. 1, Tab. 1, Zavadlav, 2013). Because none of the sampling locations was situated in the mountainous, north-western part of Slovenia that represents an important water resource, we established in 2010 additional isotope monitoring of precipitation at five ARSO meteorological stations in the Julian Alps and Karavanke including the following: Kredarica, Rateče, Bohinjska Češnjica, Zgornja Radovna and Podljubelj (Fig.1, Tab. 1, Vreča et al., 2013). At all five locations stable and radioactive water isotopes (Vreča et al., 2013, 2015b; Vreča, 2015) were monitored until July 2014. Since then, monitoring has been continued at Kredarica, Rateče and Zgornja Radovna. In autumn 2012 monitoring of oxygen and hydrogen isotope composition in Velenje was established (Fig. 1, Tab. 1, Kanduč et al., 2014) and in 2015 also in north-eastern Slovenia at the ARSO synoptic station Murska Sobota (Lojen, personal communication).

Oxygen and hydrogen in precipitation were monitored monthly also at the Union brewery in Ljubljana during the period 2003–2005 by Trček (2005, 2006), at the Postojna cave in the period 2004–2005 by Kogovšek & Urbanc (2007), at Rogaška Slatina during the period 2008–2010 by Trček & Leis (2011) and at Ilirska Bistrica and Snežnik during 2011–2012 (Mance et al., 2014). In addition, the staff of the GeoZS performed monitoring at Klariči, Korentan, Ptuj and at their institute in Ljubljana (Urbanc, personal communication). Only the isotope composition of oxygen was monitored at Ljubljana (Kleče) in the period 1997–1998 by Urbanc & Jamnik (1998), at Blatnik and Ponikve in the period 1998–1999 by

Table 2. Sampling and analytical methods. HDPE – high-density polyethylene bottles with sealing caps, 50 and 500 mL; PE – polyethylene bottles with sealing caps; b-gl. – borosilicate glass bottles with double caps, 30 or 50 mL; b-pl. – plastic bottle; IRMS – isotope ratio mass spectrometer; CO_2 equil. – water-CO_2 equilibration technique; Zn red. to H_2 – zinc reduction method; Cr red. to H_2 – chromium reduction method; LAS – laser absorption spectroscopy; H_2 equil. – water-H_2 equilibration technique; GPC – gas proportional counting; LSC-EE – electrolytic enrichment liquid scintillation counting; filt. 589/1 – sample filtered through Grade 589/1; filt. 589/3 – sample filtered through Grade 589/3; n.d. – not determined, n.r. – not reported. For sampling collectors see Figure 2.

Location		Sampling collector	Sample bottles and analytical methods			References
			$\delta^{18}O$	$\delta^{2}H$	^{3}H	
1a	Ljubljana–Bežigrad	b	PE IRMS CO_2 equil.	PE IRMS Zn red. to H_2	PE GPC	Pezdič,1999, 2003 Vreča et al., 2008
1b	Ljubljana–IJS	a	PE IRMS CO_2 equil.	PE IRMS Zn red. to H_2 IRMS Cr red. to H_2	PE GPC	
1c	Ljubljana–Reaktor	a	filt. 589/1 PE, b-gl. IRMS CO_2 equil.	filt. 589/1 PE, b-gl. IRMS Cr red. to H_2	HDPE GPC, LSC-EE	Vreča et al., 2014
2	Portorož airport (until 2002)	d	PE IRMS CO_2 equil.	PE IRMS Cr red. to H_2	n.d. GPC	Vreča et al., 2005–2007, 2009, 2011, 2015a
	Portorož airport (since 2002)	b	filt. 589/1 b-gl. IRMS CO_2 equil.	filt. 589/1 b-gl. IRMS Cr red. to H_2	HDPE GPC, LSC-EE	
3	Kozina	b	filt. 589/1 PE, b-gl. IRMS (CO2 equil.)	filt. 589/1 PE, b-ql. IRMS Cr red. to H_2	HDPE GPC, LSC-EE	Vreča et al., 2005–2007, 2009
4	Dvor	b	filt. 589/3 HDPE IRMS CO_2 equil.	filt. 589/3 HDPE LAS	n.d.	Zavadlav, 2013 JSI unpublished data
5	Postojna	b	HDPE IRMS CO_2 equil. HDPE, b-gl. LAS	HDPE, b-gl. LAS	n.d.	Zavadlav et al., 2012 Mandić, 2013 JSI unpublished data
6	Kredarica	b	filt. 589/1 b-gl. IRMS CO_2 equil. filt. 589/1 HDPE, b-gl. LAS	filt. 589/1 HDPE, b-gl. LAS	filt. 589/1 HDPE LSC-EE	Vreča et al., 2012, 2015 JSI unpublished data
7	Rateče	b				
8	Bohinjska Češnjica	b				
9	Zgornja Radovna	b				
10	Podljubelj	b				
11	Velenje	other	IRMS CO_2 equil.	IRMS H_2 equil.	n.d.	Kanduč et al., 2014
12	Murska Sobota	b	b-gl. Analysis in progress	b-gl. Analysis in progress	n.d.	Lojen, personal communication
13	Kleče	n.r.	IRMS CO_2 equil.	n.d.	n.d.	Urbanc & Jamnik, 1998
14	Blatnik	n.r.	IRMS CO_2 equil.	n.d.	n.d.	Lapanje, 2000
15	Ponikve	n.r.	IRMS CO_2 equil.	n.d.	n.d.	Lapanje, 2000

Table 2. Sampling and analytical methods – continued.

Location		Sampling collector	Sample bottles and analytical methods			References
			δ^{18}O	**δ^2H**	**^{3}H**	
16	Sinji vrh	c	n.r.	n.r.	n.d.	Trček, 2003
17	Sela na Krasu	b	HDPE IRMS CO_2 equil.	HDPE IRMS Cr red. to H_2	n.d.	Doctor, 2002
18	Selniška Dobrava	c	b-pl. IRMS CO_2 equil.	b-pl. IRMS Cr red. to H_2	n.d.	Mali, 2006, Mali & Urbanc, 2009
19	Union brewery, Ljubljana	n.r.	n.r.	n.r.	n.d.	Trček, 2005, 2006
20	Postojna cave	c	n.r.	n.r.	n.d.	Kogovšek & Urbanc, 2007
21	Rogaška Slatina	n.r.	n.r.	n.r.	n.r.	Trček & Leis, 2011
22	Postojna Karst Research Institute	d	n.r.	n.d.	n.d.	Mandić, 2013
23	Ilirska Bistrica	d	IRMS CO_2 equil.	IRMS H_2 equil.	n.d.	Mance et al., 2014
24	Snežnik	d	IRMS CO_2 equil.	IRMS H_2 equil.	n.d.	Mance et al., 2014

Lapanje (2000), and at the Karst Research Institute in Postojna (ZRC SAZU) from June 2010 to February 2011 by Mandič (2013). Detailed data (i.e. coordinates) about these locations are not reported. The monitoring of tritium in precipitation, surface and groundwater is performed at other locations in Slovenia in the frame of national programmes approved by the Slovenian Nuclear Safety Administration (Kovačič, 2015 and references therein). Results of these investigations are not discussed in this paper.

To summarize, isotope composition of monthly precipitation was monitored in the period 1981–2015 at 30 different locations in Slovenia, however none of the monitoring operated continuously at the same location during the last 35 years. Data about sampling and analytical methods used for determining isotope composition (δ^{18}O, δ^2H and ^{3}H, if measured) are summarized in Tables 1 and 2 while the mean isotope values and LMWLs are presented in Table 3.

Sampling of precipitation for isotope analysis in Slovenia

Basic data about 26 locations are summarized in Table 1, which includes all available information like coordinates, sampling period, type of sampling station and GNIP code in case that the station is already or will be included in the worldwide database. Information about type of sampling collector and water sample treatment (filtration, types of storage bottle used) are presented in Table 2. The 15 locations with known coordinates (except Murska Sobota) are shown in Figure 1 and different types of sampling collectors are presented schematically in Figure 2.

The longest isotope record is available for Ljubljana (Fig.1, Tab. 1) and is maintained by the staff of the Department of Environmental Sciences of the JSI. Samples are collected from the precipitation collector (type a in Fig. 2) as soon as possible after the precipitation event (Vreča et al., 2014). Many stations (Fig. 1, Tab. 1) are part of the Slovenian national meteorological network maintained by the staff of ARSO where precipitation samples are collected from the collector (type b in Fig. 2, Tab. 2) either three times (synoptic stations) or once per day (climatological and precipitation stations). Details about sampling at Selniška Dobrava are described in Mali (2006). They collected precipitation from a system connected by a tube to a glass bottle (type c in Fig. 2). Similar collectors with an isolated vessel buried in the soil were used at Sinji vrh (Trček, 2003), at the Postojna cave (Kogovšek & Urbanc, 2007) and at four stations maintained by the GeoZS (Urbanc, personal communication). The high-density polyethylene (HDPE) collectors containing paraffin oil to prevent evaporation during sampling were used at four locations (Fig. 2d, Tab. 2), at Portorož until 2002 (Vreča et al., 2011), at Sela na Krasu (Doctor, 2002) and at Ilirska Bistrica and Snežnik (Mance et al., 2014). The collected water was separated from the oil at the end of the month. At Postojna (Mandič, 2013)

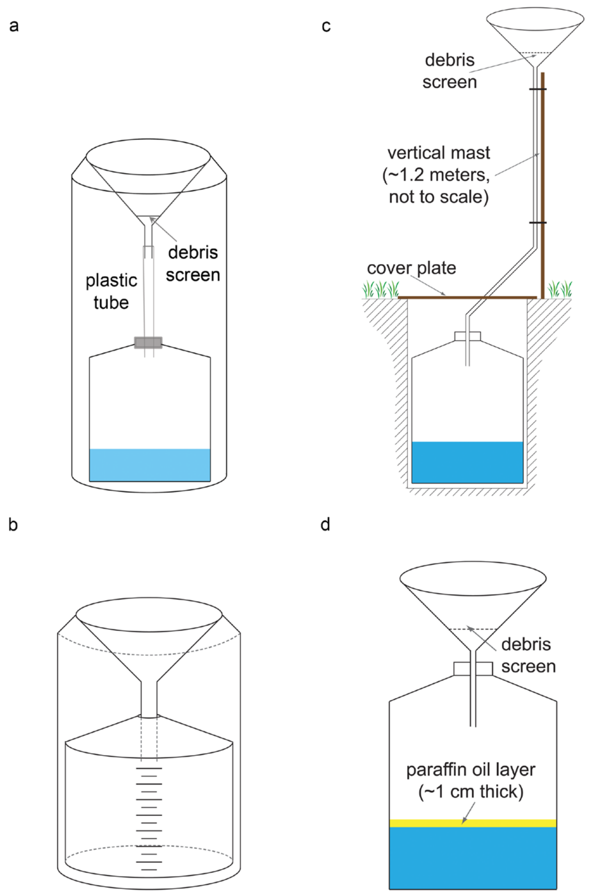

Fig. 2. Different types of collectors used for sampling of precipitation in Slovenia. a – collector used at Jožef Stefan Institute, b – collector used at meteorological stations, c – buried totalizer, d – totalizer with paraffin oil layer. Schematic presentations of type b, c and d collectors kindly provided by S. Terzer, IAEA.

precipitation was sampled also on the roof of the ZRC SAZU and integrated monthly samples were collected in a HDPE container with added paraffin oil. Walls of the collector were completely covered with aluminium foil and Styrofoam to achieve temperature stability and to prevent growth of algae. According to IAEA guidelines (Internet 3) approximately 0.5 cm film of paraffin is recommended. However, a thicker paraffin layer (approximately 1 cm) will be recommended in updated guidelines as shown schematically for sampling collector type d in Figure 2 (Terzer, personal communication). In Velenje HDPE collector was used (Kanduč et al., 2014). For Kleče, Blatnik, Ponikve, the Union brewery and Rogaška Slatina details about how the samples were collected are not given.

At the laboratory impurities (e.g. dust, particles) were removed from the samples collected at the stations Ljubljana–Reaktor, Portorož, Kredarica, Rateče, Bohinjska Češnjica, Zgornja Radovna and Podljubelj by filtration through 12–25 µm pore size ashless filter papers (Grade 589/1 Black Ribbon, Whatman, UK) before taking aliquots for the different isotope analyses (Vreča et al., 2014, 2015a). Zavadlav (2013) reports filtration of samples through 2 µm pore size ashless filters (Grade 589/3, Whatman, UK). For other sampling stations filtration of samples is not reported. Samples were stored either in polyethylene, HDPE or in borosilicate glass bottles (Tab. 2).

Analytical methods used for determining stable oxygen (δ^{18}O) and hydrogen (δ^{2}H) isotope composition

Oxygen isotope composition (δ^{18}O) was determined at all locations and in all cases the δ^{18}O was measured using the water-CO_2 equilibration technique (Epstein & Mayeda, 1953; Avak & Brand, 1995, Tab. 2). However, different IRMS were used including either a dual inlet Varian MAT 250 at JSI (Urbanc & Jamnik, 1999; Pezdič, 1999; Lapanje, 2000; Vreča et al., 2008, 2011), Finnigan DELTA^{plus} at the Joanneum Research (JR) in Graz, Austria (Mali, 2006; Mandič, 2013; Vreča et al., 2008, 2011), Thermo Finnigan DELTA^{plus} XP at the University of Rijeka (UR), Croatia (Mance et al., 2014) or a continuous flow IsoPrime IRMS at the JSI (Lojen, personal communication; Zavadlav, 2013; Zavadlav et al., 2012; Vreča et al., 2013, 2014, 2015a; Vreča, 2015). Doctor (2002) and Trček (2003, 2005, 2006) report that analyses were performed at the Institute of Groundwater Ecology (GSF) in Neuherberg, Germany but do not state the type of IRMS used for analysis. Kogovšek & Urbanc (2007), Trček & Leis (2011) report just that analyses were performed at the JR in Graz, Austria and Kanduč et al. (2014) at the National Institute of Geophysics and Volcanology (INVG) in Palermo, Italy. Investigations at Murska Sobota started in 2015 and sample analysis is in progress at the JSI. Samples collected by the GeoZS at four locations around Slovenia were analysed at the JSI (Urbanc, personal communication).

For certain samples (Tab. 2), δ^{18}O was determined by off-axis integrated cavity output laser absorption spectroscopy (LAS) (OA-ICOS, Los Gatos Research, Mountain View CA, United States of America) at the IAEA Isotope Hydrology Laboratory (IHL) in Austria according to the analytical protocol of Wassenaar et al. (2014).

Hydrogen isotope composition (δ^{2}H) was determined at 25 locations using different analytical methods. These included H_2 generated by reduction of water over hot zinc – Zn (Pezdič, 1999), reduction of water over hot chromium – Cr (Gehre et al., 1996; Morrison et al., 2001) or by water-H_2 equilibration using platinum – Pt

(Horita et al., 1989; Coplen et al., 1991, Tab. 2). Measurements were performed on different IRMS like the dual inlet Varian MAT 250 at JSI (Pezdič, 1999; Vreča et al., 2008, 2011) or the Finnigan DELTA^{plus} XP at the JR (Mali, 2006; Vreča et al., 2008, 2011, 2014, 2015a) and at the UR (Mance et al., 2014). Doctor (2002) reports that the chromium reduction method (Gehre et al., 1996) was used at the GSF, however similar as in Trček (2003, 2005, 2006) no information about the type of IRMS used for analysis is reported. Kogovšek & Urbanc (2007) and Trček & Leis (2011) report just that the analyses were performed at JR in Austria, while Kanduč et al. (2014) report that analyses were performed at the INVG. Investigations at Murska Sobota started in 2015 and sample analysis is in progress at the JSI. Samples collected by GeoZS at four locations around Slovenia are analysed at the JSI (Urbanc, personal communication).

For certain samples (Tab. 2), δ^2H was determined also by LAS at IAEA IHL according to the analytical protocol of Wassenaar et al. (2014).

Results are reported as δ values in per mill (‰) relative to the Vienna-SMOW standard (Coplen et al., 2002). Methods used in different laboratories are described in more detail in Pezdič (1999), Mali (2006) and Mandič (2013). The authors usually report that measurements were carried out together with laboratory standards calibrated periodically against international standards, as recommended by the IAEA and that the measurement precision was better than ±0.1 ‰ for δ^{18}O and ±1 ‰ for δ^2H. In some cases, better precision was reported (e.g. Trček & Leis, 2011).

Analytical methods used for determining tritium activity (^{3}H) if available together with stable isotope data

Tritium activity was monitored in the frame of SLONIP activities only at 11 locations (Tab. 2). Analyses of samples from Ljubljana, Portorož and Kozina were performed at the RBI either by the gas proportional counting (GPC) technique (Krajcar Bronič et al., 1998; Vreča et al., 2006, 2008, 2011 and references therein) or by the liquid scintillation counting technique (LSC) following electrolytic enrichment (EE) (Vreča et al., 2014, 2015a and references therein). In samples collected in the second half of 2003 in Ljubljana, Portorož and Kozina, ^{3}H activity was determined at the IHL after EE by the LSC technique (Vreča et al., 2006) while samples collected after 2010 were analysed after EE by LSC at the JSI (Vreča et al., 2014, 2015a, 2015b). Trček & Leis (2011) report only that ^{3}H measurements were performed in the Isotope laboratory HYDROSYS in Hungary.

Meteorological data

The most rational approach for monitoring isotopes in precipitation is to perform sampling at meteorological stations that are part of a national network such as the Swiss National Network for the observation of Isotopes in the Water Cycle – NISOT (Schürch et al., 2003). Therefore, the JSI cooperates with the staff of ARSO meteorological stations where meteorological data like precipitation and air temperature, are available from the ARSO database (Internet 4). We performed in the past isotope monitoring at 11 different ARSO stations (Tab.1, Fig. 1) and since 2015 sampling has been performed at six ARSO stations (Tab. 1). Unfortunately, air temperature data were not available for the majority of isotope monitoring stations including the ARSO precipitation stations: Sela na Krasu, Kozina, Dvor, Zgornja Radovna and Podljubelj, and therefore it was not possible to determine the relation between isotope composition and temperature. Precipitation data in numerical form (expressed in mm) for other than ARSO stations, except precipitation for Ljubljana–Reaktor (Vreča et al., 2014) are not reported. However, precipitation data are presented graphically by Trček (2003, 2006), Kogovšek & Urbanc (2007), and Mali & Urbanc (2009).

Data reduction

Most publications report basic descriptive statistics (mean δ^{18}O, δ^2H) while deuterium excess (*d*-excess) as defined by Dansgaard (1964) is not always calculated and reported. Even less publications report values weighted by the amount of precipitation and consequently the influence of precipitation amount at a particular location is not determined. As recommended by the IAEA (1992), the summations have to be calculated over all collected samples per year and per month over the period. The minimum required number of data is eight monthly measured samples per year and more than 70 % of total precipitation collected per year. For example, in Selniška Dobrava (Mali, 2006) these requirements were not fulfilled, many monthly data are missing and therefore caution is needed in future calculations and interpretations.

Reporting isotope data, mean isotope values and local meteoric water lines

Numerical data are evaluated and published for Ljubljana and Portorož until the end of 2010, and for the period 2011–2015 evaluation of the data is in progress. For Sela na Krasu (Doctor, 2002), Kozina (Vreča et al., 2005; GNIP database), Selniška Dobrava (Mali, 2006) and Velenje

(Kanduč et al., 2015) data are reported for the whole sampling period, while for Dvor only oxygen data for 2009 – 2010 are reported (Zavadlav, 2013). Evaluation of data collected by the JSI for the stations Kredarica, Rateče, Bohinjska Češnjica, Zgornja Radovna, Podljubelj, Dvor and Postojna for the whole sampling period is in progress. Figure 3 shows the number of evaluated or partly evaluated data for Ljubljana and the different regions of Slovenia. In the eastern part of the country, there is a deficiency of numerical data and the new data from Murska Sobota will help fill this data gap for NE part of the country.

Arithmetic and weighted means together with LMWLs as reported in publications are presented in Table 3. Complete data are only available for Ljubljana, Portorož and Kozina. Mean isotope composition of oxygen and hydrogen together with *d*-excess are reported for 13 locations, while tritium and weighted mean values are reported only rarely (Tab. 3). Arithmetic or weighted means can be further used for geostatistical evaluation of the data and modelling the geospatial distribution of water isotopes in precipitation. Vreca et al. (2010) reported the first presentation of such a map for oxygen isotope composition of precipitation over Slovenia in 2010. The spatial distribution of $\delta^{18}O$ in precipitation has been explained by a simple multiple regression model, based on the meteorological (temperature) and geographic factors (latitude and elevation) and a continuous digital map of the $\delta^{18}O$ distribution over Slovenia has been generated using GIS tools. Further evaluations of the data are in progress and will take into account data collected during the last 35 years. The review shows that the data sets, available for Slovenia during the same period, do not always overlap and therefore in spatial modelling, these gaps, have to be taken into account adequately. This is particularly important in the preparation of reliable geospatial maps and in their future implementation in water resources research, food authentication and other applications in Slovenia.

Authors report rarely local meteoric water lines (LMWL) and only in a few cases details about regression analysis are given (Tab. 3, Vreča et al. 2008, 2011, 2014, 2015a). For Ljubljana many different LMWLs are reported but users have to be aware of the details about different lines which are all close to the Global Meteoric Water Line (GMWL) defined by Craig (1961). Differences among the LMWLs are due to the different observation periods, number of data, or the type of regression calculations. These factors should be

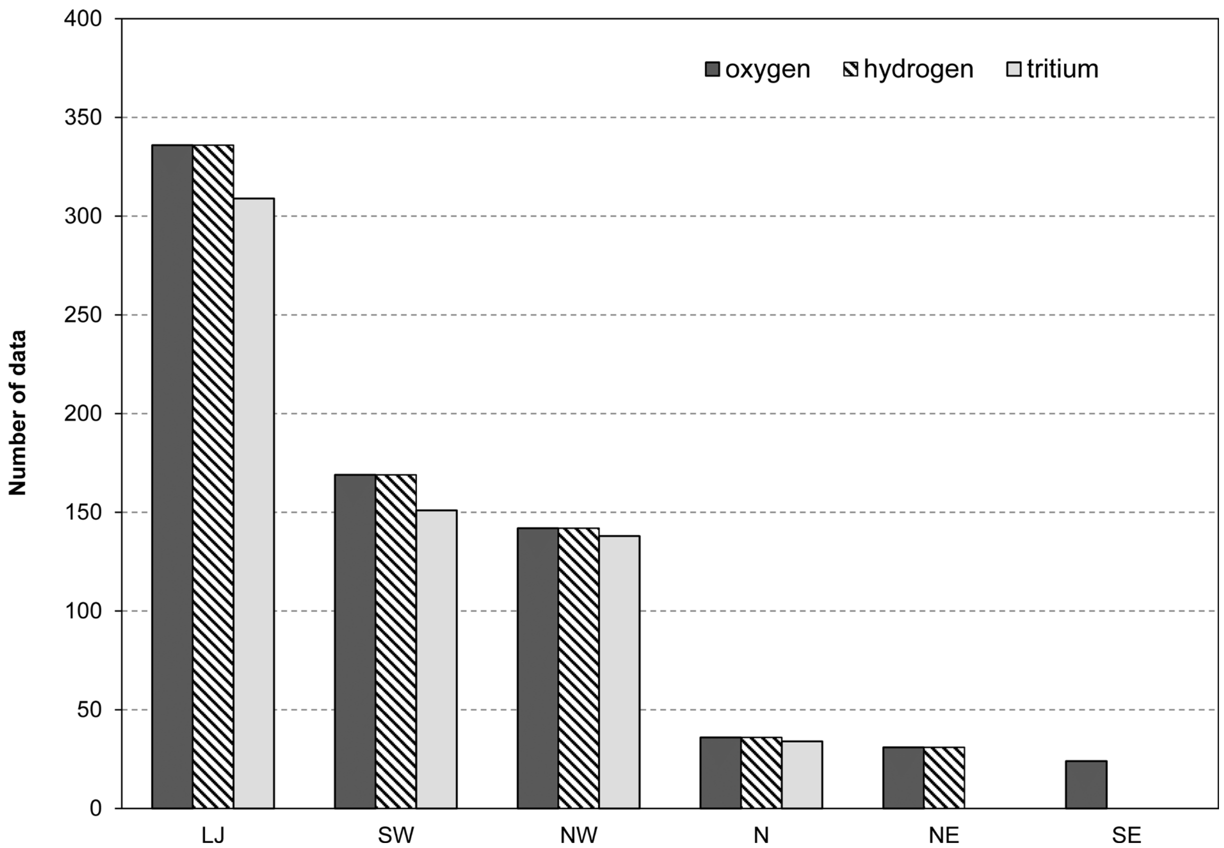

Fig. 3. Number of oxygen ($\delta^{18}O$), hydrogen ($\delta^{2}H$) and tritium (^{3}H) monthly data evaluated for Ljubljana (LJ) and different regions of Slovenia: south-western (SW – locations 2, 3 and 17 in Table 1), north-western (NW – locations 6 to 9 in Table 1), northern (N – location 10 in Table 1), north-eastern (NE – locations 11 and 18 in Table 1) and south-eastern (SE – location 4 in Table 1) part of Slovenia.

Table 3. Local meteoric water lines (LMWLs), arithmetic and weighted mean isotope values. LSF – least squares fit, RMA –reduced major axis regression (called also orthogonal regression), OLSF – ordinary least square regression, PWLSR – precipitation weighted least square regression, *– calculated from the available numeric data, n.d. – not determined, n.r. – not reported.

Location	Sampling period	LMWL	Arithmetic mean				Weighted mean				References
			$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	*d* (‰)	^{3}H (TU)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	*d* (‰)	^{3}H (TU)	
Ljubljana	n.r.	r = 0.99, n = 90 $\delta^{2}H = (8.197 \pm 0.276)\times\delta^{18}O + (10.834 \pm 2.468)$	−8.5	−60	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	Pezdič, 1999
Ljubljana	1982–1994	r = 0.99, n = 90 $\delta^{2}H = 8.83\times\delta^{18}O + 16.5$	n.r.	n.r.	n.r.	n.r.	−8.73	−60.6	n.r.	n.r.	Pezdič, 2003
Ljubljana	1981–1996	r = 0.99, n = 149 $\delta^{2}H = (8.1 \pm 0.1)\times\delta^{18}O + (11.1 \pm 0.8)$	-9.3	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	Krajcar Bronić et al., 1998
Ljubljana	1981–2006	LSF: r = 0.99, n = 290 $\delta^{2}H = (7.95 \pm 0.08)\times\delta^{18}O + (8.90 \pm 0.71)$ RMA: r = 0.99, n = 290 $\delta^{2}H = (8.06 \pm 0.08)\times\delta^{18}O + (9.84 \pm 0.71)$	−8.7 n=290	−60 n=290	9.4 n=290	16.4 n=264 9.3 n=92#	−8.57 n=290	−59.1 n=290	9.5 n=290	n.d.	Vreča et al., 2008 # - period 1998-2006
Ljubljana	2001–2003	RMA: r = 0.99, n = 36 $\delta^{2}H = (8.0 \pm 0.2)\times\delta^{18}O + (9.2 \pm 1.8)$	−8.3 n=36	−57 n=36	9.3 n=36	8.1 n=35	−8.1 n=36	−55 n=36	10.3 n=36	8.0 n=35	Vreča et al., 2006
Ljubljana	2007–2010	OLSF: r = 0.98, n = 46 $\delta^{2}H = (8.05 \pm 0.22)\times\delta^{18}O + (10.36 \pm 2.02)$ RMA: r = 0.98, n = 46 $\delta^{2}H = (8.19 \pm 0.22)\times\delta^{18}O + (11.52 \pm 1.97)$ PWLSR: r = 0.99, n = 46 $\delta^{2}H = (7.94 \pm 0.21)\times\delta^{18}O + (9.76 \pm 1.91)$	−8.6 n=46	−59 n=46	9.9 n=46	8.3 n=45	−8.7 n=46	−59 n=46	10.3 n=46	8.5 n=45	Vreča et al., 2014
Portorož airport	2001–2003	RMA: r = 0.96, n = 35 $\delta^{2}H = (7.7 \pm 0.4)\times\delta^{18}O + (7.3 \pm 2.2)$	−5.8 n=35	−38 n=35	9.2 n=35	6.9 n=34	−6.3 n=35	−40 n=35	10.3 n=35	6.3 n=34	Vreča et al., 2006

Location	Sampling period	LMWL	Arithmetic mean				Weighted mean				References
			$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	*d* (‰)	^{3}H (TU)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	*d* (‰)	^{3}H (TU)	
Portorož airport	2001–2006	LSF: r = 0.97, n = 74 $\delta^{2}H = (7.82 \pm 0.23)\times\delta^{18}O + (7.84 \pm 1.57)$	−6.5 n=74	−43 n=74	9.0 n=74	7.2 n=71	−6.6 n=71	−43 n=71	9.8 n=71	6.9 n=71	Vreča et al., 2011 Vreča et al., 2015a
		RMA: r = 0.97, n = 74 $\delta^{2}H = (8.05 \pm 0.22)\times\delta^{18}O + (9.35 \pm 1.55)$									
		PWLSR: r = 0.96, n = 71 $\delta^{2}H = (7.80 \pm 0.27)\times\delta^{18}O + (8.52 \pm 1.85)$									
Portorož airport	2007–2010	OLSF: r = 0.98, n = 47 $\delta^{2}H = (7.96 \pm 0.28)\times\delta^{18}O + (7.15 \pm 1.81)$	−6.1 n=47	−41 n=47	7.4 n=47	7.2 n=47	−6.28 n=47	−41.6 n=47	8.6 n=47	6.4 n=47	Vreča et al., 2015a
		RMA: r = 0.98, n = 47 $\delta^{2}H = (8.14 \pm 0.25)\times\delta^{18}O + (8.28 \pm 1.64)$									
		PWLSR: r = 0.99, n = 47 $\delta^{2}H = (7.87 \pm 0.28)\times\delta^{18}O + (7.97 \pm 1.87)$									
Kozina	2001–2003	RMA: r = 0.97, n = 36 $\delta^{2}H = (7.7 \pm 0.3)\times\delta^{18}O + (9.6 \pm 2.2)$	−7.2 n=36	−46 n=36	11.6 n=36	5.6 n=33	−7.8 n=36	−50 n=36	12.2 n=36	5.4 n=33	Vreča et al., 2006 Vreča et al., 2007
Kredarica	04/2010–03/2013	Data analysis in progress	−11.3 n=36	−76 n=36	14.5 n=36	7.9 n=36	n.d.	n.d.	n.d.	7.9 n=36	Vreča, 2015 Vreča et al., 2015b
Rateče	04/2010–03/2013	Data analysis in progress	−10.6 n=35	−74 n=35	11.1 n=35	7.5 n=35	n.d.	n.d.	n.d.	7.6 n=35	
Bohinjska Češnjica	04/2010–03/2013	Data analysis in progress	−8.7 n=36	−59 n=36	10.6 n=36	7.4 n=33	n.d.	n.d.	n.d.	6.8 n=33	
Zgornja Radovna	04/2010–03/2013	Data analysis in progress	−9.7 n=36	−66 n=36	11.5 n=36	7.5 n=34	n.d.	n.d.	n.d.	7.3 n=34	
Podljubelj	04/2010–03/2013	Data analysis in progress	−9.4 n=36	−65 n=36	9.7 n=36	7.8 n=34	n.d.	n.d.	n.d.	7.6 n=34	

Location	Sampling period	LMWL	Arithmetic mean				Weighted mean				References
			$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	*d* (‰)	^{3}H (TU)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	*d* (‰)	^{3}H (TU)	
Dvor	2009–2010	n.r.	−10.4 n=24	n.r.	n.r.	n.d.	n.d.	n.d.	n.d.	n.d.	Zavadlav, 2013
Postojna (location 5)	2009–2010	n.r.	−8.35	n.r.	n.r.	n.d.	n.r.	n.r.	n.r.	n.d.	Zavadlav et al., 2012
Postojna (location 5)	03/2010–12/2010	n.r.	−7.81 n=10	n.r.	n.r.	n.d.	n.r.	n.r.	n.r.	n.d.	Mandić, 2013
Postojna (location 22)	06/2010–02/2011	n.d.	−7.40 n=5	n.r.	n.r.	n.d.	n.r.	n.r.	n.r.	n.d.	Mandić, 2013
Kleče	1997–1998	n.d.	−8.47 n=10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Urbanc & Jamnik, 1998
Blatnik	08.05.–13.11.1998	n.d.	−7.25	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Lapanje, 2000
	13.11.1998–07.04.1999	n.d.	−13.89	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	07.04.–15.05.1999	n.d.	−7.87	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Ponikve	08.05.–13.11.1998	n.d.	−7.89	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Lapanje, 2000
	13.11.1998–07.04.1999	n.d.	−14.36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	07.04.–15.05.1999	n.d.	−8.75	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Sinji vrh	1999–2000	$\delta^{2}H = 8.10 \times \delta^{18}O + 13.64$	−7.00 n=11	−43.20 n=11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Trček, 2003

Location	Sampling period	LMWL	Arithmetic mean				Weighted mean				References
			$\delta^{18}O$ (‰)	δ^2H (‰)	*d* (‰)	^3H (TU)	$\delta^{18}O$ (‰)	δ^2H (‰)	*d* (‰)	^3H (TU)	
Sela na Krasu	08/1999–10/2000	OLSF: r = 0.99, n = 12 $\delta^2H = (7.22 \pm 0.31)\times\delta^{18}O + (6.62 \pm 2.15)$	–6.44 n=12	–39.9 n=12	11.7 n=12	n.d.	–6.71 n=12	–41.8 n=12	11.9 n=12	n.d.	Doctor, 2002*
		RMA: r = 0.99, n = 12 $\delta^2H = (7.28 \pm 0.28)\times\delta^{18}O + (7.05 \pm 1.97)$									
Sela na Krasu	08/1999–07/2000 (96% of annual precipitation)	n.d.	–6.50 n=10	–40.1 n=10	11.9 n=10	n.d.	–6.47 n=10	–40.0 n=10	11.8 n=10	n.d.	Doctor, 2002*
	11/1999–10/2000 (80% of annual precipitation)	n.d.	–7.08 n=9	–44.5 n=9	12.1 n=9	n.d.	–7.31 n=9	–46.2 n=9	12.2 n=9	n.d.	
Selniška Dobrava	01/2010–10/2005	r = 0.99 $\delta^2H = 7.296\times\delta^{18}O + 1.8373$	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	Mali, 2006
Selniška Dobrava	01/2010–10/2005	OLSF: r = 0.99, n = 31 $\delta^2H = (7.33 \pm 0.17)\times\delta^{18}O + (1.85 \pm 1.60)$	–8.71 n=31	–61.97 n=31	7.69 n=31	n.d.	n.d.	n.d.	n.d.	n.d.	Mali, 2006*
		RMA: r = 0.99, n = 31 $\delta^2H = (7.39 \pm 0.17)\times\delta^{18}O + (2.35 \pm 1.55)$									
Union brewery, Ljubljana	2003–2005, I. phase	n.r.	–9.07	–67.00	10.45	n.d.	n.d.	n.d.	n.d.	n.d.	Trček, 2006
	2003–2005, II. phase	n.r.	–8.12	–56.95	11.72	n.d.	n.d.	n.d.	n.d.	n.d.	
Postojna cave	2004–2005	n.r.	–9.0	n.r.	n.r.	n.d.	n.d.	n.d.	n.d.	n.d.	Kogovšek & Urbanc, 2007
Rogaška Slatina	2008–2010	r = 0.99 $\delta^2H = 8.44\times\delta^{18}O + 14.74$	n.r.	n.r.	n.r.	n.r.	n.d.	n.d.	n.d.	n.d.	Trček & Leis, 2011

taken into account in future applications. In the case of LMWLs reported by Pezdič (1999, 2003), Trček (2003), Mali (2006) and Trček & Leis (2011) for Sinji vrh, Selniška Dobrava and Rogaška Slatina it is not clear how the lines were calculated. According to the IAEA (1992) and Hughes & Crawford (2012), the linear correlations between δ^2H and δ^{18}O can be calculated by the methods usually applied in stable isotope studies – either by the ordinary least squares regression (OLSF, previously called least squares fit – LSF) or the reduced major axis (RMA, called also orthogonal) regression. More recently, Hughes & Crawford (2012) introduced the precipitation weighted least squares regression (PWLSR) method, which takes into account precipitation in a particular month. The lines are defined as local meteoric water lines ($LMWL_{OLSF}$, $LMWL_{RMA}$ and $LMWL_{PWLSR}$) and can be significantly different (Hughes & Crawford, 2012). Such an approach was in Slovenia used only by Vreča et al. (2014, 2015a) for the 2007–2010 isotope records at Ljubljana and Portorož and should be in the future used in all such investigations.

For Sela na Krasu numerical data and precipitation amount are reported and it was possible to perform additional calculations (Tab. 3). Similarly, we calculated the LMWLs for Selniška Dobrava based on data reported by Mali (2006). In both cases caution is needed in further use of the reported data and LMWLs. At Sela na Krasu sampling was performed for less than two years which is insufficient to obtain representative information about a particular location. At Selniška Dobrava sampling was performed for almost five years but only 31 monthly data are available, among them 11 collected in Autumn–Winter and 20 in Spring–Summer. Such a distribution of collected precipitation samples causes a bias of the mean values towards more positive isotope values.

Conclusions

Based on all collected information, we prepared a list of the main gaps in the research and general recommendations for future work in the frame of SLONIP. The list of main gaps includes limited information about sampling location (e.g. missing coordinates), sampling mode (e.g. type of collector, sampling period, sampling frequency, sample treatment and sample storage), and methods (e.g. instrumentation, quality control, measurement uncertainty). Different researchers have used different approaches and only rarely have the IAEA guidelines (Internet 3) been strictly followed. Often additional meteorological data and data evaluations are also missing. During the last 35 years isotope techniques and evaluation approaches have also changed and developed. The main problem is that only a limited amount of data collected at a particular station is publically available and in many cases numerical data is only presented in graphical form. In addition, only part of the data set provided by the JSI is available in the international GNIP database. This is mainly due to the lengthy and expensive measurements in the past, limited and old infrastructure and insufficient financial support in the frame of short-term projects. For this reason, the JSI has cooperated with different laboratories like the RBI from Croatia and the JR and the IAEA from Austria to collect isotope data, and other researchers from Slovenia have often cooperated with foreign laboratories. In 2015 the infrastructure at the JSI was upgraded and now enables independent continuation of monitoring of water isotopes in precipitation in Slovenia. At the JSI we intend to continue with sampling and analysing the monthly precipitation at seven locations in the frame of SLONIP and will focus on more rapid publication and accessibility of the data.

General recommendations for future work in the field of isotope in precipitation monitoring are in detail presented in the IAEA/GNIP precipitation sampling guide (Internet 3) and have been greatly improved during the last few years (update in progress). In addition, we recommend that Slovenian researchers collect samples at the ARSO stations maintained daily by the staff of the station, filtration of samples through ashless filter papers (Grade 589/1 Black Ribbon) and the storage of samples in doubly capped borosilicate glass bottles for stable isotope analysis and in HDPE bottles for tritium analysis. When researchers send samples to laboratories we also suggest they communicate with the lab in advance regarding the sampling and storage of samples and to collect all details about measurements (i.e. type of instrument, calibration and procedure, quality control, reference materials used, measurement uncertainty). Finally, it is very important to report numerical data and evaluate data according to IAEA guidelines (1992) and Hughes & Crawford (2012) and to clearly describe how the data is evaluated.

Development in the field of isotope hydrology has brought a lot of new but complex knowledge. Therefore, it is very important to collect all listed information and report it properly, particularly because nowadays precipitation isotope data are used widely in temporal and spatial investigations of the atmo-, hydro-, bio- and geosphere. Due to the importance of water isotope data it is clear that inappropriate sampling, storage, analyses and finally data evaluation can lead to wrong interpretations, for instance of spatial and temporal predictions of water isotope values at different scales.

Acknowledgements

This paper was prepared in the frame of the programme P1-0143 and Slovenian-Hungarian cooperation project N1-0054 financed by the Slovenian Research Agency and the EU project ISO-FOOD ERA Chair. The work of J. Pezdič who initiated monitoring of isotopic composition of precipitation in Ljubljana and of all colleagues from JSI, RBI, JR, IAEA, ARSO and other institutions who participated to SLONIP during 35 years is greatly acknowledged. We thank also the two reviewers for their critical revisions that helped to improve the manuscript, S. Terzer for providing schematic figures of sampling collectors, D. Kocman and J. A. Robinson for help with graphics and D. Heath for linguistic corrections.

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GEOLOGIJA 59/1, 85-98, Ljubljana 2016

http://dx.doi.org/10.5474/geologija.2016.006

Groundwater under strong influence of surface water – case study from Črneče (Northern Slovenia)

Podzemna voda pod močnim vplivom površinske vode – primer Črneč v severni Sloveniji

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Prejeto / Received 22. 6. 2016; Sprejeto / Accepted 12. 7. 2016; Objavljeno na spletu / Published online 11. 8. 2016

Key words: groundwater level maps, groundwater flow direction, hyporeic zone, floods, Drava River
Ključne besede: karte gladin podzemne vode, smer toka podzemne vode, obrežno območje, poplave, reka Drava

Abstract

The article presents an analysis of the nine-year long data set of groundwater levels measurements in the influence area of the Drava River in Črneče in the southern Koroška (Carinthia – N Slovenia). Statistical analysis of the groundwater levels fluctuations, flow rates and stages of the Drava River were performed. It is followed by analysis of the interrelation between the groundwater level observations and mutual comparison between the groundwater level and river stages. Particular emphasis is placed on the analysis of the impact of extreme flood event on 05.11.2012 on groundwater levels, which caused catastrophic flooding throughout the whole Slovenian part of the Drava River Valley. With the help of groundwater level maps it is illustrated that in the hyporeic zone of the river intensive change in the distribution of groundwater flow field is undergoing. We are dealing with both the inflow of river water in the aquifer, as the outflow of groundwater into the river, and sometimes with the flow of groundwater which is parallel to the river bank.

Izvleček

V članku prikazujemo analizo devetletnega niza podatkov meritev gladin podzemne vode na vplivnem območju reke Drave pri Črnečah na Koroškem. Podana je statistična analiza nihanja gladin podzemne vode, pretokov in pretočnih višin reke Drave. Sledi analiza medsebojnega odnosa med opazovanji podzemne vode na posameznih mestih, ter medsebojna primerjava gladin podzemne vode in pretočnih višin reke. Poseben poudarek je dan na analizi vpliva ekstremnega poplavnega dogodka dne 05.11.2012, ko je Drava poplavila po celotni dolini. S pomočjo analize kart gladin podzemne vode je prikazano, da se v obrežnem pasu reke dogajajo intenzivne spremembe njene dinamike. Opraviti imamo tako z vtokom rečne vode v vodonosnik, kot z iztokom podzemne vode v reko, ter s tokom podzemne vode, ki je vzporeden rečnemu bregu.

Introduction

Groundwater and surface waters are strongly related and very often representing boundary conditions to each other; whether groundwater is seeping into the surface stream or surface water infiltrates into the aquifer. Particularly interesting is the transition zone between both, usually referred as a bank or hyporeic zone. This zone represents important groundwater storage as well as having very important ecological role. Interactions between the groundwater and the surface water are very often studied and scientific literature about the topic is very extensive. It is a well investigated problem with the application of various methods (Kalbus et al., 2006). Results and conclusions of these studies are thoroughly summarised in various review papers (Sophocleus, 2002; Hayashi & Rosenbery, 2002).

In Slovenia, looking from regional prospective, relation between surface water and groundwater is very important. Several bigger water supply systems taping water from the aquifers are depending on the infiltrated surface water. At the same time several rivers are substantially recharged through the base flow originating from groundwater. However, in spite of the great importance of interaction between alluvial aquifers and surface waters, not many results are published. Aquifer of Ljubljansko polje is recharged through the infiltration of Sava River (Breznik, 1969; Bračič Železnik et al., 2005); the phenomena was studied by water balance methods (Andjelov et al., 2005), tracer experiments (Auersperger et al., 2005) and stable isotopes (Urbanc & Jamnik, 1998). Well known is also interaction between groundwater and surface water on Sorško polje where a phenomenon was studied by classical hydogeological methods (Žlebnik, 1975) as well as with geochemistry and stable isotopes (Urbanc & Jamnik, 2008). Infiltration of Iška River into the alluvial aquifer of Ljubljansko Barje was studied by Breznik (1975), interaction between Mura River and groundwater in the low land of Pomurje is also important (Globevnik & Mikoš, 2009) and relation between groundwater and surface water and their influence on the hydrogeological conditions in Velenje Coal Mine were thoroughly studied as well (Kanduč et al., 2010; 2014).

One of the biggest surface water courses in Slovenia is the Drava River with specific hydrological regime due to the late season melting of snow and ice in its headwaters area. Second largest Slovenian city Maribor in large part depends on the drinking water supply under the strong influence of the Drava River. To the best of the authors' knowledge the only published study in the scientific literature dealing with surface water and groundwater interaction under the influence of the Drava River in Slovenian part is a paper written by Žlebnik (1965).

In the paper as a case study relation between surface water and groundwater is represented for the area near Črneče in the northern part of Slovenia. Data of groundwater level for the analysis are coming from operational groundwater monitoring for Črneče municipal landfill which is positioned very close to the right bank of the Drava River. Groundwater level observations were performed according to the requirements enacted in Slovenian "Rules on the operational monitoring of underground water pollution" (Official Gazette RS, No. 49/2006) and are in their starting point not intended to be applicable for the observing relations between the Drava River and groundwater on its right bank. Groundwater level observations started in March 2007 with the approximate frequency of two measurements per month. At the time of paper preparation nine years of consecutive observations are available. Observations offer opportunity to study relation between groundwater in highly permeable unconfined alluvial aquifer and surface water.

For the Črneče site in the paper are presented: 1) results of groundwater level monitoring, 2) groundwater level frequency analysis, 3) representative groundwater level maps, 4) relation between river level and groundwater level, 5) relation between groundwater level and catastrophic flood event, and finally 6) interpretation and conclusions.

General settings

Geographical position

Investigated area is located in the northern Slovenia in the Drava River Valley 3 km west of the city Dravograd (Fig. 1). The groundwater monitoring network used in the study is positioned around the municipality landfill Črneče standing on the western rim of Črneško polje (Črneče field) near the village of Črneče on the right bank of the Drava River. Access to the area is through the regional road Dravograd – Libeliče.

Geomorphologicaly the Črneče site is positioned in the transition area between the flooding plain of the Drava River in the north and high river terrace in the south. Flooding plain surface is positioned at approximately 341 m a.s.l. which in this part is relatively narrow and up to 50 m wide. Flatter part of the river terrace is positioned between 366 and 372 m a.s.l. and its rim extends in the approximate direction of east-west parallel to the river. Landfill is positioned in the former gravel pit (Fig.1) where sand and gravel material was excavated from the terrace sediments (Fig. 2). Surface area of the landfill is 11,280 m^2. On the south hill Črneška gora (Črneče Mountain) is present which rises up to 1,061 m a.s.l. On the western edge of the landfill is small creek flowing in the direction from south to the north into the Drava River (Fig. 1). Exact discharge of the creek was not measured, but according to its recharge area mean discharges are in the order of 50 l/s. Surrounding area of the landfill is covered by the mixed forest. Wider area is mainly covered with the agricultural fields.

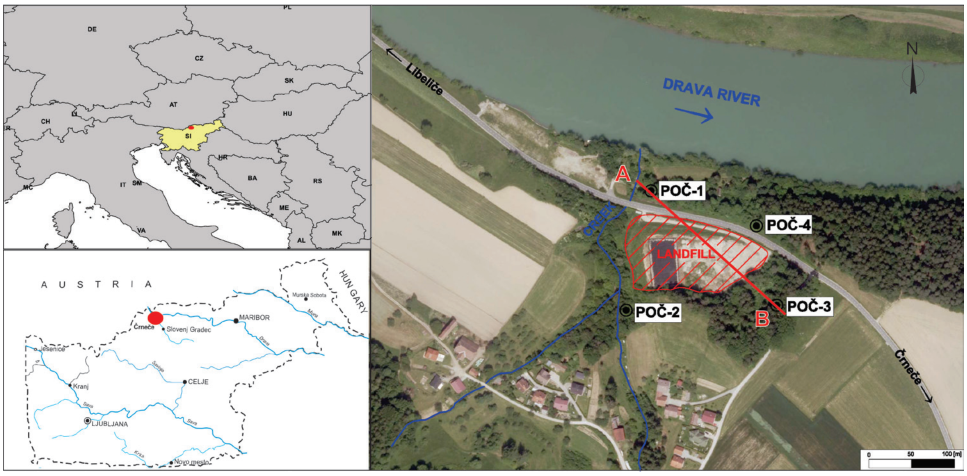


Fig. 1. Geographical position of the study site Črneče (AB – position of hydrogeological profile).

Geology of the area

Geology of the area is represented with two geological units. The bedrock consists of metamorphic rocks of Palaeozoic age above which Quaternary sediments are deposited (Fig. 2). Boreholes around the landfill reveal that in the bedrock micashist is present. According to general geologic map it consists of biotite, muscovite, quartz and plagioclase, in some parts biotite is altered by chloritisation process. It is also possible that fine to medium grained muscovite – biotite gneiss is present in the bedrock (Mioč, 1978; 1983). Bedrock surface is positioned in the interval between 332.50 and 333.00 m a.s.l. Only at the south-western corner bedrock surface is slightly higher at approximately 334.5 m a.s.l.

Basic geological map of the wider area defines four terraces (Mioč, 1978: 1983; Mioč & Žnidarčič, 1978: 1983). At the Črneče site only two terraces can be discerned; lower terrace near the Drava River and higher terrace south of the landfill. Quaternary sediments are predominantly coarse grained with some pebbles with the diameter larger than 20 cm. Sediments are poorly sorted with larger grains dispersed inside of the fine grains of sand and even sandy clay sediment. Grains consist of metamorphic and magmatic rocks with some grains of carbonate rocks. The thickness of the quaternary sediments depends on the position according to the terrace. In the western part of the investigated area the thickness of the Quaternary sediments is 11.5 m (observation borehole POČ-1, Fig. 2) but in the eastern part where surface starts to rise toward the south the depth is 27 m (observation borehole POČ-4). At the top of the terrace the thickness of Quaternary sediments is 36 m.

Groundwater monitoring network

In the groundwater monitoring network four observation boreholes are present. They are positioned in slightly deformed parallelogram around the landfill (Fig. 1) forming the inside area of 32,340 m^2. Boreholes POČ-1 and POČ-4 are positioned in the flooding plain near the Drava River. Borehole POČ-2 is positioned in the small creek valley and borehole POČ-3 is positioned on the top of the terrace.

Boreholes were made in 2005 by air-rotary drilling. They are constructed as standing open pipes equipped with PVC-U DN 100 casing used for drinking water. Filter perforation is 1 mm and no gravel pack was constructed. All boreholes were drilled 2 m deep into the bedrock where settlement tank was constructed. Observation borehole's heads are equipped with the standard type head produced by OTT Company. After completion all boreholes were cleaned with air-lift until clean water flowed out from the borehole. Boreholes are regularly cleaned by the air-lift with the frequency once per two or three years. Other technical details of observation boreholes are given in the Table 1.

Table 1. Construction data of the observation boreholes at Črneče site.

Observation borehole	Perpendicular distance from the river [m]	Altitude of observation borehole head [m a.s.l.]	Depth [m]	Interval of filters [m]
POČ-1	39	344.12	13.5	5.5 – 11.5
POČ-2	183	352.44	20.0	10.0 – 18.0
POČ-3	142	368.00	38.0	24.0 – 36.0
POČ-4	55	359.89	29.0	21.0 – 27.0

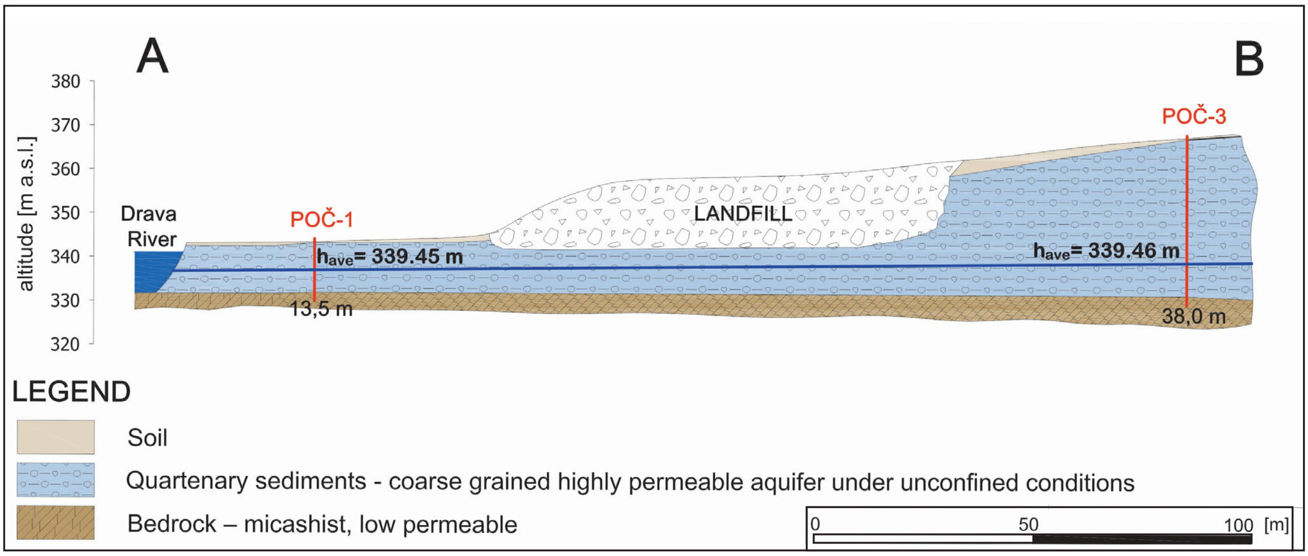


Fig. 2. Hydogeological profile (for the position see Fig. 1).

Data sets

Following data sets are available for the analysis; groundwater level observations at the Črneče landfill site, discharge level and discharge data at gauging station Črneče on the Drava River and discharge level measurements at Dravograd hydropower plant. Available data sets differ among each other in the number of available data. Not all direct comparisons between different sets can be made. Differences in the data sets are the consequence of data availability for the analysis and conditions under which gauging stations were operated in the past.

Groundwater level measurements at the landfill site Črneče started on 21.03.2007. Available data set of groundwater level measurements spans until the end of the year 2015 (last measuring date 21.12.2015). Measurements are performed with the manual groundwater dipper by the staff of Municipality Supply Company of Dravograd on nearly regular frequency of two weeks. On observation boreholes POČ-1 and POČ-2 data set consist of 210 measurements and on observation boreholes POČ-3 and POČ-4 data set consists of 208 measurements.

Environmental Agency of Slovenia - ARSO is managing discharge gauging station Črneče on the Drava River (LON 14.98870865°; LAT 46.59820803°) which is positioned on the right bank of the river in the air distance of 540 m from the landfill observation borehole POČ-1. Zero level of the gauging station (z_0) is defined at 333.765 m a.s.l. Contributing area of the gauging station is represented by the surface of 12,057 km^2 and it is positioned at the change of 432.48 km from the confluence with the Danube River. Station started operation in year 2007; however, data are only partially available (ARSO, 2016b). The gauging station Črneče is specific because it is positioned in the damming area of the hydropower plant Dravograd which is in the downstream direction in the distance of 3,750 m; consequently at some times backward flow in the river bed is present influencing the accuracy of the calculated discharges.

At the time of paper preparation two sets of data were available for the gauging station Črneče. One set of data originates from the web hydrological archive of surface waters (ARSO, 2016b); there only average daily discharges for the period 01.01.2012 to 31.12.2012 and daily average stage data from 01.01.2014 to 31.12.2014 are available. Second set of data, not available on the web page, was obtained directly from ARSO. In this set average daily discharge data for the years 2011 to 2013 are available and therefore for analysis complete data set of average daily discharges for the period from 01.01.2011 to 31.12.2014 can be used. In this data set 968 daily data are available with the data gap between 01.01.2013 to 08.05.2013. In the data set available directly from ARSO are also daily (average) stage data. They are available for the period from 10.04.2009 to 31.08.2014, altogether 1,612 data. In the record two data gaps are present; first from 27.12.2009 to 04.06.2010 and second from 05.11.2012 to 09.05.2013; the latter is the consequence of catastrophic flood event which destroyed gauging station. After the reconstruction of the gauging station zero gauging level (z_0) has changed to 333.46 m a.s.l. This happens to represent step change in the time series of stage data causing none-homogeneity of data. Additionally other step change was detected in the data between 31.12.2011 and 01.01.2012. All step changes were manually corrected to the levels similar at stable hydrological regime before the catastrophic flood event. Such manual homogenisation procedure is justified with further analyses where only relative reactions of groundwater to changes in river regime were observed.

Gauging station HE Dravograd is operated by the hydropower plant Dravograd and discharges are transferred to the data base of ARSO where they are available on the web hydrological archive of surface waters (ARSO, 2016c). The gauging station (LON 15.02349159°; LAT 46.58695904°) is positioned on the dam of the hydropower plant. Zero level of the gauging station is not defined. Catchment area of the gauging station is represented by the surface of 12,071 km^2 and it is positioned at the change of 428.82 km from the confluence with the Danube. Station started with the operation in year 1952; however discharge data are available from 01.01.1965 until 31.12.2014; altogether 18,259 data. Year 1967 was removed from our analysis due to spurious data.

Methods

Only simple methods were used for analyses. Descriptive statistics, duration curves, indicator diagrams and kriging procedures are briefly described as follows.

Descriptive statistics were calculated for analysed data sets. First quartile value is assigned with the index 25 (e.g. for groundwater level h_{25}, for the discharges Q_{25}) and third quartile with the index 75. Interquartile range IQR is defined as a difference between third and first quartile.

Duration curves are based on the ranking of values from the lowest (i=1) to the highest (i=N). Relative frequency F in % of certain observation is defined as F = 100/(N+1) where N is total number of observations. Duration represents share of total observation period with the groundwater level lower than certain value.

Groundwater level indicator diagram is represented as a scatter plot where in each axis data from one of the neighbouring observation boreholes are plotted.

Groundwater level maps were drawn with the help of kriging procedure implemented in the software Surfer 10 (GoldenSoft Inc., 2011). Results of the kriging procedure were transferred into AutoCAD MAP 3D (Auto Desk, 2014) where manually corrected surface was generated whenever it was necessary due to artificial shapes in groundwater generated by the kriging procedure.

Results and interpretation

Drava River discharges

Reliable estimates of the Drava River discharges can be made at the gauging station HE Dravograd. Exception are minimum discharges which are difficult to estimate reliably. From the data analysis follow that two periods in the record are present; first from 1965 to 1995 and second from 1995 to 2014 (Fig. 3). Such behaviour indicates strong none-homogeneity in data series. For the period 1965 to 1995 minimum monthly discharge of 71.0 m^3/s was measured on 06.02.1972; this is also minimum value for the minimum average daily discharge. For this period average minimum monthly discharge was 184.5 m^3/s. After 1995 the appearances of minimum monthly discharges changed, sharp drop in the behaviour of minimum discharges is present (Fig. 3). Until the end of the observation period 0 m^3/s discharges are reported 112 times, before that period no reports are available on zero discharges; among 228 records available during this second period zero discharges represent a share of 49 %. For the period 1995 to 2014 average minimum monthly discharge is 38.0 m^3/s and minimum average daily discharge calculated from averaged daily discharges was 58.9 m^3/s. Two possible explanations for such change in the behaviour of minimum monthly discharges are possible. First, it indicates that that discharge over the dam of hydropower plant was not present and that there was no flow in the river above the dam, therefore stage of the river was also stable. Another possibility for such behaviour is change in the gauging profile or the discharge measuring method, however this is highly unlikely.

Average daily discharge for the period 1965 – 2014 is 260 m^3/s with Q_{25} of 158 m^3/s and Q_{75} of 322 m^3/s. For the period of 1965 to 1995 average discharge is 264.1 m^3/s and for the period 1995 to 2014 average discharge is 254.3 m^3/s. Absolute record value for the maximum discharges is 2,570 m^3/s measured on 05.11.2012 when catastrophic flood happened. This discharge is much larger compared to the discharge of 1,961 m^3/s recorded on 20.08.1966. Catastrophic event of November 2012 must be regarded as separate and exceptional event discussed further in more details. If we do not consider catastrophic event of 2012 the average maximum monthly discharge in the period 1965 – 2014 is 509 m^3/s.

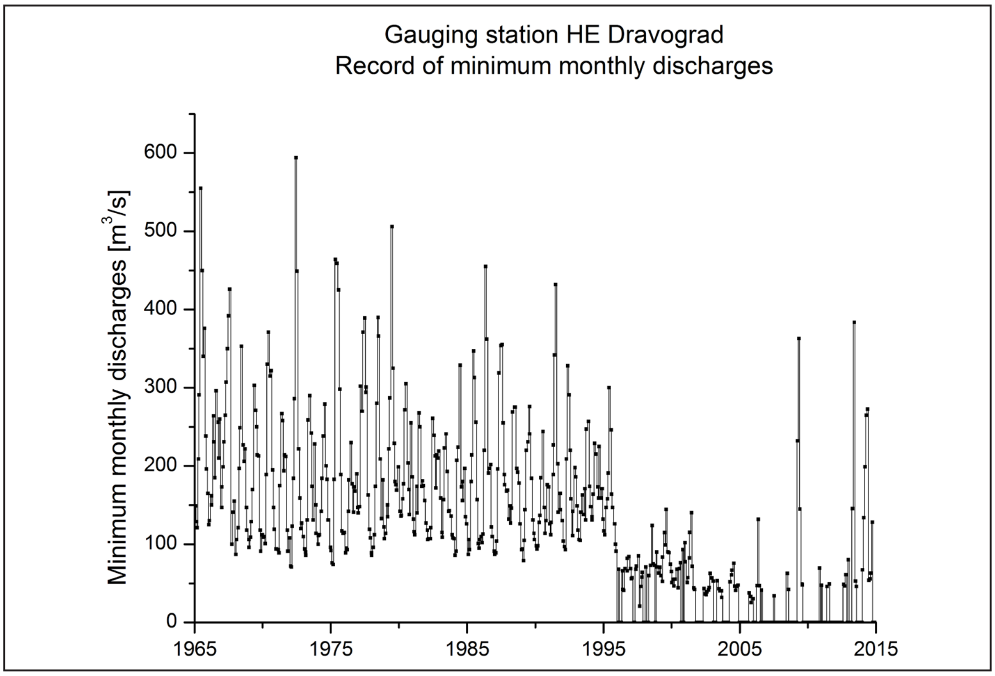


Fig. 3. Minimum monthly discharges at gauging station HE Dravograd

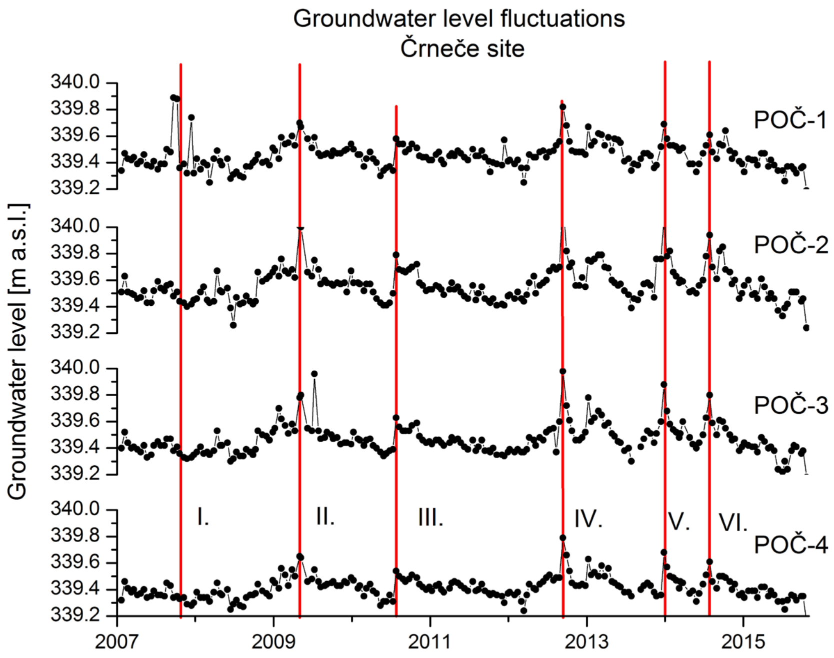


Fig. 4. Groundwater level fluctuations at Črneče site marked with significant hydrological events.

At Črneče gauging station in the period between 2011 – 2013 average daily discharge was 277.9 m^3/s, for the same period at gauging station HE Dravograd average daily discharge was 272.0 m^3/s. Comparing both gauging stations relative difference represents 0.9 % which from the accuracy point of view is negligible.

Groundwater level fluctuations

Descriptive statistics of groundwater fluctuation for the period from 2007 to the end of 2015 are given in the Table 2 and graphically time series are represented in Fig. 4. From the comparison of median and average values it follows that distribution of groundwater levels is symmetrical because values are nearly identical. Ranges are showing that amplitude of the groundwater fluctuation is rather small; the largest fluctuation is observed at the observation borehole POČ-2 which is positioned near small creek flowing to the Drava River, the smallest fluctuations are observed for the observation boreholes POČ-1 and POČ-4 which are in close vicinity of the river. Calculations of first quartile values h_{25} and third quartile values h_{75} are showing the interquartile range IQR is very small, the largest is again for the observation borehole POČ-2, but for the POČ-1 and POČ-4 observation boreholes fluctuations are also very small. This means that during the majority of the observation period 50 % of all the time, groundwater is very stable and fluctuates only for several centimetres.

Table 2. Descriptive statistics of groundwater level fluctuations

Descriptive statistics [m]	Observation boreholes			
	POČ-1	POČ-2	POČ-3	POČ-4
min	339.19	339.24	339.18	339.16
h_{25}	339.39	339.47	339.39	339.36
median	339.45	339.55	339.45	339.41
average	339.45	339.57	339.46	339.41
h_{75}	339.50	339.63	339.52	339.46
max	339.89	340.20	339.98	339.79
range	0.70	0.96	0.80	0.63
IQR	0.11	0.16	0.13	0.10

Several significant hydrological events with relatively fast rise of groundwater level can be detected from the Fig. 4 where six events are marked with vertical lines. Some of these events can not be detected in all observation boreholes. Event I. from November 2007 can be detected only in the observation borehole POČ-1. In the entire observation period for this borehole it is the highest detected groundwater level of 339.89 m a.s.l. Event II. was detected in June 2009 and event III. was detected in September 2010. The most important event detected in all observation boreholes is marked as IV. and is concomitant to catastrophic flood of November 2012. Unfortunately the measurement had been taken four days after the maximum flood stage when groundwater level was already in the declining stage. Exact flood related peak at maximum is not known. The event V. was detected in February 2014 and event VI. at the end of the year 2014.

Stable groundwater levels can be also illustrated with the duration curve. In the Fig. 5 only the duration curve for observation borehole POČ-1 is illustrated because other observation boreholes are showing similar behaviour. The

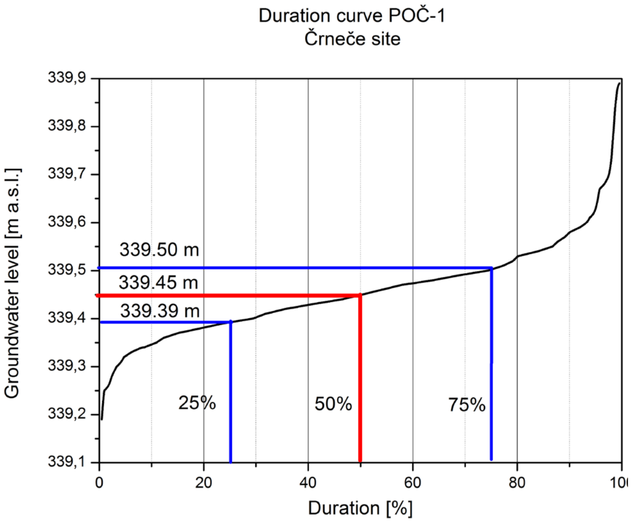


Fig. 5. Duration curve of groundwater level for observation borehole POČ-1

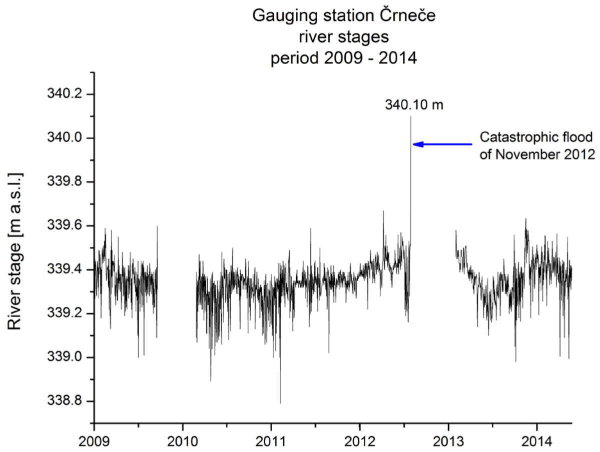


Fig. 6. River stages at Črneče gauging station

duration curve has a profound S shape illustrating that events at both extremes are very rare; low and high values are appearing only occasionally.

River stages fluctuations

Fluctuations of river stages at the gauging station Črneče for the period from 10.04.2009 to 31.08.2014 are illustrated on the Fig. 6. Maximum stage of 340.10 m a.s.l. was recorded on 05.11.2012 as a consequence of the catastrophic flood. After this event station was not in the operation until May 2013. Minimum stage of 338.79 m a.s.l. was recorded on 18.05.2011. Total difference between maximum and minimum stage is only 1.21 m. In the rest of the diagram rather fast fluctuations, short drops or short rises can be observed. Such behaviour is illustration of the river level damming at hydropower plant Dravograd, showing that stage is relatively constant and at the same time changes in the stage are fast. Amplitudes of fluctuations are changing rather fast but usually they are not exceeding 0.4 m.

Groundwater level indicator diagrams

For detection of groundwater level dynamics four groundwater level indicator diagrams were drawn on the Fig. 7; three diagrams are representing comparison with the groundwater levels in the borehole POČ-1 and the fourth represents comparison between groundwater levels between observation boreholes POČ-4 and POČ-3. In all diagrams line 1:1 is drawn.

In the Fig. 7A comparison between POČ- 1 and POČ-2 is represented. Borehole POČ-1 is positioned near the Drava River and observation borehole POČ-2 is positioned in the creek valley near the rim of the upper terrace. In the diagram nearly all data points are positioned above the line 1:1 indicating that groundwater level in the borehole POČ-2 in majority of cases is higher than in the borehole POČ-1, therefore it can be interpreted as an observation borehole which is positioned in upstream position. Only some small number of points are positioned below the 1:1 line indicating that groundwater levels at those observation times in borehole POČ-1 were higher. According to the position of this borehole such high groundwater levels can be only the consequence of the Drava River higher stages. Some data points in the upper part of the diagram are showing that in the observation borehole POČ-2 groundwater is much higher than in the borehole POČ-1 which is the consequence of the relatively fast inflow of the groundwater from the background of the borehole POČ-2 and also infiltration of the creek water into the aquifer.

In the diagram of Fig. 7B comparison between observation boreholes POČ-1 and POČ-3 is shown. Observation borehole POČ-3 is positioned on the top of the terrace. Data points in majority are positioned around 1:1 line indicating that groundwater level relation between boreholes is changing; sometimes groundwater level in the borehole POČ-1 is higher than in the borehole POČ-3 and reverse. Some data points are positioned out of the line 1:1; those well below the line 1:1 are indicating flooding water intruding from the Drava River and those above the line 1:1 are indicating water coming from the southern hinterland of the terrace.

In the diagram of Fig. 7C relations between groundwater levels in the observation boreholes POČ-1 and POČ-4 are shown. Both boreholes are positioned bellow the terrace and are very close to the Drava River. Therefore, it is interesting that nearly all the data points are positioned below line 1:1 showing groundwater levels in POČ-4 are slightly lower than in the POČ-

1 which indicates that the later is positioned in the upstream position. Again in the lower right part of the diagram some data points are indicating direct influence of the Drava River on observation borehole POČ-1 but at the same time this influence is not detected in the borehole POČ-4.

On the diagram of Fig. 7D comparison between observation boreholes POČ-4 and POČ-3 is shown. Both boreholes are forming profile which is perpendicular to the Drava River. Nearly all data points are positioned above the line 1:1 indicating that in majority nearly all observations in observation borehole POČ-3 are higher than in the observation borehole POČ-4 showing POČ-3 is in the upstream direction. Only few observation data are positioned bellow the line 1:1. They are measured at relatively low water conditions indicating when groundwater level in the aquifer is at very low level river water penetrate much further in the aquifer.

Relation between groundwater level and river stage

For the comparison between the Drava River stages and groundwater level observation borehole POČ-1 was chosen (Fig. 8). POČ-1 observation borehole is taken because it is the closest observation borehole to the river. Reported the Drava River stages from the ARSO data base (ARSO, 2016b) were slightly shifted for 0.1 m higher to have direct comparison between groundwater level and stages. The shift was estimated on the comparison between average levels and stages. In the diagram with vertical lines are indicated important hydrological events (see Fig. 4).

From the diagram in Fig. 8 follows that groundwater levels and stage levels are related. But relation between groundwater levels and river stages is not straightforward; there is no direct correlation which indicates that groundwater level in the borehole POČ-1 is the only consequence of

Groundwater level indicator diagrams

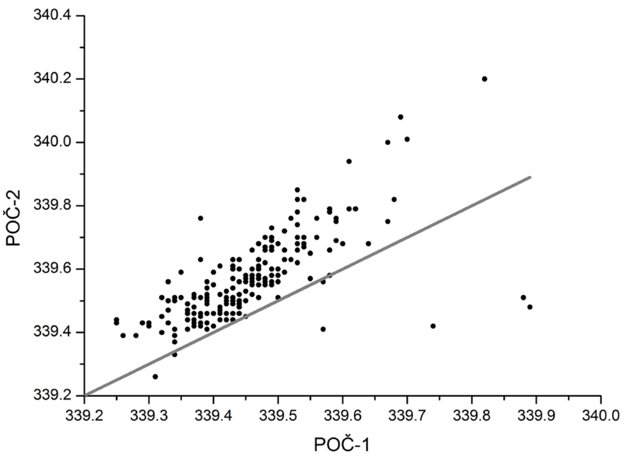


Fig. 7A. Relation between observations in boreholes POČ-1 and POČ-2.

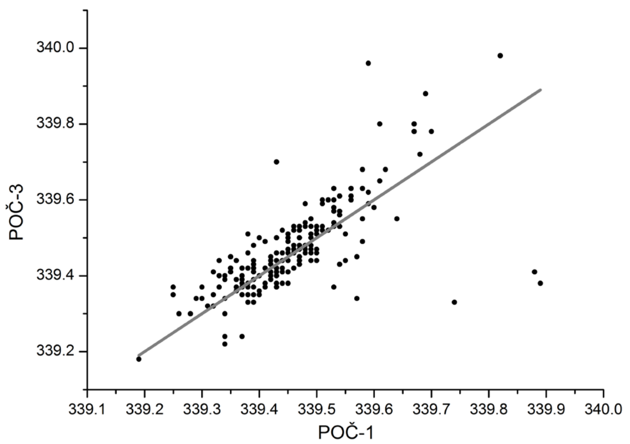


Fig. 7B. Relation between observations in boreholes POČ-1 and POČ-3.

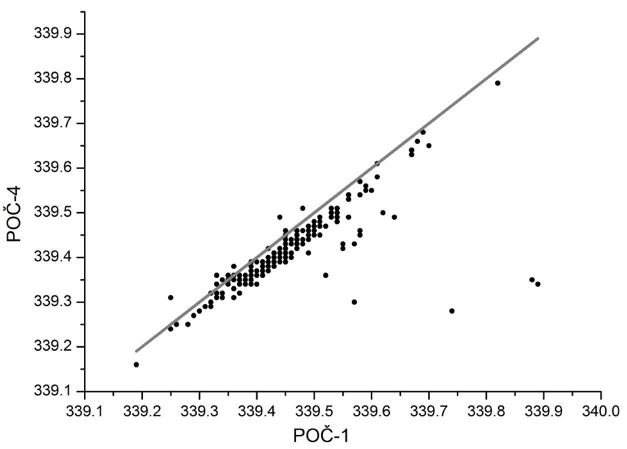


Fig. 7C. Relation between observations in boreholes POČ-1 and POČ-4.

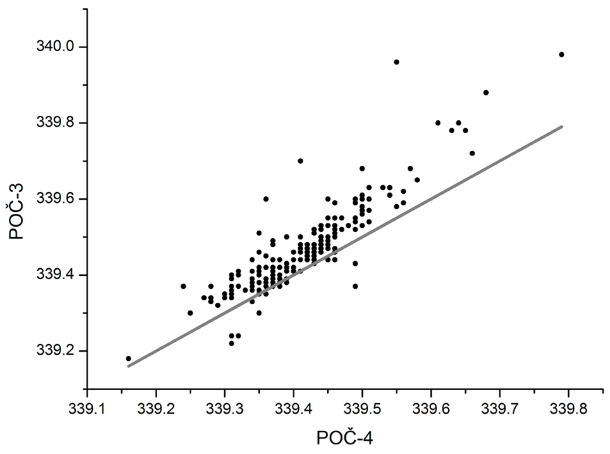


Fig. 7D. Relation between observations in boreholes POČ-4 and POČ-3.

the Drava River stages and fluctuation. There is indication that sometimes the Drava River stage is higher than groundwater level and reverse and there is practically no direct equilibrium with the same levels and stages. Lowering of the stages in the river causes lowering in the groundwater level and rising stages in the river is causing rising in the groundwater levels. Diagram also indicates that changes in the groundwater levels in the aquifer are slower than in the changes of the river stages; influences of the river are damped. Changes in the river stages in the sense of lowering and rising are too fast to be reflected fully in the groundwater levels. Groundwater level in the borehole POČ-1 is also influenced also by the inflow from the south. Among detected hydrological events (see also Fig. 4) all events are caused by higher river stages. For the event V. river stage data are not available.

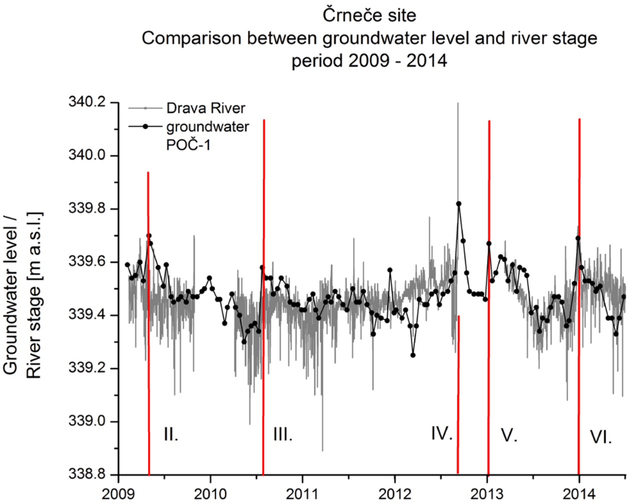


Fig. 8. Comparison between groundwater level in observation borehole POČ-1 and river stages at gauging station Črneče.

Catastrophic flood event in November 2012

During the observation period in November 2012 an exceptional flood event occurred. On 05.11.2012 discharge record values at Dravograd were reached. High flood wave caused damage of the gauging station Črneče which stopped working. According to the data set for gauging station HE Dravograd available at hydrological archive (ARSO, 2016c) record discharge was 2570 m^3/s but later analyses reveal somehow different estimates. According to Kobold (2013) and Kobold and co-workers (2013) discharges were higher than 2,600 m^3/s, Anzeljc & Kobold (2013) estimated discharge at gauging station Črneče on 2,669 m^3/s. Estimated return period was around 100 years. Such discharge was the consequence of the heavy rainfall from 04.11.2012 and 05.11.2012 falling on the snow which started to thaw. The discharges at gauging station started to rise fast in the morning at 3 a.m 05.11.2012 and reached their peak between 12 and 15 p.m. of the same day. Record discharge caused severe flooding in the down-stream direction along the valley and several settlements were severely damaged. High flood peak and sharp discharge rises were the consequence of improper emptying of the hydropower plant reservoirs in the upstream direction in Austria (Anzeljc & Kobold, 2013). By analysis it was also estimated how the discharges will behave if there will be no intervention with fast emptying of reservoirs behind the dams in Austria. Discharge will be in the interval between 1,790 and 1,980 m^3/s with the return period of around 20 years and the peak arrival to the site between 14 and 21 a.m. on 05.11.2012. (Anzeljc & Kobold, 2013).

Detailed diagram of the November 2012 event is illustrated in the Fig. 9. Due to the malfunction of the gauging station it is not known if the area around observation boreholes POČ-1 and POČ- 4 during the event was flooded. Unfortunately, groundwater level measurements were performed only 4 days after the flood peak and the exact level of groundwater during the flooding is not known. From the diagram (Fig. 9) follows that flood influenced groundwater levels but these influences quickly fade out. High groundwater levels probably last only few days after flood event.

We suppose that groundwater monitoring data from November 2012 until January 2015 are representing drainage of the aquifer. At the same time we conceptually assume that aquifer is linear reservoir where the draining curve can be described by the exponential equation. If we extrapolate this curve groundwater level at the peak of the flood

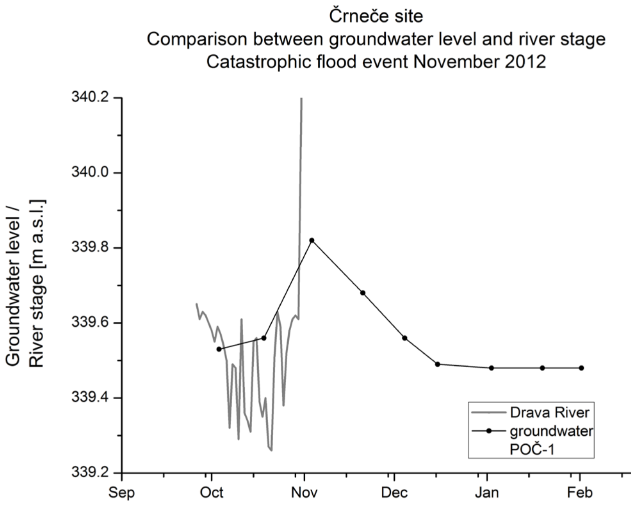
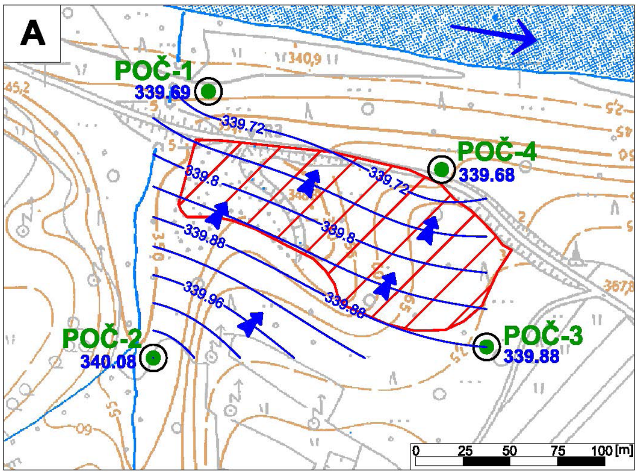


Fig. 9. Comparison between groundwater level in observation borehole POČ-1 and river stages at gauging station Črneče during flood event in November 2012.

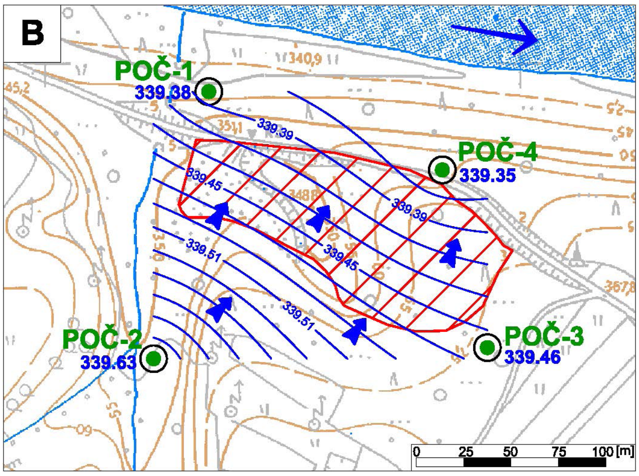
event can be estimated. The value obtained with extrapolation is 339.85 m a.s.l. which is surprisingly low. We can question extrapolation procedure but it somehow shows that if the flood event was relatively short it has no profound influences on the groundwater levels; the flood has influence on the groundwater but consequent rise of groundwater level was not substantial.

Groundwater level maps

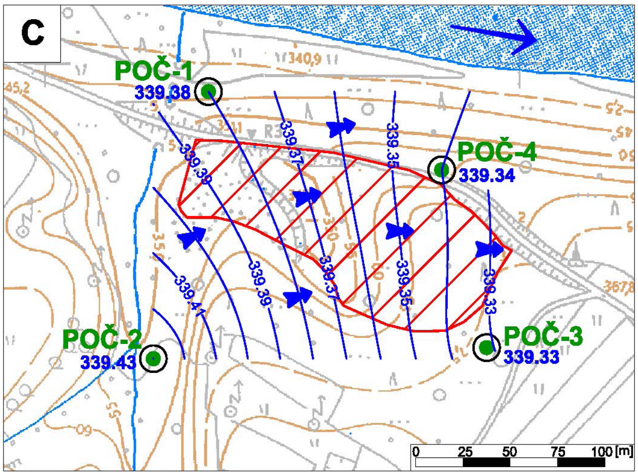
Based on the groundwater level observation it is possible to reconstruct the groundwater level maps. In spite of the fact that groundwater fluctuation in the observation boreholes is not exceeding 1.0 m dynamics of groundwater is diverse and several realisations of groundwater surface were detected.



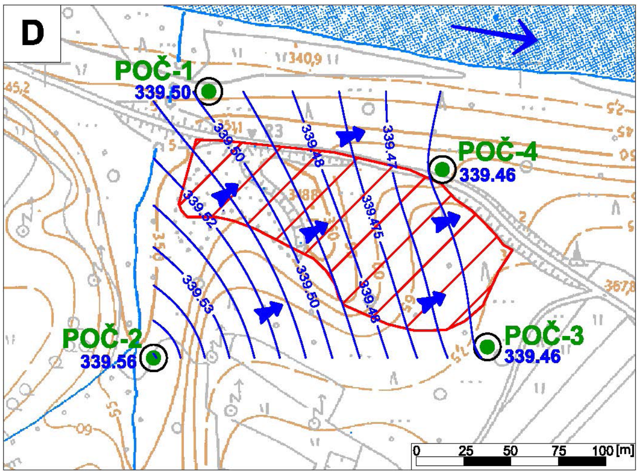
Groundwater level map of the typical high level conditions - 24.02.2014



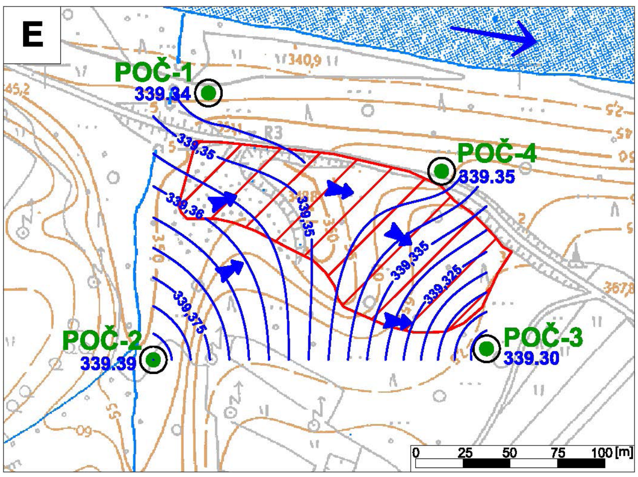
Groundwater level map of the typical low level conditions - 09.02.2009



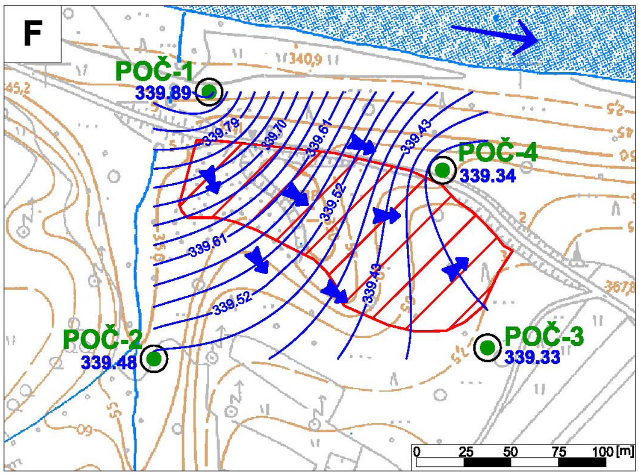
Groundwater level map as a result of water infiltration from the creek and river at high stage 19.07.2007



Groundwater level map as a result of water infiltration from the creek and low river stage 16.09.2011



Groundwater level map as a result of water infiltration from the creek and river when creek is at low water conditions 25.09.2013



Groundwater level map of the strong river influence - 19.11.2007

Fig. 10. Groundwater level maps at different hydrological conditions.

For the understanding of the groundwater surface shape at the Črneče site it is important to recognise boundary conditions. In the northern part the Drava River is present and small creek flowing from the south to the river represents western boundary. Due to the altitude which rises to the south and terrace sediments, it is expected that from there gravity induced recharge is present. To the east boundary is open and some hundreds meters away possible boundaries are not known to us. Typical and the most interesting reconstructed situations are represented on the Figs. 10 A – F.

In Figs. 10A and 10B most frequent situations of groundwater level are present. In the Fig. 10A situation at high groundwater level conditions is present and in Fig. 10B at low water conditions. In both cases groundwater is flowing from the south to the north recharging the Drava River. From the boundary conditions in the west of the map it is evident that water from the creek is infiltrating into the aquifer stabilising groundwater level at that part. At higher groundwater level (Fig. 10A) hydraulic gradient is slightly higher (2.7×10^{-3}) comparing to lower groundwater level represented in the Fig. 10B (1.7×10^{-3}).

Situations represented in Figs. 10C and 10D are showing conditions where groundwater level is at the same time under the influence of water infiltrating from the creek and water infiltrating from the Drava River. Groundwater flow direction is deflected more to the east direction comparing to predominant flow directions shown previously on Figs 10A and 10B. The deflection from this direction depends on the intrusion of water from the Drava River; if the river is at higher stage more water is flowing into the aquifer from the riverbed, and if river stage is lower less water is infiltrating from the riverbed. At the situation on Fig. 10C there is more influence from the Drava River than in the case represented on the Fig. 10D.

Last two situations shown on Figs. 10E and 10F are very rare, they happened only few times. In the Fig. 10E situation is represented where strong groundwater flow parallel to the bank of the Drava River is present. Groundwater is flowing transversally from observation borehole POČ-1 towards POČ-3 and at the same time infiltration of surface water from the creek is present.

Last situation presented in the Fig. 10F is also very rare. It represents sudden intrusion of river water into the aquifer. In observation borehole POČ-1 groundwater is rather high and in other boreholes low and consequently from northwest corner river water is dispersing into the aquifer. These data are indicating that river infiltrates into the aquifer and flows in the direction NW-SE from observation borehole POČ-1 to POČ-4 and POČ-3. Such behaviour of groundwater flow was detected also with the indicator diagram on Fig. 7D. No data are available about the presence of water in the creek at the time of map 10F, but the creek was probably dry or at very low water conditions and no infiltration was present from its bed allowing river to intrude further into the aquifer.

Interpretation of groundwater dynamics

Groundwater flow field in the aquifer on the right bank of the Drava River at the Črneče site is the consequence of the interrelation between infiltrating water from the river and inflow of groundwater from the southern hinterland. Three main flow directions are present; first is inflow from the Drava River, second is infiltration of water from the creek and third is inflow of groundwater from the south. Groundwater level maps are showing that infiltration from the creek bed is influencing groundwater level on the west. If stage of the river is low than groundwater flow direction is parallel to the creek bed and it has direction from the south to the north. If stage of the river water is higher, than groundwater on the northern part, near the bank, falls under the influence of the river which intrudes into the aquifer. Inflow of the river water into the aquifer is dependant on the relative position between the river stage and groundwater level. If this difference is small than infiltrating river water pushes groundwater incoming from the south to the east direction and groundwater infiltrating river water is flowing parallel to the river bank. If the river stage becomes much higher water from the river is infiltrating further into the aquifer.

The Drava River is damming the groundwater and this is, together with relatively high permeability of the aquifer and its unconfined conditions, the main cause why relatively low groundwater hydraulic gradients are present at all events. In spite of the low hydraulic gradients, strong changes in the groundwater flow directions are present and changes are such that nearly all directions of flow are possible. Predominant groundwater flow is from the south to the north; very often groundwater flow parallel to the river bank from west to east direction is present. Sometimes on rare occasions fast intrusion of river water into the aquifer happens and in this case water from the river penetrates farer into the aquifer, first flowing from north to south and later from northwest to southeast.

Conclusions

Detailed study of the groundwater level fluctuations near the bank of the Drava River shows that in spite of the fact that high resolution data of groundwater level and river stages are not available, many important characteristics of groundwater fluctuation in the bank zone can be discerned. Groundwater flow in the area under the influence of the river must be observed and interpreted in three dimensions. We have illustrated that groundwater flow is changing due to the conditions not only in the river but also in the recharge area outside of the river influences. On the combination of all conditions at the aquifer boundaries depends what groundwater surface will form and to which direction groundwater will flow.

In the future Črneče site can represent useful polygon for further research on the interrelation and interdependencies between surface water and groundwater. As we have shown groundwater flow in the influence area on the rivers' bank must be observed from the spatial and three dimensional points of view. It remains open how equipotential lines inside of the aquifer are distributed under the river stage and groundwater inflow changing conditions. This can be solved only with the help of three dimensional numerical models. Understanding of the processes can be also improved by the introduction of continuous measurements of groundwater level fluctuations as well as river stages fluctuations gaining more detailed information on changes. Further insights can also be possible with the help of geochemical studies. Available data based on the chemical status of groundwater and sampling of stable isotopes during different hydrological events can be very helpful.

Acknowledgement

Municipality Supply Company of Dravograd (Javno komunalno podjetje Dravograd d.o.o.) is greatly acknowledged for allowing us to use their data. Hermina Ivanuša Šket from National Laboratory for Health Environment and Food from Maribor is acknowledged for the long and fruitful cooperation on the monitoring projects. Dr. Mira Kobold and staff of the Department for hydrological analyses and prognoses, ARSO (Sektor za analize in prognoze površinskih voda, ARSO) are acknowledged for making data of Črneče and HE Dravograd gauging stations available. The paper is part of the activities guided under the research program "Groundwater and geochemistry" (P1-0020) of Geological Survey of Slovenia financially supported by Slovenian Research Agency. The paper has been prepared by the senior author during his stay supported by CEEPUS scholarship in summer 2016 at Department of Applied Geology, Eötvös Loránd University, Budapest (HU).

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GEOLOGIJA 59/1, 99-114, Ljubljana 2016
http://dx.doi.org/10.5474/geologija.2016.007

Stanje izkoriščanja geotermalne energije in nekateri zanimivi dosežki v geotermalnih raziskavah in razvoju v svetu

The state of exploitation of geothermal energy and some interesting achievements in geothermal research and development in the world

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Prejeto / Received 29. 6. 2016; Sprejeto / Accepted 13. 7. 2016; Objavljeno na spletu / Published online 11. 8. 2016

Ključne besede: geotermalna energija, geotermalna elektrika, neposredna raba geotermalne energije, geotermalne toplotne črpalke, svet, Slovenija, znanstveno-tehnološki dosežki

Key words: geothermal energy, geothermal electricity, direct use of geothermal energy, geothermal heat pumps, World, Slovenia, scientific-technological achievements

Izvleček

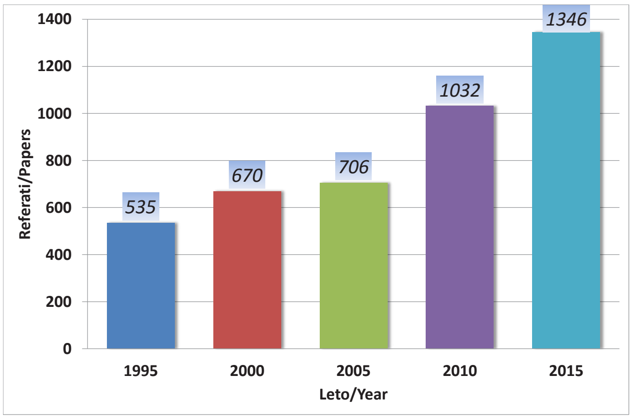
Pričujoči pregledni članek prikazuje najnovejše stanje izkoriščanja geotermalne energije v svetu in primerjavo s prejšnjim obdobjem, tako v proizvodnji električne energije kot v različnih kategorijah neposredne rabe. Proizvodnja elektrike iz geotermalnih elektrarn s skoraj 12,8 GW_e moči se odvija v 26 državah in je ob koncu leta 2014 dosegla 73.700 GWh. To je še vedno le 0,31 % vse proizvedene elektrike na svetu in pri tem bo zanimivo spremljati bodoči delež. V zadnjem petletnem obdobju je bil razvoj hiter predvsem v državah, kjer je bil le-ta v preteklosti počasnejši in, seveda, z ugodnimi geološkimi (tektonskimi) pogoji (Islandija, Kenija, Nova Zelandija, Turčija itd.). Neposredna raba geotermalne energije zajema bistveno več držav, danes kar 82, čeprav je med njimi nekaj takšnih, kjer se to odvija skoraj zgolj z geotermalnimi toplotnimi črpalkami (GTČ) na energijo plitvega podzemlja (Finska). Inštalirana moč v neposredni rabi znaša 70.885 MW_t in izkoriščena geotermalna energija, vključno z GTČ, kar 592.638 TJ/leto (ob koncu 2014). V izkoriščeni energiji prevladuje delež GTČ s kar 55,2 %, sledijo bazenski kompleksi za kopanje in plavanje z balneologijo z 20,2 %, ogrevanje prostorov s 15,0 % (večina za daljinsko ogrevanje), ogrevanje rastlinjakov in tal s 4,9 %, itd. V drugem delu prikazujemo nekaj zanimivih tehnoloških in znanstvenih novosti pri raziskavah in izkoriščanju geotermalne energije.

Abstract

The article presents the latest status of geothermal energy use worldwide and the comparison with the previous period, both in electricity generation as well as in the various categories of direct use. Electricity production takes place in 26 countries and has at the end of 2014 reached 73,700 GWh from geothermal power plants with nearly 12.8 GW of installed power. This is still only 0.31 % of the total electricity produced in the world and it will be interesting to monitor the future share of geothermal energy in doing so. In the last 5-year period the development was particularly rapid in countries where it was slower in the past and, however, with favorable geological (tectonic) conditions (Iceland, Kenya, New Zealand, Turkey, etc.). Direct use of geothermal energy covers a significant number of countries, today there are 82, although some of them are such where it takes place almost solely by geothermal (ground-source) heat pumps (GHP) on shallow subsurface energy (Finland). Installed capacity in the direct use is 70,885 MW_t and geothermal energy used, including the GHP, is 592,638 TJ/year (end of 2014). Within the used energy the share of GHP dominates with 55.2 %, followed by the bathing and swimming pools complexes incl. balneology by 20.2 %, space heating by 15.0 % (the majority of it is district heating), heating of greenhouses and soil with 4.9 %, etc. The second part presents some interesting technological and scientific innovations in exploration and exploitation of geothermal energy.

Uvod

Raznolika dejavnost v raziskavah in razvoju potencialnih geotermalnih polj kakor tudi izkoriščanje in tehnologija rabe geotermalne energije se v svetovnih razmerah še nadalje nezadržno širi, kar je pokazal tudi zadnji svetovni geotermalni kongres v Melbournu v aprilu 2015 (WGC, 2015, v Gutiérrez-Negrín, 2015). To se je videlo tudi po številu sprejetih referatov v primerjavi s prejšnjimi kongresi (sl. 1).



Sl. 1. Rast svetovnega geotermalnega kongresa v smislu sprejetih referatov (Horne, 2015).

Fig. 1. The growth of the World Geothermal Congress in terms of papers accepted (Horne, 2015).

Znova se je izkazalo, da so indirektne in površinske metode (geofizika, geokemija in geologija) še naprej zelo pomembne v raziskavah in upravljanju geotermalnih virov. Številni referati o raziskavah kažejo, kako dejavno in zahtevno je iskanje novih virov. Poleg tega še nikoli ni bilo toliko referatov namenjenih raziskavam v zvezi s izboljšanimi geotermalnimi sistemi (angl. Enhanced Geothermal Systems, EGS) kot ravno na tem kongresu. Čeprav so potekali v zadnjem desetletju številni projekti na več celinah, so poglavitne težave, vezane na vrtanje in stimulacijo rezervoarja, upočasnile razvoj te tehnologije. Kot rezultat je danes v poskusnem obratovanju le nekaj demonstracijskih pilotnih elektrarn (v ZDA in Avstraliji), med stalno delujočimi pa sta sedaj edini Soultz-sous-Forêts (Renski tektonski jarek) v Franciji, in Habanero v severovzhodnem delu Južne Avstralije, njuna skupna inštalirana moč pa je 2,5 MW_e.

Proizvodnja električne energije iz geotermalne energije v svetovnem merilu ni ravno vsepovsod prisotna, saj se še vedno večinoma odvija le v državah, ki ležijo na robovih aktivnih tektonskih plošč. Bistveno bolj je razširjena neposredna raba geotermalne energije, namreč v kar 82 državah na vseh petih celinah (od skupno 204 držav sveta). Zanimivo je, da je na vsaki celini razmerje med inštalirano močjo geotermalnih elektrarn in proizvedeno elektriko približno enako. Obe Ameriki in Azija (brez Oceanije) proizvedejo skupaj preko 65 % vse geotermalne elektrike. Glede neposredne rabe pa je znatno padlo razmerje inštalirane kapacitete glede na izkoriščeno energijo za vso Ameriko, saj je tam 27,7 % vse svetovne inštalirane moči in le 16,9 % vse svetovne izkoriščene geotermalne energije v neposredni rabi. To je posledica visokega deleža geotermalnih toplotnih črpalk z nizkim faktorjem izkoristka (razpoložljivosti) za tovrstne enote v ZDA in Kanadi, kar velja sicer tudi v mnogih evropskih državah.

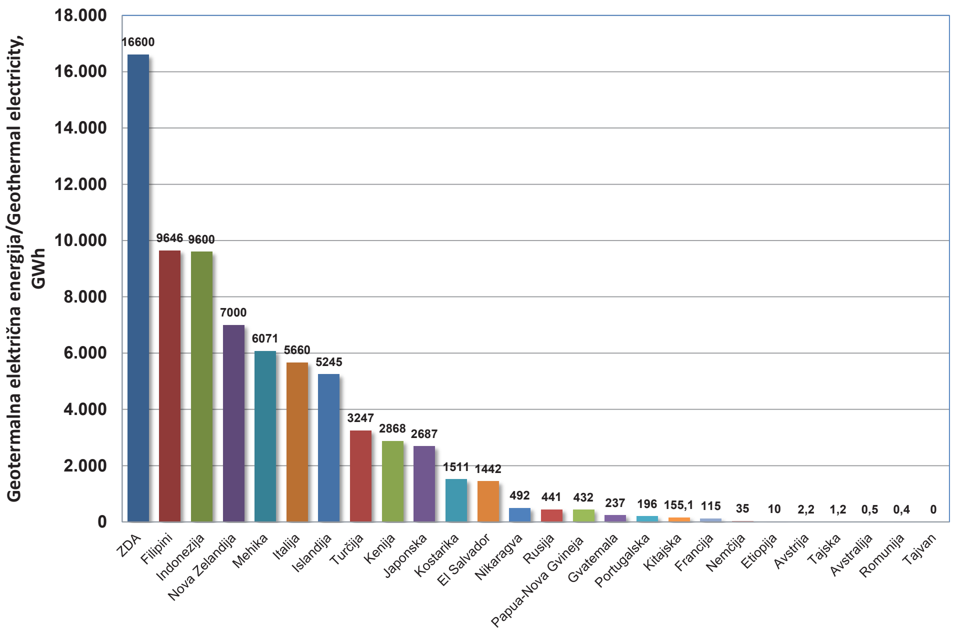
Izkoriščanje geotermalne energije v letu 2014

Številke o izkoriščanju geotermalne energije, tako za proizvodnjo električne energije kot za njeno neposredno rabo, prikazujemo v preglednicah 1 do 5 in slikah 2 do 8 šele za leto 2014, saj so Bertani (2016) ter Lund & Boyd (2016) z zbiranjem svetovnih podatkov zaključili, z dopolnitvami vred, že v juniju 2015.

Proizvodnja električne energije iz geotermalne energije

Električno energijo iz geotermalnih virov proizvajajo v 26 državah, pri tem sta Grčija in Argentina zaprli svoji elektrarni zaradi neznanih okoljskih in ekonomskih razlogov že pred letom 2010. Vendar sta do leta 2020 obe napovedali postavitev novih geotermalnih elektrarn z močjo 40 oziroma 30 MW_e. Poleg tega postavitev prvih geotermalnih elektrarn napoveduje še precej drugih držav (Bertani, 2015, 2016; IGA, 2016): Alžirija, Argentina, Armenija, Bolivija, Kanada, Čile, Češka, Djibuti, Dominika, Ekvador, Grčija, Honduras, Hrvaška, Madžarska, Indija, Iran, Latvija, Montserrat, Nizozemska, Nevis, Peru, Poljska, Slovaška, Španija, Švica in Velika Britanija. Predvsem v evropskih državah naj bi šlo skoraj izključno za binarne elektrarne. Parno-prevladujoči vir (suha para) se seveda lahko izkorišča neposredno na turbinah, medtem ko se mora vir vroče vode z znižanjem tlaka bliskovito upariti, da se proizvaja para (za opis tehnologije glej članek Rajver in sod. (2012)). Nizkotemperaturni viri, ki prevladujejo v evropskih geotermalnih sistemih, s temperaturo večinoma pod 150 °C, zahtevajo uporabo sekundarnega fluida z nizkim vreliščem za ustvarjanje pare v binarni ali t.i. ORC (angl. Organic Rankine Cycle) elektrarni. Potem ko para zapusti turbino, se navadno uporablja mokri ali suhi hladilni stolp za kondenzacijo pare, da se do skrajnosti poveča temperaturni padec med prihajajočo in odhajajočo paro ter tako poviša učinkovitost delovanja.

Proizvedena elektrika je na svetu porazdeljena glede na tip elektrarn takole (Bertani, 2015): 23 % elektrarne na suho paro, 41 % na enojno uparitev, 19 % na dvojno uparitev, 2 % na trojno uparitev, 12 % na binarni in kombinirani cikel, 2 % na hibridne in 1 % na znižani tlak. Ob koncu leta 2014 je celotna svetovna kapaciteta vseh elektrarn znašala 12.731 MW_e, proizvedena električna energija iz njih pa 73.694 GWh. Slika 2 kaže proizvedeno električno energijo iz geotermalne



Sl. 2. Proizvedena električna energija (GWh) iz geotermalne energije v svetu po državah. Skupno proizvedene elektrike je 73.694 GWh ali 0,31 % svetovne neto proizvodnje (23.536.500 GWh). Podatki so večinoma za leto 2014 (Bertani, 2016).

Fig. 2. Produced electricity (GWh) from geothermal energy worldwide per countries. Total energy is 73,694 GWH or 0.31 % of world net production (23,536,500 GWh). Data are mostly for 2014 (Bertani, 2016).

energije za vseh 26 držav, kot je bilo poročano v letu 2015. Podatke za vodilne države v proizvodnji elektrike iz geotermalne energije kaže tabela 1. Eden od pomembnih vidikov razvoja geotermalnih elektrarn je delež njihovega prispevka v državni in regionalni kapaciteti ter proizvodnji električne energije določenih držav. Kar osem držav in tri regije vodijo v takšnem prispevku z več kot 10 % proizvedene električne energije iz geotermalnih elektrarn (tab. 2). Omenimo lahko, da za celotno Italijo veljata deleža 0,8 % (v kapaciteti) oziroma 1,9 % (v proizvedeni elektriki), denimo za Mehiko le 1,7 % oziroma 2,3 %, in za ZDA le 0,3 % oziroma 0,5 % (samo za Kalifornijo pa 4,4 % proizvedene elektrike).

Tabela 1. Vodilne države v proizvodnji elektrike (podatki veljajo večinoma za leto 2014) iz geotermalne energije z vsaj 100 MW_e inštalirane moči elektrarn (Bertani, 2015, 2016).

Table 1. Leading countries in electricity generation (data mostly for 2014) from geothermal energy with at least 100 MW_e of installed capacity (Bertani, 2015, 2016).

Država/Country	**Inštalirana moč/ Installed capacity (MW_e)**	**Letna proizvedena energija/Annual electricity produced (GWh)**
ZDA/USA	3450	16600
Filipini/Philippines	1870	9646
Indonezija/Indonesia	1340	9600
Nova Zelandija/New Zealand	1005	7000
Mehika/Mexico	1058	6071
Italija/Italy	916	5660
Islandija/Iceland	665	5245
Turčija/Turkey	407	3247
Kenija/Kenya	636	2868
Japonska/Japan	520	2687
Kostarika/Costa Rica	207	1511
El Salvador	204	1442
Nikaragva/Nicaragua	159	492

Tabela 2. Delež kapacitete geotermalnih elektrarn v skupni inštalirani moči elektrarn in v proizvodnji električne energije iz geotermalnih elektrarn v izbranih državah in regijah, po poročanju v 2015 (Bertani, 2016).

Table 2. Proportion of the capacity of geothermal power plants (PPs) in a total installed capacity of PPs and in the electricity production from geothermal PPs in selected countries and regions, as reported in 2015 (Bertani, 2016).

Država ali regija/ Country or Region	**% državne ali regionalne kapacitete/ % of national or regional capacity (MW_e)**	**% državne ali regionalne električne energije (GWh/leto)/ % of national or regional electricity (GWh/yr)**
El Salvador	13,7	24
Filipini/Philippines	11,4	14
Francija/France*, Guadaloupe	9	9
Indonezija/Indonesia	3,4	4,5
Islandija/Iceland	25,8	29
Italija/Italy*, Toskana/Tuscany	25	33
Kenija/Kenya	27,2	50
Kitajska/China*, Tibet	25	25
Kostarika/Costa Rica	7,4	15
Nikaragva/Nicaragua	13,5	10
Nova Zelandija/New Zealand	10,4	16,2
Papua-Nova Gvineja/ Papua-New Guinea	7,1	13
Portugalska/Portugal*, Azori/Azores	22	22

*Številke veljajo le za omenjene regije v označenih državah. Za Tibet odstotka nista točno znana. / Numbers are only valid for the above mentioned regions in the designated countries. Tibet percents are not exactly known.

Slika 3 kaže precej drzno napoved v dvigu inštalirane kapacitete geotermalnih elektrarn na svetu do leta 2020, ki jo Bertani (2016) temelji na številnih načrtih v državah, ki doslej še niso postavile nobene geotermalne elektrarne ter na številnih zarisanih in po dolgotrajnih raziskavah že ovrednotenih projektih, katere naj bi končno pretvorili v dejanske elektrarne. Ta izziv bo, kot pravi Bertani (2016), sposoben pokazati celotni geotermalni skupnosti jasen znak o možnosti in pripravljenosti geotermalne industrije biti eden od najpomembnejših dejavnikov med obnovljivimi viri energije na bodočem trgu elektrike. Bertani (2016) je prav tako ocenil pričakovane geotermalne cilje za leto 2050:

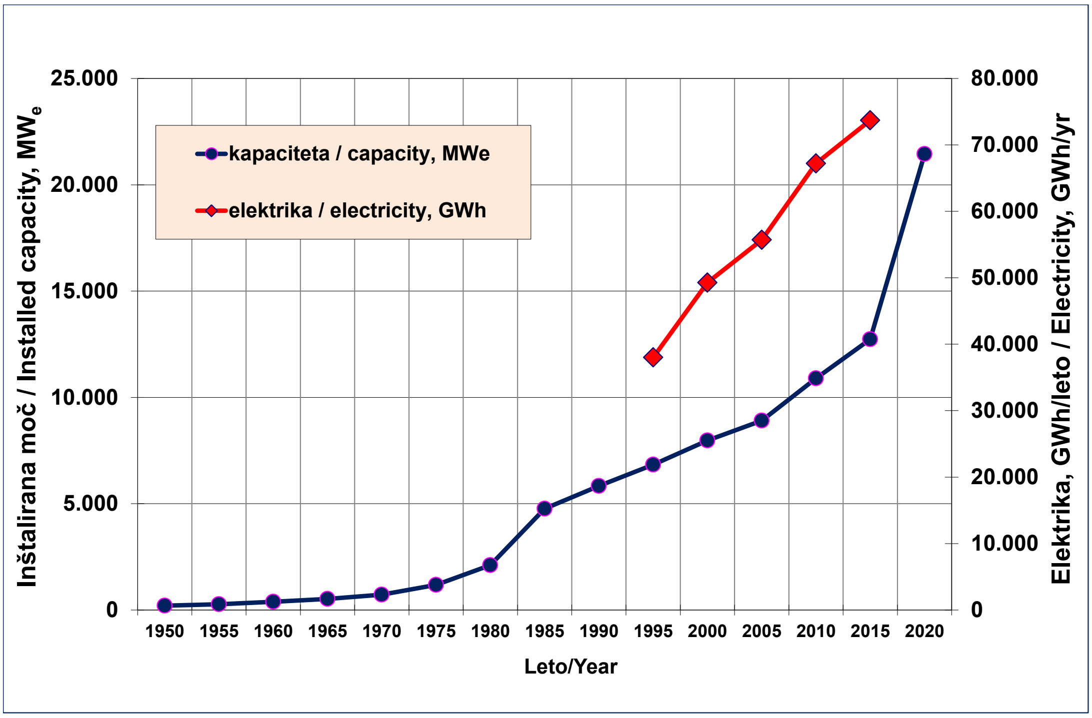
- iz hidrotermalnih virov: 70 GW_e , oziroma
- skupno 140 GW_e (vključno z EGS sistemi in drugimi nekonvencionalnimi viri)

Če bi bil dosežen cilj 140 GW_e, bi bilo možno proizvajati do 8,3 % skupne svetovne elektrike samo iz geotermalne energije, kar bi pokrilo potrebe 17 % svetovnega prebivalstva. Še več, približno 40 držav, večinoma v Afriki, Srednji in Južni Ameriki ter na pacifiškem območju, bi lahko 100 % pokrilo svoje potrebe po elektriki iz geotermalne energije. Ocenjena kapaciteta 21,4 GW_e za leto 2020 (sl. 3) je v skladu z dolgotrajno napovedjo za standardna hidrotermalna polja. Vseeno pa je morda ta napoved preveč optimistična, glede na to, da je Bertani (2010) še pred šestimi leti za leto 2015 napovedal za vse elektrarne na svetu skupno inštalirano moč 18.500 MW_e, od katerih pa smo še precej oddaljeni.

V letu 2015 so postavili in priključili v omrežje še nekaj sto MW_e iz novih elektrarn, tako da je stanje ob koncu 2015 znašalo okrog 13,2 GW_e (Sawin et al., 2016). Prav zanimivo bo videti, koliko se bo skupna kapaciteta približala napovedanemu cilju. Omenimo lahko tudi to, da je na Japonskem gradnja novih geotermalnih elektrarn skorajda zastala, japonski proizvajalci turbin in druge opreme za geotermalne elektrarne pa so zelo dejavni drugod po svetu in zasedajo prva tri mesta. Naštejmo pet najpomembnejših proizvajalcev na svetu: Toshiba, Mitsubishi, Fuji (vsi trije Japonska), Ormat (Izrael in ZDA) in Ansaldo-Tosi (Italija).

Neposredna raba geotermalnih virov

Za svetovni pregled sta Lund & Boyd (2016) zbrala podatke iz 65 držav, ki izkoriščajo geotermalno energijo za neposredno rabo toplote. K temu sta dodala še druge vire informacij iz 17 držav, ki niso poročale za zbornik kongresa WGC 2015. Neposredna raba geotermalne energije se odvija v 82 državah, kar je porast glede na 78 držav, poročanih leta 2010. Nove dežele, ki so tokrat poročale o neposredni geotermalni rabi, so Grenlandija, Madagaskar, Pakistan in Saudska Arabija. Ocenjena inštalirana termična moč za neposredno rabo ob koncu leta 2014 je bila 70.885 MW_t, kar je skoraj 46,2 % porast glede na 2010, z rastjo 7,9 % letno in s faktorjem razpoložljivosti 0,265. Izkoriščena toplotna energija v direktni rabi ob koncu leta 2014 je tako znašala 592.638 TJ/leto (164.635 GWh/leto



Sl. 3. Inštalirana moč (levo) in proizvedena elektrika (desno) iz geotermalne energije od leta 1950 do 2020 v svetu; podatki za proizvedeno elektriko pred letom 1995 so pomanjkljivi ali neznani (Bertani, 2016). Točke kažejo na leta, ko so bile vrednosti poročane na svetovnih kongresih, dejansko pa veljajo za leto prej (n.pr. za leto 2014 in ne za 2015, za 2009 in ne za 2010, itd.).

Fig. 3. Installed capacity (left) and produced electricity (right) from geothermal energy from 1950 up to 2015; data for electricity before 1995 are incomplete or unknown (Bertani, 2016). Points indicate the year when values were reported at the WGC, in fact they are subject to the previous year (e.g. 2014 and not for 2015, 2009 and not 2010, etc.).

ali 14.155 ktoe/leto), kar je porast za 39,8 % glede na 2010 in z letno rastjo 6,9 % (sl. 4). Delež izkoriščene geotermalne energije v direktni rabi znese le 0,104 % vse proizvedene primarne energije v svetu (13.541 Mtoe v letu 2013; podatki po IEA, 2015). Porazdelitev izkoriščene geotermalne energije po kategorijah rabe kaže tabela 3.

Kar 89 % vse izkoriščene energije za ogrevanje prostorov gre za daljinsko ogrevanje. »Ostale rabe« so kategorija, ki zajema različne rabe, katerih podrobnosti so pomanjkljive, vključuje pa gojenje živali in alge spiruline ter izločanje soli. V kategoriji »Taljenje snega in hlajenje (klimatizacija)« prevladuje taljenje snega. Vsa privarčevana energija v letu 2014 znaša 52,8

Kategorija neposredne rabe/ Category of direct use	**Kapaciteta/ Capacity (MW_t)**	**Energija (TJ/leto)/ Utilization (TJ/year)**	**Izkorišč. energija v % / Used energy in %**	**Faktor razpol./ Capacity factor**
Geotermalne toplotne črpalke/ Geothermal heat pumps*	50258	326848	55,2	0,206
Kopanje & plavanje, vklj. balneologija/ Bathing & swimming, incl. balneology	9143	119611	20,2	0,415
Ogrevanje prostorov, vklj. daljinsko ogrev./Space heating, incl. district heating	7602	88668	15,0	0,370
Rastlinjaki & pokrito gretje tal/ Greenhouse heating	1972	29038	4,9	0,467
Ribogojništvo/ Aquaculture pond heating	696	11953	2,0	0,545
Industrijska procesna toplota/ Industrial uses	614	10454	1,8	0,540
Taljenje snega & hlajenje/ Snow melting & cooling**	360	2596	0,4	0,229
Sušenje v poljedeljstvu/ Agricultural drying	161	2030	0,3	0,400
Ostale rabe/Other uses	79	1440	0,2	0,578
SKUPAJ	**70885**	**592638**	**100**	**0,265**

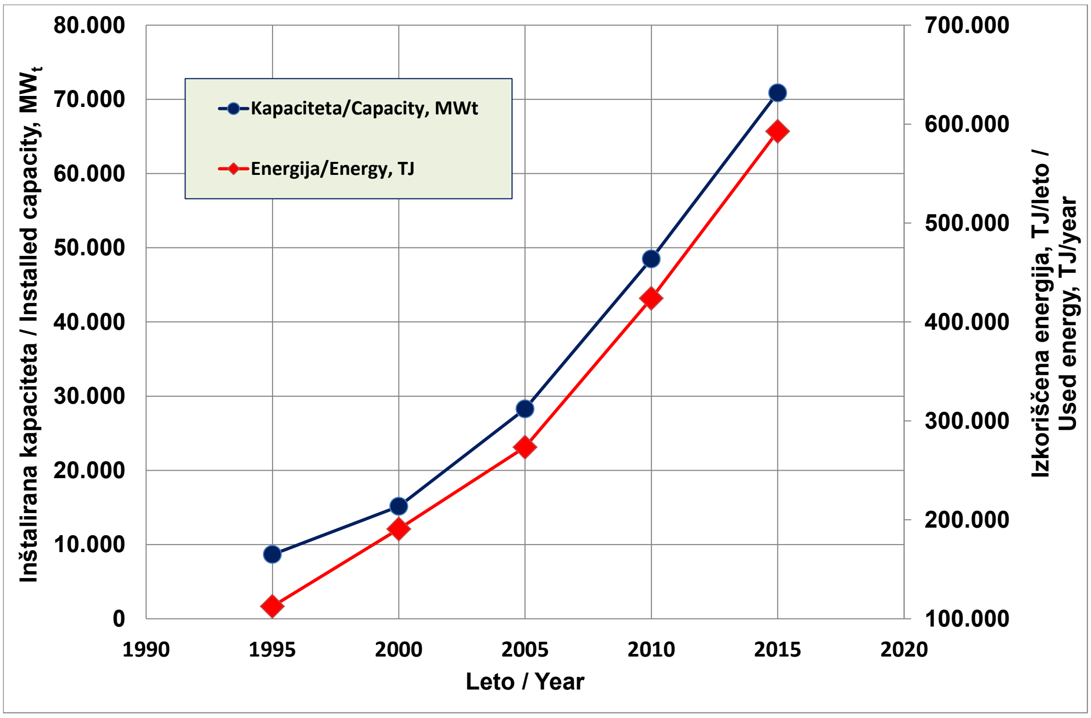
Tabela 3. Povzetek različnih kategorij neposredne rabe v svetu v letu 2014 (poročano v 2015), podatki po Lund & Boyd (2016).

Table 3. Summary of the various categories of direct use worldwide in 2014 (reported in 2015), according to Lund & Boyd (2016).

Opombe / Remarks:

*faktor razpoložljivosti za GTČ velja samo v načinu gretja / Capacity factor for GHPs applies only in heating mode.

**samo za taljenje snega: 307 MW_t in 2.323 TJ/leto/for snow melting only: 307 MW_t and 2.323 TJ/yr.



Sl. 4. Neposredna raba geotermalne energije v obdobju od 1995 do 2015 z inštalirano kapaciteto (levo) in izkoriščeno energijo (desno); po Lund & Boyd (2016). Točke kažejo na leta, ko so bile vrednosti poročane na svetovnih kongresih, v resnici pa veljajo za leto prej (n.pr. za leto 2014 in ne za 2015, za 2009 in ne za 2010, itd.).

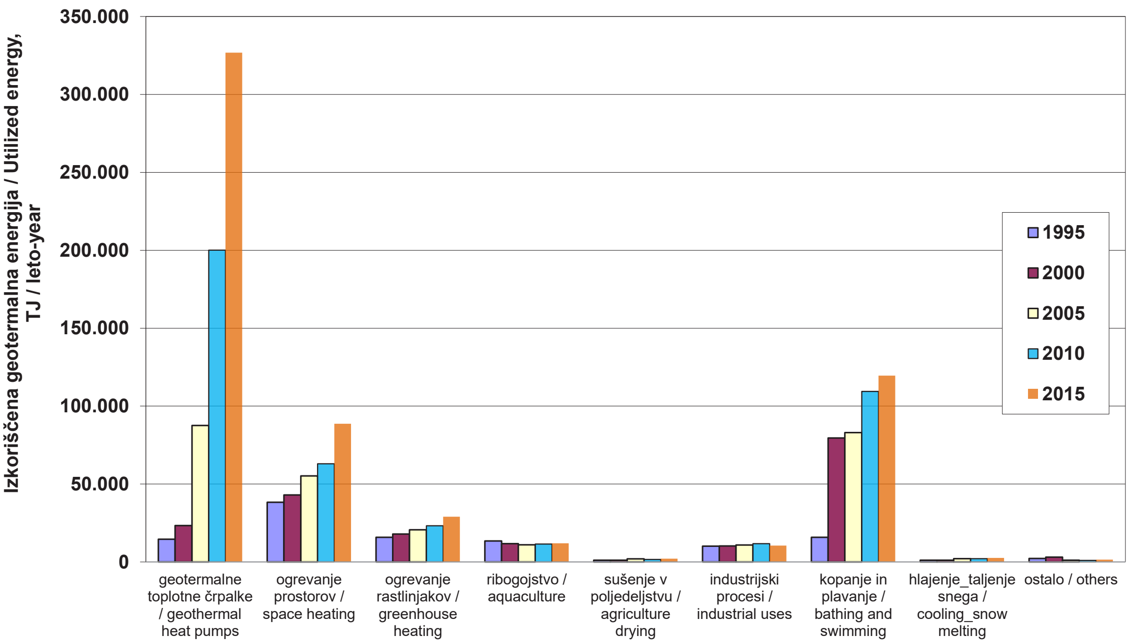
Fig. 4. Direct use of geothermal energy in the period from 1995 to 2015 with an installed capacity (left) and utilized energy (right); after Lund & Boyd (2016). Points indicate the year when values were reported at the WGC, in fact are subject to the previous year (e.g. 2014 and not for 2015, 2009 and not 2010, etc.).

milijonov ton naftnega ekvivalenta (toe) ali 352 mil. sodčkov nafte, kar je preprečilo izpust v ozračje 46,1 milijonom ton ogljika in 149,1 milijonom ton CO_2, to pa zajema tudi privarčevanje za pogon geotermalnih toplotnih črpalk (GTČ) v hladilnem načinu (v primerjavi z rabo pogonskega goriva za proizvodnjo elektrike v ta namen).

Neposredna raba geotermalnih virov se primarno odvija za ogrevanje prostorov in hlajenje. Navadno zajema temperature virov pod 150 °C. Glavna prednost takega izkoriščanja v nizko do srednjetemperaturnem razponu je, da so ti viri bolj razširjeni in obstajajo v vsaj 82 državah v ekonomsko dosegljivih globinah. Tipična oprema vsebuje: črpalke v vrtini in obtočne črpalke, toplotne izmenjevalce, cevovode za prenos in porazdelitev termalne vode, opremo za odvzem toplote, vršne in pomožne energetske obrate (običajno na fosilna goriva) za znižanje izrabe geotermalnega fluida in znižanje števila potrebnih vrtin, ter sisteme za odstranitev izrabljenega fluida (reinjekcijske vrtine). Omenjeni faktor razpoložljivosti 0,265, kar ustreza 2321 uram polne obremenitve letno, je nižji od poročanih faktorjev v letu 2010 (0,28), v letu 2005 (0,31) in v letu 2000 (0,40). Nižji faktor in nekoliko nižja stopnja rasti za letno neposredno rabo geotermalne energije sta posledica številčnega porasta inštalacij geotermalnih toplotnih črpalk, ki kažejo nizek faktor razpoložljivosti, in ta je sedaj 0,21 v svetovnem povprečju.

Pet držav z največjo inštalirano močjo (MW_t) v neposredni rabi, vključno z GTČ, so: Kitajska, ZDA, Švedska, Turčija in Nemčija, ki predstavljajo 65,8 % svetovnih zmogljivosti. Pet držav z najvišjo letno izkoriščeno energijo (TJ / leto) v neposredni rabi, vključno z GTČ, so: Kitajska, ZDA, Švedska, Turčija in Islandija, ki zajemajo 63,2 % svetovne rabe. Seveda pa pregled podatkov glede površine ali prebivalstva držav pokaže, da prevladujejo manjše (in bogatejše) države, zlasti skandinavske. V "top pet" se potem za inštalirano moč (MW_t / prebivalstvo) uvrščajo: Islandija, Švedska, Finska, Norveška in Švica; in glede letne rabe energije (TJ / leto / prebivalstvo): Islandija, Švedska, Finska, Nova Zelandija, Norveška (Lund & Boyd, 2016).

Druga znatna sprememba od leta 2010 je velik porast enot geotermalnih toplotnih črpalk (GTČ) na vir toplote tal oz. plitvega podzemlja. Rastoče zavedanje in priljubljenost GTČ imata najbolj značilen vpliv na neposredno rabo geotermalne energije. Letna izkoriščena energija z enotami GTČ se je povišala 1,63-krat, inštalirana moč pa 1,52-krat glede na 2010 (sl. 5). Kategorija GTČ tvori največji delež v skupni inštalirani kapaciteti neposredne rabe (70,90 %) in v skupni letni izkoriščeni energiji (55,15 %). Skupno ekvivalentno število 12-kW postavljenih enot toplotnih črpalk (kar je tipična nazivna moč v ZDA in večjem delu Evrope) je okrog 4.190.000 v 48 državah, največ v ZDA, Kanadi, Evropi in na Kitajskem. To je 52 % porast glede na število



Sl. 5. Primerjava izkoriščene geotermalne energije (v TJ/leto) po kategorijah neposredne rabe za leta poročanja od 1995 do 2015; po Lund & Boyd (2016). Skupna letno izkoriščena energija je znašala po letih poročanja: 1995: 112,4 PJ, 2000: 190,7 PJ, 2005: 273,4 PJ, 2010: 423,8 PJ in 2015: 592,6 PJ.

Fig. 5. Comparison of geothermal energy (TJ/year) per category of direct use for the reporting year from 1995 to 2015; after Lund & Boyd (2016). The total annual utilized energy for reporting years was: 1995: 112.4 PJ, 2000: 190.7 PJ, 2005: 273.4 PJ, 2010: 423.8 PJ and 2015: 592.6 PJ.

enot GTČ v letu 2010. Vodilne države v številu postavljenih enot in v inštalirani moči (MW_t) so: ZDA, Kitajska, Švedska, Nemčija in Francija, glede izkoriščene energije pa: Kitajska, ZDA, Švedska, Finska in Nemčija (tab. 4). Velikost posameznih enot sega od 5 kW za individualne hiše do več kot 150 kW za industrijske in javne stavbe. V ZDA je večina enot dimenzionirana za vršno hlajenje in predimenzionirana za gretje, izjema so severne zvezne države. Zato se zanje ocenjuje poprečno 2000 ekvivalentnih ur delovanja v polni obremenitvi letno. V Evropi je večina enot dimenzionirana za gretje, pogosto pa so enote GTČ dimenzionirane za pokrivanje osnovne obremenitve ter z dodatnimi fosilnimi gorivi za vršne obremenitve. Kot rezultat so GTČ lahko v delovanju do 6000 ekvivalentnih ur v polni obremenitvi za gretje na leto, kot je to primer v nordijskih državah (posebno na Finskem). Drugod je število ur nižje. Če niso bile poročane dejanske številke, sta Lund & Boyd (2016) uporabila vrednost 2200 ur/leto (in višje za nekatere severne države) za izračun izkoriščene energije. Hladilni način (obremenitev) ni bil upoštevan kot geotermalno koriščenje, ker se v takem primeru toplota vrača v podzemlje ali v podzemno vodo. Seveda pa ima hlajenje vlogo v nadomestitvi fosilnih goriv in zmanjšanju emisij toplogrednih plinov.

Tabela 4. Vodilne države v svetu glede inštaliranih geotermalnih toplotnih črpalk (MW_t) in z njimi izkoriščena plitva geotermalna energija (TJ/leto); po Lund & Boyd (2016).

Table 4. Leading countries worldwide in terms of installed geothermal heat pumps (MW_t) and their exploited shallow geothermal energy (TJ/year); after Lund & Boyd (2016).

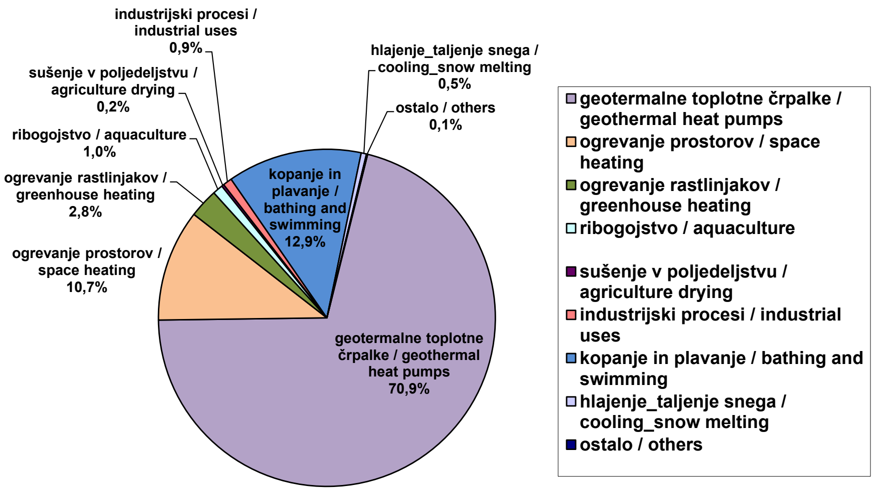
Država/Country	MW_t	Država/Country	TJ / leto-year
ZDA/USA	16800	Kitajska/China	100311
Kitajska/China	11781	ZDA/USA	66670
Švedska/Sweden	5600	Švedska/Sweden	51920
Nemčija/Germany	2590	Finska/Finland	18000
Francija/France	2010	Nemčija/Germany	16200

Sliki 6 in 7 kažeta odstotne deleže različnih kategorij neposredne rabe geotermalne energije v svetu. Lund & Boyd (2016) sta poskusila ločeno prikazati individualno ogrevanje prostorov in daljinsko ogrevanje, toda to je bilo pogosto težko. Zato je njun najboljši približek, da daljinsko ogrevanje predstavlja 88 % inštalirane moči in 89 % letne izkoriščene energije od celotne kategorije »ogrevanje prostorov« (Lund & Boyd, 2016).

Ogrevanje prostorov, kjer z 89 % prevladuje daljinsko ogrevanje, se odvija v 28 državah. Vodilne v daljinskem ogrevanju glede letne energetske rabe geotermalne energije so: Kitajska, Islandija, Turčija, Francija in Nemčija, v individualnem ogrevanju prostorov pa: Turčija, ZDA, Italija, Slovaška in Rusija (skupno 28 držav).

Ogrevanje rastlinjakov in pokrito gretje tal se s koriščenjem geotermalne energije odvija v 31 državah (3 manj kot pred petimi leti), prednjači pa gojenje zelenjave in cvetja. Vodilne države v letni energijski rabi so: Turčija, Rusija, Madžarska, Kitajska in Nizozemska. Večina držav ni poročala o razlikovanju med pokritimi rastlinjaki in nepokritim talnim gretjem. S pomočjo poprečne potrebne energije (iz WGC 2000), ki znaša 20 TJ/leto/ha, skupna izkoriščena geotermalna energija za rastlinjake 29.038 TJ/leto ustreza približno površini 1.452 ha vseh ogrevanih rastlinjakov na svetu (kar je porast za 12,6 % glede na leto 2010). Razvite države v tej panogi čutijo močno konkurenco iz držav v razvoju zaradi tamkajšnje cenejše delovne sile.

Koriščenje geotermalne energije za **ribogojništvo** omenjajo v 21 državah, vodilne so: ZDA, Kitajska, Islandija, Italija in Izrael. Tilapia (afriška sladkovodna riba), losos in postrv so prevladujoče vrste gojenih rib, ponekod pa gojijo še tropske ribice, jastoge, morske rakce,



Sl. 6. Kategorije neposredne rabe geotermalne energije v 2014 (leto poročanja je 2015), porazdeljene v odstotkih skupne inštalirane kapacitete (Lund & Boyd, 2016).

Fig. 6. Categories of direct use of geothermal energy in 2014 (reporting year is 2015), distributed as a percentage of the total installed capacity (Lund & Boyd, 2016).

(jamske) kozice in aligatorje. Glede na energetsko rabo v ZDA so izračunali, da je potrebno 0,242 TJ/leto/tono ribe (ostriž, brancin in tilapia) z rabo termalne vode v nepokritih ribnikih. Torej poročana geotermalna energetska raba ustreza 49.393 tonam letne proizvodnje rib, kar je za 3,8 % več od poročanih številk v 2010.

O rabi geotermalne energije za **sušenje pridelkov v poljedeljstvu** poročajo iz 15 držav (pred petimi leti je bilo 13 držav), in sicer za sušenje različnih zrn, zelenjave in sadja. Značilni primeri so: morske alge (Islandija), čebula (ZDA), pšenica in druge žitarice (Srbija), sadje (El Salvador, Gvatemala, Mehika), nemška detelja (Nova Zelandija), kokosova moka (Filipini) in stavbni les (Mehika, Nova Zelandija, Romunija). Največ geotermalne energije izkoristijo na Kitajskem, v ZDA in na Madžarskem. Za to kategorijo rabe se izkorišča 24,2 % več geotermalne energije glede na 2010.

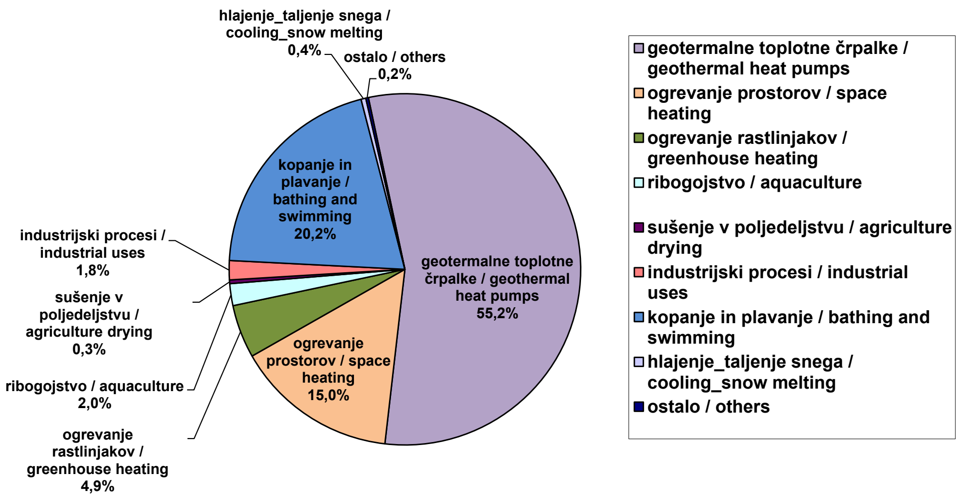
Za **industrijsko procesno toploto** koristijo geotermalno energijo v 15 državah. Ta dejavnost je energetsko potratna in ponavadi deluje celo leto, zato ima ta kategorija enega najvišjih faktorjev izkoristka (0,54). Primeri vključujejo: sušenje betona (Gvatemala), gaziranje brezalkoholnih pijač in ustekleničenje vode (Bolgarija, Srbija, ZDA), pasterizacija mleka (Romunija, Nova Zelandija), industrija usnja (Srbija), kemijsko obarjanje snovi (Bolgarija, Poljska, Rusija), izločanje CO_2 (Islandija, Turčija), procesiranje papirne kaše in papirja (Nova Zelandija), izločanje joda in soli (Vietnam) ter proizvodnja borata in borove kisline (Italija). V Sloveniji se žal ne izkorišča več v industriji usnja na Vrhniki, katere ni več, tamkajšnji termalni vir pa uporablja drugo podjetje za ogrevanje prostorov.

Taljenje snega in hlajenje prostorov s pomočjo geotermalne energije je omejeno na manjše število držav, večinoma za taljenje snega na pločnikih in ulicah. Postavitve omenjajo na Islandiji, v Argentini, na Japonskem, v ZDA in v manjši meri še na Poljskem in v Sloveniji. Približno 2,5 milijona m^2 površin se ogreva na svetu, večina na Islandiji (74 %). Toplotna moč, potrebna za taljenje, znaša glede na primere v ZDA in na Islandiji od 130 do 180 W/m^2. Hlajenje prostorov (klimatizacija) se odvija v petih državah (Japonska, Bolgarija, ZDA, Slovenija, Alžirija). Toplotne črpalke v hladilnem načinu niso upoštevane, ker pri tem le vračajo toploto v podzemlje ter torej ne izkoriščajo geotermalne energije.

Skoraj vsaka država, ki rabi geotermalno energijo, jo koristi tudi za **kopanje in plavanje (vključno z balneologijo)**, teh pa je vsaj 70, avtorja pregleda pa omenjata še razvoj v Maleziji, Mozambiku, Singapurju in Zambiji. Vendar se v velikem številu ta raba vrši na način, da puščajo termalno vodo krožiti neprestano ne glede na rabo (na primer tudi ponoči, ko so bazeni zaprti). Posledično so lahko dejanske številke za porabo in kapaciteto visoke. Največ energetske rabe imajo na Kitajskem, Japonskem (t.i. onsen, kar je termin za tople izvire v japonščini, zajema pa zunanje in notranje kopeli), v Turčiji, Braziliji in Mehiki.

Ostale rabe geotermalne energije omenjajo v 13 državah in vključujejo gojenje živali, gojenje spiruline, izločevanje soli, sterilizacijo steklenic, ponekod pa še gaziranje brezalkoholnih pijač. Najvišja energetska raba je na Novi Zelandiji (namakanje, zaščita pred mrazom, turistični parki).

Najznačilnejše kategorije rabe v državah z največjo proizvodnjo so podane v tabeli 5. Porazdelitev izkoriščene geotermalne energije v neposredni rabi po državah z vsaj 2500 TJ vključno z GTČ kaže slika 8.



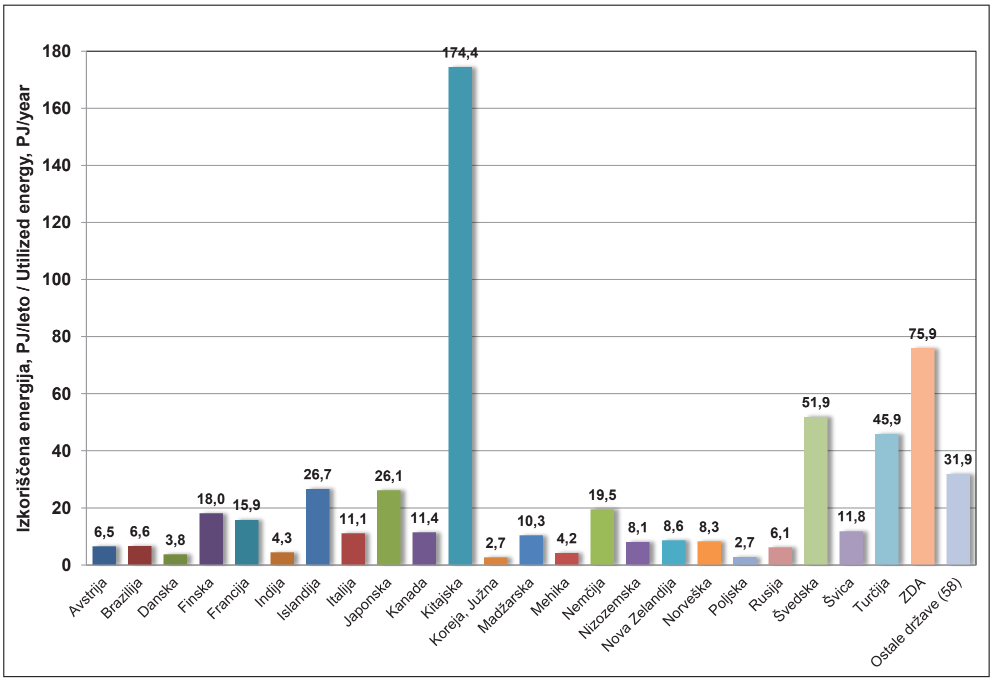
Sl. 7. Kategorije neposredne rabe geotermalne energije v 2014 (leto poročanja je 2015), porazdeljene v odstotkih skupne izkoriščene energije (TJ / leto), po Lund & Boyd (2016).

Fig. 7. Categories of direct use of geothermal energy in 2014 (reporting year is 2015), distributed as a percentage of the total utilized energy (TJ / year), after Lund & Boyd (2016).

Država/Country	MW_t	GWh/leto-year	TJ/leto-year	Najvažnejše kategorije rabe/ The most important use categories
Kitajska/China	17870	48435	174352	GTČ, daljinsko ogrevanje, balneologija/ GHP, district heating, balneology
ZDA/USA	17416	21075	75862	GTČ/GHP
Švedska/Sweden	5600	14423	51920	GTČ/GHP
Turčija/Turkey	2937	12748	45892	bazeni, rastlinjaki, daljinsko ogrevanje/ swimming pools, greenhouses, district heating
Islandija/Iceland	2040	7422	26717	daljinsko ogrevanje/district heating
Japonska/Japan	2186	7259	26130	kopanje & plav. (onsen topli izviri)/ bathing & swimming (onsen hot springs)
Nemčija/Germany	2849	5426	19531	GTČ, daljinsko ogrevanje/ GHP, district heating
Finska/Finland	1560	5000	18000	GTČ/GHP
Francija/France	2347	4408	15867	GTČ, daljinsko ogrevanje/ GHP, district heating
Švica/Switzerland	1733	3288	11839	GTČ/GHP
Kanada/Canada	1458	3164	11388	GTČ/GHP
Italija/Italy	1355	3074	11065	zdravilišča-bazeni, ribogojstvo/ spas-swimming pools, aquaculture
Madžarska/Hungary	906	2852	10268	zdravilišča-bazeni, rastlinjaki/spas-swimming pools, greenhouses
Nova Zelandija/New Zealand	487	2395	8621	industrijska procesna raba, bazeni/ industrial uses, swimming pools
Norveška/Norway	1300	2295	8260	GTČ/GHP

Tabela 5. Vodilne države v neposredni rabi geotermalne energije z vsaj 2.000 GWh/leto, stanje v letu 2014, podatki po Lund & Boyd (2016).

Table 5. Leading countries in the direct use of geothermal energy by at least 2,000 GWh/year, the situation in 2014, data after Lund & Boyd (2016).



Sl. 8. Porazdelitev izkoriščene geotermalne energije (PJ/leto) v neposredni rabi po državah z vsaj 2.500 TJ (stanje v 2014, poročano v letu 2015), podatki po Lund & Boyd (2016).

Fig. 8. Distribution of utilized geothermal energy (PJ/year) in the direct use by countries with at least 2,500 TJ (situation in 2014, reported in 2015), data after Lund & Boyd (2016).

Glede izkoriščanja **geotermalne energije v Sloveniji** znaša inštalirana kapaciteta za neposredno rabo okrog 202,2 MW_t, letna izkoriščena geotermalna energija pa 1218,1 TJ ali 338,4 GWh (stanje na 31. dec. 2015) vključno z geotermalnimi toplotnimi črpalkami (Rajver in sod., 2016). Raba termalne vode za različne namene se odvija pri 34 uporabnikih iz 56 proizvodnih vrtin (njihova skupna globina je 48,84 km) in treh naravnih termalnih izvirov. Skupna kapaciteta vrtin in izvirov je 65,62 MW_t, s katerimi so v letu 2015 izkoristili 486 TJ geotermalne energije. Samo prispevek geotermalnih toplotnih črpalk na toploto plitvega podzemlja znaša 136,64 MW_t oziroma 732,1 TJ/leto. Imamo okrog 9350 delujočih enot GTČ različnih nazivnih grelnih moči. Od teh je okrog 312 večjih sistemov z nazivno močjo nad 20 kW, ki prispevajo 24,0 MW_t in 132,7 TJ izkoriščene toplote. Različne vrste uporabe zajemajo: individualno ogrevanje prostorov (pri 19 uporabnikih), daljinsko ogrevanje (3 uporabniki), klimatizacijo/hlajenje (4 uporabniki), ogrevanje rastlinjakov (4 uporabniki), kopanje in plavanje z balneologijo (27 uporabnikov), taljenje snega (2 uporabnika) ter geotermalne toplotne črpalke (v povezavi s plitvo geotermijo).

Najzanimivejši znanstveno-tehnološki dosežki pri iskanju in razvoju geotermalnih virov

Vrtanje v magmo na Islandiji s ciljem ustvariti magmatski EGS sistem

Med mnogimi zanimivimi in pomembnimi projekti izstopajo raziskave za superkritičnimi fluidi. Nadaljuje se namreč islandski globoki vrtalni (raziskovalni in razvojni) projekt IDDP, ki raziskuje možnost, kako znatno povečati termično (in električno) moč geotermalnih vrtin z izkoriščanjem visokoentalpijskih superkritičnih geotermalnih fluidov iz globin 4 do 5 km pri temperaturah 400 do 600 °C (Friðleifsson in sod., 2015). Cilj je povišati proizvodno moč na vrtino za 10-krat. Prvi resni poskus leta 2009, ko so želeli priti 4 do 5 km globoko v superkritični rezervoar z vrtino IDDP-1 (sl. 9) na geotermalnem polju Krafla (severna Islandija), so morali zaključiti pri »samo« 2096 m globine, potem ko so zavrtali vročo magmo riolitne sestave z nad 900 °C. Z namenom proizvajati paro iz vroče kontaktne cone z magmatsko intruzijo pri temperaturi nad 500 °C so vrtino opremili s cementirano 9 5/8 colsko (244,5 mm) »žrtvovano« (zavestno izgubljena) zaščitno cevitvijo do globine 1950 m znotraj 13 5/8 colske (346,1 mm) proizvodne cevitve enake globine. V odseku od 1950 do 2072 m so postavili 9 5/8 colsko režasto (slotirano) cevitev, od tam pa do globine 2096 m pustili odprto 12 1/4 colsko (311,1 mm) vrtino (cóla ali palec, angleško *inch*, znaša 2,54 cm).

Sl. 9. Izlivalni poskus iz vrtine IDDP-1 v nov. 2011 pri temperaturi, ki se je dvignila do 450 °C. V prvih urah je bila para sive barve zaradi produktov korozije (Friðleifsson in sod., 2014; slika iz Markusson & Hauksson, 2015).

Fig. 9. Flowing test from the well IDDP-1 in November 2011 at a temperature, which increased to 450 °C. In the first hours the steam was gray due to corrosion products (Friðleifsson et al., 2014; figure from Markusson & Hauksson, 2015).

Med dveletnim izlivnim poskusom je vrtina IDDP-1 postala najbolj vroča proizvodna geotermalna vrtina na svetu s temperaturo kar 450 °C iztekajoče superpregrete pare na ustju pri visokih tlakih (40 do 140 bar). Koncentraciji HCl s 100 mg/kg pare in kremenice z 62 mg/kg pare nakazujeta na temperature do 550 °C. Superpregreta para vsebuje tudi žveplene sestavine, ki so se izločale po kondenzaciji pare. To vpliva negativno (korozija) na uporabnost pare (Hauksson & Markusson, 2013). Proizvodni poskusi so pokazali, da je vrtina zmožna proizvajati do 36 MW_e, odvisno od koncepta sistema turbine. Med in po izlivalnih poskusih so izvedli niz pilotnih poskusov za proizvodnjo elektrike, ki so dali izjemne rezultate v ravnanju z magmo v geotermalnem sistemu: (a) uspeli so zavrtati v staljeno kamnino pri temperaturi nad 900 °C in vrtalno opremo izvleči iz nje; (b) projekt je uspel ustvariti visoko prepustnost s hidravlično stimulacijo z vtiskanjem hladnega vrtalnega fluida v kontaktno avreolno kamnino (hydrofracking); (c) uspeli so vstaviti zaščitno cevitev in s cementom obložiti del odprte vrtine; (č) proizvedli so superpregreto paro iz kontaktne avreole pri temperaturnem svetovnem rekordu za geotermalno vrtino; (d) projekt je pokazal, da se nevaren kemizem fluida lahko varno obvlada z ravnanjem s paro, kar omogoča, da se para neposredno vòdi v konvencionalne parne turbine, in (e) ustvarjen je bil prvi svetovni magmatski EGS (izboljšani geotermalni sistem), kar je bilo potrjeno z vtiskovalnim (reinjekcijskim) poskusom sledenja po zaključenih poskusih izlivanja. Vrtino IDDP-1 so morali leta 2012 dokaj nenadno ohladiti zaradi poškodb ventilov, zato so poskusi izlivanja in pilotne študije končane (Friðleifsson et al., 2015). Obilo premaganih tehničnih ovir med vrtanjem in naknadnim izlivalnim poskusom je zelo koristnih za nadaljevanje IDDP programa. V teku so priprave za vrtanje in testiranje vrtine IDDP-2 pri Reykjanesu (JZ Islandija), kateri bo najbrž še pred letom 2020 sledila vrtina IDDP-3 pri Hengillu (južna Islandija).

Nova vrtalna tehnika, ki temelji na izstrelitvi hipersoničnih izstrelkov

Ameriško vrtalno podjetje HyperSciences (ZDA) je pridobilo patent za novo tehniko izdelave vrtin s ponavljajočim streljanjem izstrelkov s hitrostjo 2 km/s, kar povzroči eksplozijo z ustvarjeno luknjo. Ta tehnika je po trditvah proizvajalca desetkrat hitrejša od tradicionalnega vrtanja. Tehnologija, znana kot »pospeševalnik zabijalca«, je načeloma zmožna pospeševanja izstrelkov do hitrosti nad 8 km/s. Na zadnjem koncu naprave se nahaja velik bat v veliki plinski komori, na sprednji strani pa je majhna cev s projektilom. Vsak projektil naj bi se izstrelil z visoko hitrostjo in pri tem uparil vse kar zadene na poti. Pri tem vstopa v vrsto cevi, ki vsebujejo mešanice zraka in gorljivih plinov. Ko izstrelek potuje skozi pline, jih oblika izstrelka stisne, plini za izstrelkom se vžgejo ter ga s tem pospešijo naprej do hitrosti več kilometrov na sekundo. S to hitrostjo izstrelek uniči in upari katerokoli zadeto kamnino ali usedlino, ostanke kamnine pa posesajo ven iz vrtine Princip sistema vrtanja je prikazan na sliki v oglasu v IGA NEWS (2015, 101, str. 27) in na tam omenjenem spletu (INTERNET 1).

Tehnologija pospeševanja predmetov do zelo visokih hitrosti je dobro uveljavljena. NASA že desetletja izvaja hiperhitrostne raziskave v prizadevanjih eksperimentalno raziskati udarce asteroidov, ki se običajno dogodijo pri hitrosti nekaj deset kilometrov na sekundo. Ponavadi plinske puške uporabljajo vodik namesto zraka, ker je omejevalni dejavnik za končno hitrost izstrelka to, kako hitro se lahko udarni val širi skozi plin (z drugimi besedami hitrost zvoka), to pomeni skoraj štirikrat hitreje v vodiku kot je to v zraku. Sedaj delajo na možnosti dodajanja plastičnih eksplozivov, tako da se poveča globino strela. Prav tako upajo, da bi "puško" lahko z zaporednimi streli uporabili v doseganju geotermalnih virov v globinah do 3,2 km.

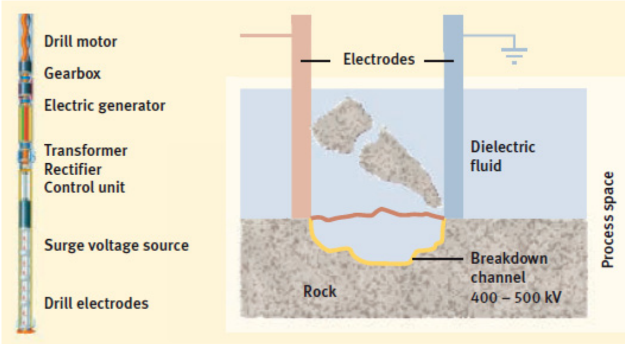
Nov proces, ki uporablja visoko napetost za globoko geotermalno vrtanje

Vrtalne dejavnosti lahko znesejo do 90% investicijskih stroškov v geotermalnih projektih. Z obstoječimi komercialnimi metodami vrtanje skozi trde magmatske in metamorfne kamnine napreduje počasi, vrtalna dleta pa se hitro obrabijo. Znanstveniki na tehnološki univerzi v Dresdnu (Nemčija) razvijajo alternativni postopek za vrtanje s pomočjo visokonapetostnih sunkov (impulsov), ki zdrobijo kamnino (sl. 10). Ta metoda povzroči majhno obrabo vrtalnih svedrov in lahko omogoči do 30 % nižje vrtalne stroške. Vsaka tehnična izboljšava in zmanjšanje stroškov v postopku vrtanja »pripelje« nove geotermalne rezervoarje v bolj gospodarni doseg (IGA NEWS, 2016, 102, str. 29).

Pri vrtanju s procesom električnega sunka (electric impulse technology, EIT), se postavita dve elektrodi pod površjem na plast ustrezne kamnine. Skozi njih se sprožijo 400 kV sunki. V kanalu, kjer sunek razpada, se tlak in temperatura v kamnini povečata in kamnina razpade. Dobljene izvrtanine se odstranijo z neprevodno vrtalno tekočino. EIT sveder je bil uspešno preizkušen na poskusni napravi pod pogoji, podobnim v vrtini. Cilj stalno napredujočega projekta je razviti celovit sistem za vrtanje in ga preskusiti v dejanski vrtini.

Kroglice DNK kot geotermalni sledilci

Pot podzemnih tokov vode ali slanice, ki jo injektiramo skozi geotermalne vrtine v rezervoar, je možno testirati z nizom sledilcev (markerjev), od kemikalij in radioaktivnih elementov do



Sl. 10. Shematična struktura EIT vrtalnega svedra (levo) in princip procesa (desno) (INTERNET 2, MILLES, 2015, Avtorska pravica: © Technische Universität Dresden).

Fig. 10. Schematic structure of the EIT drill bit (left) and the process principle (right) (INTERNET 2, MILLES, 2015, Credit: © Technische Universität Dresden).

fluorescenčnih barvil. Toda rezultati več metod si lahko nasprotujejo. Sledilci se lahko ujamejo v pasteh ali uničijo; lahko so ostanki iz preteklih poskusov. Kot pravi Roland Horne (Univ. Stanford, CA, ZDA) bi se radi zapletom izognili z uporabo DNK. S specifičnimi DNK »oznakami« – čeprav se lahko tudi izgubijo – bo mogoče poznati natančno, kje je bilo sledilo injicirano in kdaj (IGA NEWS 2015, 101, str. 28).

Na podlagi dosežkov znanstvenikov, ki poskušajo ohraniti dolge DNK kode, je Horneova geotermična ekipa uporabila kratke, sintetične DNK fragmente za sledenje toka vode. DNK ima edinstven vzorec okoli sto osnovnih parov, in se zvije okoli drobcene kremenaste (silicijeve) kroglice. Ekipa je postavila kremenasto (silicijevo) lupino okoli DNK, da jo zaščiti. V geotermalnem rezervoarju je okolje zelo neprijazno, z visokimi pritiski in temperaturami, ki lahko sežejo preko 300 °C. Doslej so DNK kremenaste kroglice preživele šest ur pri 300 °C v laboratoriju, vendar niso bile terensko preiskušane. Hornova ekipa ima še nekaj dela v zaščiti DNK pri dolgih terenskih poskusih. Njihov naslednji korak je zagotoviti več vzdržljivosti v pogojih visoke toplote, da se iznajdejo žilavi, zanesljivi in točni sledilci. Če bodo »oznake« uspešne v terenskih poskusih, bo to ob poznavanju lokacij največjih razpok in najboljših vrtin omogočilo pametne investicije v razvoj geotermalnih virov. Tedaj se (globoke) geotermalne raziskave lahko izvedejo skoraj kjerkoli.

Močno geotermično segrevanje pod ledenim pokrovom na zahodni Antarktiki

Raziskovalci na univerzi Santa Cruz (CA, ZDA) so ugotovili presenetljivo visoko količino toplote, ki priteka proti dnu ledene plošče na zahodni Antarktiki iz globokih geotermalnih virov (IGA NEWS, 2015, 101, str. 29). Rezultati, objavljeni julija 2015 v spletni reviji *Science Advances* (IGA NEWS, 2015, 101, str. 29), zagotavljajo pomembne podatke raziskovalcem, ki poskušajo napovedati usodo ledene plošče. Ta se sooča s hitrim taljenjem v zadnjem desetletju.

Študija se opira na zbrane podatke v velikem antarktičnem vrtalnem projektu WISSARD (Whillans Ice Stream Subglacial Access Research Drilling). Raziskovalna ekipa je uporabila posebno termično sondo za meritve temperatur v sedimentih pod sub-ledeniškim jezerom Whillans, ki leži pod okoli 800 m ledu (sl. 11 in 12). Po vrtanju skozi ledeni pokrov v januarju 2013 s posebnim vrtalnikom na vročo vodo so raziskovalci spuščali sondo skozi vrtino, dokler se ni zaustavila v sedimentih pod sub-ledeniškim jezerom. Pri tem so merili temperaturo v različnih globinah, ki je pokazala na skoraj 5-krat višji geotermični gradient od tistega, ki ga običajno najdemo na drugih celinah. Rezultati kažejo na relativno hiter tok toplote proti dnu ledene plošče.

Visok toplotni tok pod zahodno antarktično ledeno ploščo lahko pomaga pojasniti prisotnost jezer pod njo in zakaj se kosi ledene plošče gibljejo hitreje kot običajni tokovi ledu. Vzrok zanj je možna prisotnost kopice vročih točk (jeder vulkanov) v skorji pod dnom Antarktike. Menijo, da voda na dnu ledenih tokov deluje kot mazilo, ki pospeši gibanje delov plošč, in pri tem nosi velike količine ledu ven na plavajoče ledene police na robovih ledene plošče. Ker je bila geotermična meritev le na eni lokaciji, sklepajo, da se toplotni tok lahko krajevno spreminja.

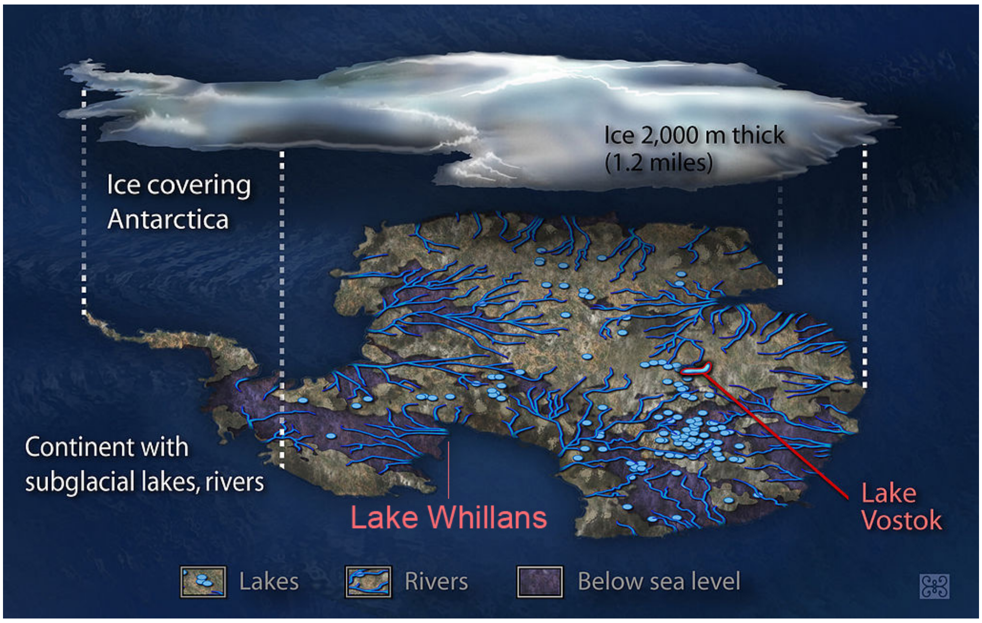
Geotermično segrevanje prispeva k taljenju bazalnega ledu, ki s tem dobavlja vodo v mrežo sub-ledeniških jezer in mokrišč, za katere so znanstveniki odkrili, da se nahajajo pod velikim predelom ledene plošče. V ločeni študiji, objavljeni leta 2015 v reviji *Nature* (Iga News, 2015, 101, str. 29), je mikrobiološka ekipa projekta WISSARD poročala o bogatem in raznolikem mikrobnem ekosistemu v jezeru.

Izmerjen geotermični toplotni tok v novi študiji je bil približno 285 ± 80 mW/m^2. Raziskovalci so merili tudi navzgor usmerjen toplotni tok skozi zahodno antarktično ledeno ploščo, ki je približno 105 ± 13 mW/m^2 (Fisher et al, 2015). Leto kasneje so izvedli meritve na osnovi sipanja laserske svetlobe v kablu z optičnimi vlakni. Kombinacija meritev pod ledom in v njem je omogočila izračun stopnje, s katero nastaja staljena voda na dnu ledene plošče na mestu vrtine, in ta znaša približno 1,27 cm (pol inča) letno. Izmerjen toplotni tok je 4-krat višji od svetovnega povprečja in bi lahko stalil iz ledu na dnu te plošče do 35 km^3 vode na leto (Fisher et al, 2015).

Model, ki simulira super-kritične geotermalne rezervoarje

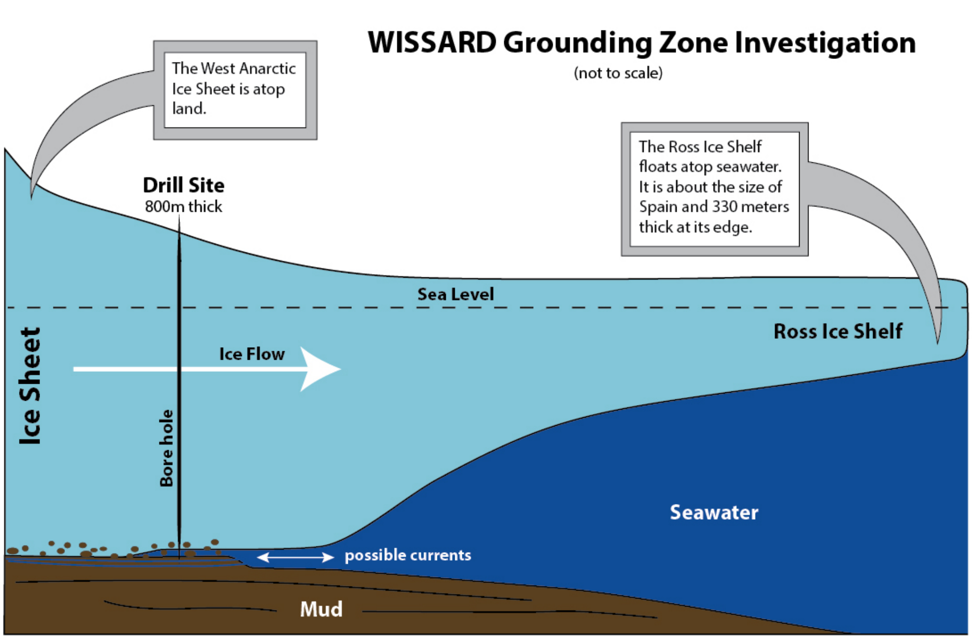
V letu 2008 so islandski raziskovalci, ki delajo na islandskem globokem vrtalnem projektu (IDDP), medtem ko so iskali še bolj vroče geotermalne rezervoarje, odkrili rezervoar izjemno vroče vode, ki ima potencial bistveno razširiti proizvodnjo geotermalne električne energije (Iga News, 2015, 101, str. 30). Sedaj so na inštitutu ETH v Zürichu prvič izdelali simulacijo, kako nastajajo takšni rezervoarji. Napovedujejo, da so ti naravni pojavi razširjeni v vulkanskih območjih, kot so na Japonskem in Novi Zelandiji.

Neposredno nad magmatskim telesom so raziskovalci odkrili doslej edinstven geotermalni rezervoar z vodo - tak, v katerem so temperature dosegle 450 °C. Tako stanje znanstveniki imenujejo superkritično stanje. Voda postaja superkritična pri segrevanju nad 374 °C, in od te točke se začne obnašati kot zmes plina in tekočih faz. Dve fazi postaneta neločljivi in nerazpoznavni, kar privede do fluida, ki je lahko tako gost kot tekočina, istočasno pa teče z lahkoto tako hitro kot plin. Voda, ki jo ogreva magmatska intruzija do superkritične temperature, vsebuje dovolj toplotne energije, da z eno vrtino lahko



Sl. 11. Umetnikov koncept sub-ledeniškega okolja na Antarktiki (Internet 3; Avtorska pravica: Zina Deretsky, NSF).

Fig. 11. An artist's conception of the Antarctic subglacial environment (Internet 3; Credit: Zina Deretsky, NSF).



Sl. 12. Presek čez območje vrtine SLW (Subglacial Lake Whillans) na ledeni plošči na zahodni Antarktiki (Internet 4).

Fig. 12. Cross section through the area of the borehole SLW (Subglacial Lake Whillans) on an ice sheet in the western Antarctica (Internet 4).

zagotovimo 35 MW_e moči. Znanstveniki na ETH so se odločili simulirati ta nenavaden geotermalni sistem z novim računalniškim modelom, tako da sedaj razumejo kako se pojavlja, pod kakšnimi pogoji nastaja in kje raziskovati za drugimi takšnimi sistemi. Simulacije nudijo realistično predstavitev obnašanja tega rezervoarja, čeprav so zadržali model kar se da enostaven z le nekaj parametri. Njihov model ponazarja, katera vzajemna delovanja so potrebna med različnimi geološkimi faktorji, kot so: prepustnost matične kamnine in temperatura pri kateri ta kamnina postaja plastična ter globina intruzije za idealne pogoje, da nastane rezervoar. To znanje pomaga osredotočiti iskanje za takšnimi rezervoarji. Sedaj želijo raziskovalci razširiti to metodo. Kot del projekta Sinergia, s financiranjem iz SNSF (Swiss National Science Foundation), želijo tesneje sodelovati z geofiziki, da ugotovijo, če se lahko ti rezervoarji odkrijejo s seizmičnimi tehnikami.

Viri zlata in srebra v geotermalnih sistemih

Skupina raziskovalcev iz ZDA in Nove Zelandije je pokazala, da obstajajo velika nahajališča zlata (Au) in srebra (Ag) v vsaj šestih geotermalnih rezervoarjih pod več vulkani na severnem otoku Nove Zelandije (Iga News, 2015, 101, str. 30). V svojem prispevku (Simmons et al., 2016) ekipa opisuje preiskavo v geotermalnih sistemih v Taupo vulkanski coni (v obliki črke V) in koliko plemenite kovine naj bi se skrivalo tam spodaj. V tej coni so območja prenašanja in usedanja plemenitih kovin. Zlato in srebro se namreč obarjata (usedata) v vročih vrelcih, v podzemnih hidrotermalno spremenjenih kamninah in v cevovodih z dvofaznimi fluidi v povezavi s proizvodnimi vrtinami. Slednje je posledica izgub plinov zaradi hitre uparitve in adsorpcije v žveplenih fazah bogatih z arzenom (As) in antimonom (Sb). Količine sedimentiranega zlata v podzemnih kamninah lahko presežejo nekaj 100.000 unč (unča: = 31,1 g). Toda zdi se, da so koncentracije zelo nizke stopnje (< 1 ppm Au). Usedline visoke stopnje nastajajo v vročih vrelcih, vsebujejo namreč > 500 ppm Au in > 700 ppm Ag, toda manjše zaloge kovin (< 10.000 unč Au) in zelo visoka vrednost ohranitve izloča te lokacije kot potencialne vire.

Vzorčenje proizvodnih vrtin je pokazalo, da imajo globoke rezervoarske vode koncentracije Au od < 0,1 do > 20 ppb in koncentracije Ag od < 2 do > 2000 ppb. Omejeni podatki kažejo, da bi pri skromnih koncentracijah proizvodne vrtine lahko proizvedle letno 0,3 do 3,0 kg Au, vrtine na območju Rotokawe pa celo 19–70 kg Au/leto. Pri skromnih koncentracijah Ag bi proizvodne vrtine lahko letno proizvedle 3–100 kg Ag, vrtine v krajih Mokai in Rotokawa pa kar 680–7500 kg Ag/leto. Skupne količine vodnega zlata in srebra v geotermalnih rezervoarjih bi lahko bile reda velikosti 10.000 unč Au in več 100 tisoč unč Ag ali celo več.

Potrebne so nove tehnologije za pridobivanje plemenitih kovin iz fluidnega pretoka v proizvodnih vrtinah brez poseganja v proizvodnjo geotermalne energije, da bi bila neprestana ekstrakcija kovin izvedljiva. Druga možnost je, da pustimo, da se plemenite kovine kopičijo v dvofaznih cevovodih, in jih nato poberemo v intervalih, ki ustrezajo delovanju parnega geotermalnega polja (Broadlands-Ohaaki) in ki so optimalni z vidika dobičkonosnosti.

Vrtanje najbolj vroče geotermalne vrtine na svetu v Italiji

Raziskovalci in tehnologi iz vse Evrope so združili moči v sledenju skupnega cilja, da postane potencialno najbolj energetsko bogata vrtina na svetu realnost. Globoka vrtina se bo vrtala v Larderellu v Toskani (Italija), za projekt pa je namenjenih 15,6 milijona € raziskovalnih sredstev (Iga News, 2016, 102, str. 23).

Projekt DESCRAMBLE (Drilling in dEep, Super-CRitical AMBients of continental Europe) vòdi globalni proizvajalec zelene energije Enel Green Power. Cilj je izvleči največ možne energije iz vrtine. Izjemna vročina globoko pod Toskano pomeni, da bodo tako pritiski kot temperature tik na tisti meji, čemur so tudi inovativne tehnologije trenutno kos. Do sedaj so v tako ekstremnih pogojih temperature in tlaka uspeli delno nadzorovati vrtino le na Islandiji v vrtini IDDP- 1. Nekaj posebnega se zgodi, ko temperatura doseže 374 °C, tlak pa je 218-kratni zračni tlak na površini. Naletimo na tisto, čemur pravimo superkritična voda. Ni ne tekočina in niti ne para. Pojavlja se v fizikalni obliki, ki vključuje obe fazi, kar pomeni, da privzame povsem nove lastnosti.

Superkritični fluid se obnaša kot močna kislina, saj bo uničil karkoli, vključno elektroniko in vrtalno opremo. Ima pa tudi svoje prednosti. Ob uspešno izvedeni vrtini je lahko proizvodnja energije iz nje celo desetkrat višja kot pa voda in para dosežeta iz standardne geotermalne vrtine. Prav tako se lažje pretaka skozi razpoke in pore kamnin. Lahko prenaša v raztopini dragocene minerale na površje.

Operacija vrtanja zahteva visoko napredne tehnične priprave. Zaradi tega bo glavni tehnološki preboj najprej modeliran v posebej izdelanem simulatorju. To je SINTEF Petroleum Research že razvil za vrtanja za nafto in plin v napravi, podobni letalskemu simulatorju. Simulator bo podal vse razpoložljive podatke o načrtovani vrtini in njeni lokaciji.

Superkritični fluid mora biti pod nadzorom. Za čimbolj natančno napoved, kako se bo ta tekočina obnašala tako v globini v vrtini kot na njeni poti proti površju, se mora celoten proces modelirati v simulatorju toka. Simulator toka "LedaFlow" omogoča analizo bolj podrobnih in kompleksnih scenarijev toka, ki vključujejo t.i. večfazni prenos, kjer se nafta, plin in voda vsi pretakajo po istem cevovodu.

Medtem ko se nadaljuje delo na modeliranju in simulaciji naprednih operacij vrtanja, se še ena raziskovalna skupina spoprijema z drugačnimi težavami. Razvili bodo specialno sondo in jo spustili v vrtino, da izmerijo, kako dobro se vrtina obnaša in če zdrži temperature do 450°C in zelo visoke tlake. V ta namen razvijajo po meri zasnovano visoko temperaturno elektroniko, zaprto v neke vrste termos flaško, imenovano tudi Dewar flaška. Posoda mora biti dobro izolirana za zaščito merilnega instrumenta v njeni notranjosti v razmerah meritev v vrtini v trajanju nekaj ur pri temperaturah 250 do 450 °C. Takrat jeklo postaja krhko, plastika in elektronika pa odpovesta ali pa se pričneta taliti. Običajno elektronika deluje le kratek čas pri temperaturah nad 200 °C. Sedaj delajo s proizvajalci na izdelavi baterij, varnih za uporabo pri teh temperaturah. Projekt se je začel v Pisi sredi maja 2016, vrtanje se bo predvidoma pričelo v jeseni 2016.

Tabela 6. Porazdelitev neposredne rabe geotermalne energije po celinah; po Lund & Boyd (2016).

Table 6. The distribution of the direct use of geothermal energy by continent; after Lund & Boyd (2016).

Celine/Continents	**Število držav/ # Countries**	**%MW$_t$**	**%TJ/ leto-year**
Afrika/Africa	8	0,2	0,4
Ameriki/Americas	16	27,7	16,9
Azija/Asia	18	35,8	43,9
Evropa*/Europe*	37	35,6	37,3
Oceanija/Oceania	3	0,7	1,5

*Vključuje CIS države (Armenija, Belorusija, Gruzija, Rusija in Ukrajina)/Includes CIS countries (Armenia, Belarus, Georgia, Russia and Ukraine).

Zaključni komentarji

Geotermalna energija lahko kot povsod prisotna trajnostna in obnovljiva energija nadomešča druge oblike energijske rabe, posebej fosilna goriva, ki so ekološko gledano najbolj problematična, a prispevajo v svetovni preskrbi s primarno energijo več kot 80 %. Nekaj držav izstopa kot glavne koristnice geotermalnih fluidov za neposredno rabo (Kitajska, ZDA, Japonska, Islandija in Nemčija), seveda pa je bil razvoj v večini držav počasen. To ni presenetljivo, saj so geotermalni energiji glavni tekmec razmeroma poceni fosilna goriva, začetni stroški geotermalnih projektov pa so visoki. V mnogih državah so vseeno izvajali potrebne temeljne raziskave, izvedli inventure in ovrednotili svoje vire kot pripravo na razvoj, ko bo gospodarska situacija boljša in bodo vlade in privatni investitorji videli koristi v razvoju domačega obnovljivega energetskega vira. Porazdelitev neposredne rabe geotermalne

Tabela 7. Znatni doprinosi neposredne rabe geotermalne energije k državnemu gospodarstvu; po Lund & Boyd (2016).
Table 7. Significant contributions of direct-use geothermal energy to a country's economy; after Lund & Boyd (2016).

Islandija/Iceland	90 % stavbnega prostora je ogrevano / 90 % of building space heating
Japonska/Japan	2000 onsenov, 5000 javnih kopališč, 1500 hotelov s 15 mil. turistov letno / 2000 onsens, 5000 public baths, 1500 hotels serving 15 million guests / year
Švedska/Sweden	20 % stavb je ogrevano s sistemi GTČ / 20 % of building heated using GHPs
Švica/Switzerland	90.000 inštaliranih enot GTČ (ca 3 enote/km^2) / 90,000 geothermal heat pumps installed (≈3 units/km^2)
Tunizija/Tunisia	244 ha ogrevanih rastlinjakov / 244 ha of greenhouses heated
Turčija/Turkey	90.000 stanovanj je ogrevano v 16 mestih – blizu 30 % vseh stanov. enot / 90,000 apartment residences heated in 16 cities-approaching 30 % of the total units
ZDA/USA	1,4 milijona enot GTČ (7 % letna rast) / 1.4 million geothermal heat pumps (7.0 % annual growth)

energije po celinah sveta je v tabeli 6. Vodilni celini sta Azija in Evropa z 18 oziroma 37 državami, ki izkoriščajo geotermalno energijo v direktnih aplikacijah.

Poleg visokotemperaturnih se uporabljajo tudi nizko do srednjetemperaturni geotermalni viri v kombiniranih toplotnih-električnih obratih (angl. combined heat and power plant, CHP) za soproizvodnjo toplote in elektrike, kjer vroče vode, pogosto s temperaturami pod 100 °C, sprva peljejo skozi binarno ORC (Organic Rankine Cycle) elektrarno, nato za kaskadno ogrevanje prostorov, bazene, rastlinjake in/ali ribogojstvo, preden se jih vrača nazaj v vodonosnik. CHP projekti zagotovo povečajo izkoriščenost vira in izboljšajo ekonomiko projekta, kot se je pokazalo na Islandiji, v Avstriji in Nemčiji, kakor tudi na oregonskem tehnološkem inštitutu (Klamath Falls, ZDA).

V 42 državah sveta je bilo v zadnjih petih letih (2010 – 2014) izdelanih skupno 2218 novih vrtin, tako za namen neposredne rabe (38,7 %) kot proizvodnjo elektrike (48,8 %), in to v skupni globini 9.534,5 km, kot navajata Lund & Boyd (2015, 2016). To nam poda poprečno globino 4,3 km/vrtino, ki je 4-krat večja globina, kot je bila v obdobju 2005 – 2009. Tu niso zajete številne plitve vrtine za toplotne črpalke. Države, v katerih so izdelali za več kot 100 km vrtin, so: Madžarska, Kitajska, Kenija, Turčija, ZDA, Mehika, Filipini in Nova Zelandija. Največ vrtin po globinskih kilometrih je bilo izdelanih v Aziji (48,4 % in 1074 vrtin). Nadalje je bilo v 52 državah razporejeno 34.000 človek-leto dela v geotermiji in v geotermalne projekte v 49 državah je bilo vloženih 20 milijard US dolarjev, največ v Aziji (44 %). Glede prispevka geotermalne neposredne rabe k nacionalnemu energetskemu proračunu izstopa nekaj držav, vsaka s svojimi posebnostmi (tabela 7). Večina porasta te rabe se zelo jasno pripisuje geotermalnim toplotnim črpalkam. Razvoj bo v bodoče vseboval večji poudarek na obratih (elektrarnah) za kombinirano toploto in elektriko, posebno na tistih, ki bodo uporabljale nižjetemperaturne fluide do 100 °C. Največji porast bo zajemala inštalacija in uporaba GTČ, ker se le-te lahko uporabljajo kjerkoli v svetu, kot se je pokazalo v Švici, Skandinaviji, Avstriji, Nemčiji, na Madžarskem, v Kanadi, ZDA in še kje.

Sedanja nizka cena fosilnih goriv, predvsem nafte, zavira razvoj rabe geotermalne energije v nekaterih državah, vendar je pričakovati, da to ne bo dolgo trajalo, in bo geotermalna energija v naslednjih desetletjih postajala konkurenčna fosilnim gorivom. Prav tako so zelo pomembne okoljske koristi z njeno rabo, zato je pričakovati boljše razumevanje in sprejemljivost te vrste obnovljivega vira energije kakor tudi ostalih tovrstnih virov. Zato je pomembno širiti poznavanje o koristnosti rabe geotermalne energije, njene različne možne uporabe in okoljske koristi, ki iz nje izhajajo. V Sloveniji skoraj vse kategorije rabe geotermalne energije iz termalne vode kažejo v zadnjih petih letih stagnacijo v izkoriščanju te energije, izjema je ogrevanje rastlinjakov. Stalno rast beleži seveda tudi izkoriščanje plitve geotermalne energije s sistemi GTČ.

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GEOLOGIJA *59/1*, 115-116, Ljubljana 2016

Nova knjiga

Urednika: Nina RMAN & Matevž NOVAK, 2016: **70 geoloških zanimivosti Slovenije.** Geološki zavod Slovenije, Ljubljana: 204 str.

Geološka stroka letos praznuje pomembno obletnico – 70 let delovanja Geološkega zavoda Slovenije (GeoZS). Dogodki, posvečeni temu jubileju, se bodo odvijali skozi vse leto, začeli pa so se z odkritjem spomenika »70ka«, ki ga sestavlja sedem značilnih slovenskih kamnin, ter izidom knjige »70 geoloških zanimivosti Slovenije«.

V preteklosti so slovenski geologi že skušali približati našo stroko širši javnosti. Leta 1958 so tako izšli Geološki izleti po Sloveniji in leta 1961 Geološki izleti po ljubljanski okolici prof. dr. Antona Ramovša. Dobrih dvajset let kasneje je prof. dr. Stanko Buser z velikim optimizmom in navdušenjem načrtoval Slovensko geološko transverzalo. Nastal je vodniček k njenemu prvemu delu – Vodnik poti Jezersko-Tržič-Jesenice ter oštevilčene oznake po predvideni trasi, a žal brez komentarja ali tabel z razlagami na terenu. Vrzel sta nekoliko zapolnila oba geoparka, ki predstavljata bogato geološko dediščino Mežice s Karvankami ter Idrije z okolico. Miniti pa je moralo preko 30 let, da držimo v rokah publikacijo, ki na poljuden, a kljub temu strokoven način, predstavlja zanimive geološke pojave iz vseh delov Slovenije.

Zahtevnega projekta sta se kot gonilna sila lotila urednika dr. Nina Rman in dr. Matevž Novak.

K delu sta pritegnila še 25 soavtorjev iz različnih geoloških inštitucij: Geološkega zavoda Slovenije, Oddelka za geologijo Naravoslovnotehniške fakultete, Prirodoslovnega muzeja, Zavoda republike Slovenije za varstvo narave ter nekatere posameznike, tehnično vodstvo pa je prevzel GeoZS. Knjižica je zastavljena kot turistični vodnik, namenjena vsem, ki jih zanimajo tudi geološke zanimivosti našega ozemlja. V roke jo bodo lahko vzele družine, ki načrtujejo nedeljski izlet, v nahrbtnik jo bodo dodali planinci, ki na poti radi gledajo tudi »pod noge«, prav bo prišla šolam in društvom, ki bi svoje dejavnosti želeli oplemenititi s spoznavanjem »v živo«, predvsem pa vsi tisti, ki po naši deželi hodijo z odprtimi očmi in srcem ter si želijo spoznati vedno nekaj novega in drugačnega. Slovenija je kljub svoji majhnosti geološko izredno pestra – od Alp, Panonske ravnice in Sredozemlja je v kamninah zabeleženih tri milijarde let zgodovine. Našo pozornost lahko pritegnejo različne kamnine, fosili in minerali, ki jih skrivajo, vodna in rudna bogastva, posebne geomorfološke oblike in končno tudi muzeji, ki hranijo nekatere še posebej zanimive primerke – od meteorita do fosilnih morskih konjičkov. Geološki turistični vodnik je tako namenjen spoznavanju raznolike zgradbe Slovenije, predvsem pa geološko stroko na nevsiljiv, poljuden način predstavlja in razlaga širši javnosti. Cilj publikacije je ne le povečati prepoznavnost geologije, temveč tudi širiti razumevanje pomena njenih ugotovitev za vsakdanje življenje.

Avtorji so se potrudili, da so poiskali geološke zanimivosti prav v vseh delih Slovenije. Razdelili so jo na regije – osrednjeslovensko, zasavsko, gorenjsko, goriško, obalno-kraško, primorsko-notranjsko, jugovzhodno, podravsko, pomursko in koroško, ter v njih opisali skupno 70 tipičnih geološko zanimivih turistično-izletniških točk. Večina jih je lahko dostopnih, nekatere so opremljene tudi z informativnimi tablami in drugim učnim gradivom. Namenoma so izpustili nekatere znamenitosti, dodatno pa so vključili šest muzejskih primerkov.

Vodnik je zastavljen jasno in pregledno. V uvodnem delu je pojasnjen izbor geoloških zanimivosti, uporaba vodnika in kar je še posebej pomembno – geobonton. Sledi legenda simbolov, ki obiskovalca pri vsaki od točk opozori, na kakšno vrsto pojavov naj bo pozoren. Zelo dobrodošlo je poglavje, ki na kratko, a kljub temu dovolj sporočilno in strokovno korektno, podaja geološko zgodovino Slovenije. Sledi opis posameznih točk, ki se vedno prične z izsekom geološke karte obravnavane regije. Za posamezno opazovališče je podan dostop opisno, s koordinatami, na topografski karti in s kodo QR na spletnem zemljevidu, fotografija pojava, njegova zavarovanost ter besedilo, ki povzema glavne značilnosti in posebnosti. Zelo dobrodošle so tudi skice in detajlne fotografije, ki dodatno pomagajo pri razumevanju ter v nekaterih primerih odkrijejo tisto, kar s prostim očesom ni vidno. Na koncu knjižice sledi spisek javnih in registriranih zasebnih geoloških zbirk v Sloveniji, kakršnega do sedaj še nismo imeli. Zagotovo bo pripomogel k temu, da bodo zbirke pridobile številnejše obiskovalce, njihovi lastniki in upravljavci pa priznanje za svoje delo. Podatki o zbirkah se sproti osvežujejo in so prosto dostopni na spletni strani http://www.geo-zs.si/?option=com_content&view=article&id=172. Za najbolj radovedne je za vsako od opisanih točk pripravljen tudi izbor poljudne in strokovne literature.

Snovalci projekta so opravili zares odlično delo, ki bo pripomoglo k umeščanju geološke stroke v širšo javnost. Avtorjem zato iskrene čestitke, z željo, da nadaljujejo z enakim zagonom.

Nina Zupančič

Poročila

Mednarodna delavnica o ledenih jamah "IWIC VII"
Postojna, 16.–22. 05. 2016

Polona VREČA

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V Postojni je v času od 16. do 22. maja 2016, na Inštitutu za raziskovanje krasa (IZRK) ZRC SAZU potekala sedma mednarodna delavnica o ledenih jamah IWIC VII (International Workshop on Ice Caves), ki se je je udeležilo približno 40 raziskovalcev. Delavnico so pod vodstvom A. Mihevca organizirali sodelavci IZRK ZRC SAZU v sodelovanju s Komisijo za jame v ledenikih in firnih ter jame z ledom (Comission on Glacier, Firn and Ice Caves), ki deluje v okviru Mednarodne speleološke zveze (International Speleological Union). Prva tovrstna delavnica je potekala v Romuniji leta 2004, nato pa so na dve leti sledila srečanja na Slovaškem, v Rusiji, v Avstriji, v Italiji, v ZDA in letos v Sloveniji. Glavni cilji srečanja v Postojni so bili predstavitev rezultatov raziskav, izmenjava spoznaj in izkušenj tudi v obliki terenskih ekskurzij po dinarskem in alpskem krasu ter spodbujanje tako nacionalnega kot mednarodnega povezovanja.

Delavnica se je pričela v ponedeljek, 16. 5. 2016, s spoznavnim sprejemom, na katerem so udeleženci delavnice lahko okusili led iz Velike ledene jame v Paradani. Torek, 17. 5. 2016, se je pričel z uradno otvoritvijo delavnice s pozdravnimi govori A. Mihevca, kot glavnega organizatorja IWIC VII, predstojnika IZRK ZRC SAZU T. Slabeta, glavne tajnice Mednarodnega speleološkega združenja N. Zupan Hajna in V. Maggija, predsednika Komisije za jame v ledenikih in firnih ter jame z ledom. Sledile so predstavitve M. Ogrina in sodelavcev o podnebju slovenskega gorskega sveta s poudarkom na temperaturnih razmerah v mraziščih, N. Buzjaka in sodelavcev o geografski porazdelitvi in vrstah ledenih jam na Hrvaškem, M. Temovskega o ledenih jamah v Makedoniji, A. Pflitscha in sodelavcev o klimatoloških raziskavah ledeniških jam na vulkanih Mount Hood in Mount Rainier v ZDA, S.-E. Lauritzena s sodelavci o dinamiki ledene jame Svarthammar na Norveškem in A. Mihevca o periglacialnih pojavih v jamah s primeri iz Slovenije. V popoldanskem času je potekala ekskurzija v Skedneno jamo in ogled jam in ostalih pojavov na severnem obrobju Planinskega polja.

V sredo, 18. 5. 2016, smo najprej poslušali predavanje N. Zupan Hajna, ki je predstavila zanimivo kraško depresijo na območju Snežnika, nato pa so sledila predavanja C. Meyer, ki je predstavila metodo CALCFLOW, ki se lahko uporabi za določanja toka zraka s pomočjo merilcev temperature, F. Scota, ki je s sodelavci predstavil model kroženja zraka in rezultate topografskih meritev v jami Grotta del Gelo na vulkanu Etna v Italiji, R. Collucija in sodelavcev o odzivu bilance ledu v ledenih jamah na območju kaninskega masiva na naraščajoče ekstremne dogodke v Julijskih Alpah in M. Stauta s sodelavci o recentnih spremembah količine ledu v Ledeni jami pri Planini Viševnik, severno od Bohinjskega jezera. V nadaljevanju je J. Košutnik predstavil rezultate raziskav spreminjanja volumna ledu v nekaterih ledenih jamah v Sloveniji, G. Brick je predstavil ledene jame v pripovedih iz male ledene dobe, F. Sauro nas je seznanil z rezultati večletnega projekta laserskega skeniranja in monitoringa ledene jame Cenote v Dolomitih v Italiji, A. Persoiu s sodelavci pa je predstavil uporabo stabilnih izotopov v raziskavah jamskega ledu s poudarkom na sledenju sprememb zračne vlage v vzhodni Evropi.V popoldanskem času smo obiskali Škocjanske jame in si ogledali brezstropo jamo v Lipovi dolini. V četrtek, 19. 5. 2016, smo dopoldan poslušali predavanja in predstavitve posterjev, popoldan pa je bil organiziran obisk Postojnske jame. Predavanja je pričel S. Polak, ki je predstavil migracije jamskih hroščev kot odziv na temperaturna nihanja v ledeni jami in sicer Jami jugozahodno od Mašuna na Snežniku, F. Pappi je predstavila rezultate ekoloških raziskav epikraških združb v Snežni jami na planini Arto v osrednji severni Sloveniji na območju Raduhe, S.-E. Lauritzen pa še speleogenezo jame Svarthammar na Norveškem. Sledile so predstavitve posterjev in sicer C. Itcus o pestrosti bakterij ter porazdelitvi bakterij in arhej v ledenem bloku v jami Scarisoara v Romuniji, Z. Kerna o stratigrafiji in spremembah količine ledu v Kugini ledenici na Velebitu na Hrvaškem ter o izotopskih raziskavah kriogenih karbonatnih mineralov v jami Scarisoara v Romuniji, M. Gomez-Lende o termičnih razmerah v ledenih jamah Picos de Europa v severni Španiji, L. Øvreas o mikrobiomu iz kronološke sekvence v ledeni jami Svarthammar na Norveškem, V. Maggija o preliminarnih rezultatih analize 7,8 m dolgega jedra ledu iz jame Vasto v jugovzhodnih Alpah, R. Collucija o mikroklimatskih razmerah v jami Buso del Valon ter o novem seznamu ledenih jam na območju jugovzhodnih Alp, in J. Košutnika o mejnikih raziskovanja ledenih jam v Sloveniji, od Valvasorja do Pavla Kunaverja. Sledili sta še predavanji Z. Kerna o radiokarbonskih analizah organskih delcev iz ledenega bloka v dvorani Saarhalle, jama Mammuthöhle v Avstriji in M.

Luetscherja o identifikaciji prisotnosti jamskega ledu v preteklosti s pomočjo kriogenih jamskih karbonatov v alpskih jamskih sistemih. Ob koncu predavanj je V. Maggi na kratko predstavil delo Komisije za jame v ledenikih in firnih ter jame z ledom in glavne cilje komisije med katere sodijo tudi karte ledenih jam tako na nacionalnem kot regionalnem nivoju.

Sledili sta še celodnevni ekskurziji z ogledom dveh ledenih jam v Sloveniji. V petek, 20. 5. 2016, je potekala celodnevna ekskurzija z obiskom Velike ledene jame v Paradani in visokega krasa na Trnovski planoti vključno z ogledom Smrekove drage, na dnu katere se pojavlja permafrost. V soboto, 21. 5. 2016, pa je potekala še ekskurzija v Snežno jamo na planini Arto, ki leži na južnem pobočju Raduhe. Za vse ekskurzije so organizatorji pripravili podrobne opise, ki so bili objavljeni v zborniku skupaj s povzetki predavanj in posterjev.

Sedma mednarodna delavnica o ledenih jamah v Postojni je bila zelo poučna in je omogočila druženje z domačimi in tujimi raziskovalci ter veliko izmenjav zanimivih informacij, predvsem med terenskimi ekskurzijami po dinarskem in alpskem krasu. Naslednja delavnica o ledenih jamah bo leta 2018 v Španiji.

Letna skupščina Slovenskega združenja za geodezijo in geofiziko (SZGG)

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V Ljubljani je 28. januarja 2016 na Fakulteti za gradbeništvo in geodezijo potekala letna skupščina Slovenskega združenja za geodezijo in geofiziko (SZGG), po skupščini pa je potekalo enaindvajseto srečanje z naslovom »Raziskave s področja geodezije in geofizike – 2015«. SZGG je združenje, ki povezujejo zelo različne profile strokovnjakov, ki se ukvarjajo z raziskavami Zemlje, tudi geologov, in omogoča zanimivo izmenjavo različnih znanj.

V okviru skupščine je najprej podal kratko poročilo o delu v preteklem letu predsednik združenja R. Čop, ki mu je sledilo poročilo tajnika združenja M. Kuharja ter podelitev priznanj SZGG mlajšim raziskovalcem, M. Sečniku za področje hidrologije in O. Strletu za področje geodezije. V okviru SZGG deluje osem sekcij, katerih vodje so hkrati predstavniki Slovenije v mednarodnih združenjih, ki delujejo v okviru Mednarodne zveze za geodezijo in geofiziko (International Union of Geodesy and Geophysics – IUGG). Predstavniki posameznih sekcij so predstavili kratka poročila o delu v preteklem letu: B. Stopar (Sekcija za geodezijo), P. Zupančič (Sekcija za seizmologijo in fiziko notranjosti Zemlje), M. Kobold (Sekcija za hidrologijo), M. Miklavec (Sekcija za geomagnetizem) in P. Vreča (Sekcija za kriosfero). Predstavitve so dostopne na http://www.fgg.uni-lj.si/sugg/ .

Sledilo je strokovno srečanje, na katerem je štirinajst predavateljev predstavilo rezultate raziskovalnega dela. S. Šebela je predstavila rezultate raziskav Črne jame, ki je najhladnejša jama v Postojnskem jamskem sistemu, A. Gosar je predstavil skalne podore, ki so nastali ob potresu leta 1998 v Krnskem pogorju in možnost njihove uporabe za oceno seizmičnih intenzitet po Environmental Seismic Intensity lestvici (ESI 2007), B. Strajnar je na primeru letalskih opazovanj Mode-S MRAR in prognostičnega modela ALADIN-Slovenija predstavil kaj in zakaj določa vpliv opazovanj na kvaliteto vremenskih napovedi, M. Mole, pa je prikazala rezultate raziskav atmosferskih procesov v Vipavski dolini, ki so bile opravljene na osnovi razširjanja aerosolov. Sledila so predavanja M. Sečnika o video kontrolnem sistemu prehajanja rib v ribji stezi pri zapornici na Ambroževem trgu in na jezu pri Fužinskem gradu v Ljubljani, M. Triglav Čekada, ki je prikazala rezultate laserskega skeniranja Slovenije in njegove uporabe pri določanju akumulacijskih reliefnih oblik v slovenskem visokogorju s katerim so identificirali prvi fosilni kamniti ledenik pod Rutarškim Vršičem v Sloveniji, R. Čopa o absolutnih meritvah zemeljskega magnetnega polja, A. Rojca o sončnih ciklih in turističnem gospodarstvu Slovenije, A. Trobec o raziskavah strukture sedimentnega morskega dna v Strunjanskem zalivu s podpovršinskim sonarjem, P. Pavlovčič Prešeren o modeliranju plimovanja trdne Zemlje za geodetsko določanje 3D položaja točk kombinirane geodetske mreže in K. Zabret, ki je prikazala vpliv fenološke faze, trajanja padavinskega dogodka ter mikrostrukture padavin na proces prestrezanja padavin. Nadalje je O. Sterle predstavil stanje horizontalne komponente državnega koordinatnega sistema D96, M. Zlata Božnar je prikazala nov algoritem in namensko orodje za analizo dnevnih ciklov npr. sončnega obsevanje ("sončnica"), za analizo onesnaženja z delci PM10 ("onesnažnica"), za analizo rože vetrov ("vetrovnica") in za analizo vremenske napovedi ("vremenčica"). Zborovanje se je zaključilo s predavanjem A. Mihevca o uporabi lidarskih posnetkov v geomorfologiji krasa na primeru več brezstropih jam v Lipovih dolinah, v Lozi, pri Povirju in v podgorskem krasu. Prispevki so objavljeni v Zborniku referatov SZGG 2015 in so dostopni na http://www.fgg.uni-lj.si/sugg/.

Predstavitev Slovenskega geološkega društva in letno poročilo za leto 2015

Matevž NOVAK

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Slovensko geološko društvo (SGD), s sedežem na Dimičevi ul. 14 v Ljubljani, je strokovno združenje slovenskih geologov. Kot nevladna in neprofitna organizacija prostovoljno združenih strokovnjakov in ljubiteljev geologije si je za temeljni cilj postavilo napredek znanosti in prakse na področju vseh vej geologije, kar je zapisano tudi v njegovem statutu. Društvo zato prireja javna predavanja, strokovne ekskurzije, razstave, znanstvene sestanke in delavnice, skrbi za popularizacijo geologije in za vključevanje geoloških ved v osnovnošolske in srednješolske učne programe, sodeluje pri prizadevanjih za varstvo okolja in pri izdelavi zakonskih aktov in normativov s področja geologije, sodeluje tudi z drugimi strokovnimi društvi v Sloveniji in tujini in je vključeno v več mednarodnih organizacij.

Na občnem zboru SGD, 9. oktobra 2014 v Ankaranu, so bili izvoljeni novi organi društva: predsednik Matevž Novak, podpredsednik Timotej Verbovšek, tajnica Nina Rman, blagajničarka Bernarda Bole, in člani izvršnega odbora Miloš Markič, Matija Križnar, Petra Žvab Rožič, Luka Gale in Nadja Zupan Hajna. Izvoljeni organi imajo 4 letni mandat, zato v letu 2015 ni bilo volitev. V okviru društva delujejo naslednje sekcije: *Sekcija za geokemijo* (predsednica Mateja Gosar), *Skupina za sedimentarno geologijo* (predsednik Adrijan Košir), *Sekcija za mineralogijo* (predsednik Miha Jeršek) in *Sekcija za geološko dediščino* (predsednica Martina Stupar). Razširjeni izvršni odbor sestavljajo predsedniki sekcij, nadzorni odbor (Špela Goričan, Miloš Bavec in Vladimir Vukadin) in častno razsodišče (Katica Drobne, Jernej Pavšič in Dragomir Skaberne).

V preteklih letih je društvo delovalo v skladu z določili društva in programom dela, ki je bil sprejet na IO društva v vsakem koledarskem letu. Večina zastavljenih aktivnosti in ciljev programa je bila v letu 2015 realizirana.

Strokovna predavanja

Ladislav Palinkaš (Univerza v Zagrebu), »Sv. Jakob *Pb-Zn rudno ležište, Mežica na Medvednici«*, 24. februar 2015 ob 17. uri v Ljubljani na Oddelku za geologijo NTF, Privoz 11.

Jure Žalohar, »Omega-Teorija; nova fizikalna teorija potresov«, 2. april 2015 ob 17. uri v Ljubljani na Oddelku za geologijo NTF, Privoz 11.

Helmut Weissert (ETH Zürich), »*Pelagic sediments – archives for ocean and climate history*«, 21. april 2015 ob 18. uri v Ljubljani v Prešernovi dvorani SAZU, Novi trg 4. Predavanje je organizirala Skupina za sedimentarno geologijo, ki deluje tudi kot sekcija SGD in je potekalo v okviru International Association of Sedimentologists (IAS) Lecture Tour 2014-2015.

Adrien Moulin (CEREGE, Aix en Provence), »*Active tectonics of the Alps-Dinarides junction: Quantitative morphology, fault kinematics and implications for the Adria microplate geodynamics*«, 20. maj 2015 ob 17:30. uri v Ljubljani na Oddelku za geologijo NTF, Privoz 11.

Dogodek v počastitev 200-letnice smrti naravoslovca Balthasarja Hacqueta s predavanjema Mihaela Brenčiča in Jožeta Čarja je bil izveden 29. oktobra ob 17. uri v Ljubljani na Oddelku za geologijo NTF, Privoz 11.

Strokovna posvetovanja, seminarji in okrogle mize

Seminar *Kako do zaposlitve* za študente geologije je bil na pobudo Luke Galeta izveden 23. januarja 2015 med 14. in 19. uro v Ljubljani na Oddelku za geologijo NTF, Privoz 11. Seminar sta sestavljala dva dela. Prvi del je bil delavnica s sledečimi temami: Kaj me čaka po diplomi (vodila A. Kastelic), Življenje in agonije mladega raziskovalca (vodila L. Korat), Kako pripraviti življenjepis & Moj prvi intervju (vodil G. Mesarić iz Moja zaposlitev d.o.o.), Geolog kot samostojni podjetnik (vodil T. Verbič). Drugi del je bil okrogla miza, na kateri so sodelovali predstavniki inštitutov in podjetij, kjer zaposlujejo geologe (GeoZS, IRGO, ELEA), pedagoško osebje NTF in drugi poklicni geologi. Seminarja se je udeležilo 45 študentov.

Slovensko geološko društvo je bilo soorganiza-tor *22. posvetovanja slovenskih geologov*, ki je potekalo 30. novembra 2015 v Ljubljani na Oddelku za geologijo NTF, Privoz 11. Na posvetovanju je bilo predstavljenih 48 predavanj in 16 posterjev. Slovensko geološko društvo je sodelovalo tudi z dvema posterjema s predstavivijo projektov KINDRA in INTRAW. Spletna stran posvetovanja je: http://web.geo.ntf.uni-lj.si/22-posvet-geologov/Home

Mednarodno delovanje SGD in članstvo v tujih in domačih zvezah

SGD je včlanjeno v tuje zveze: European Federation of Geologists (EFG), International Union for Quaternary Research (INQUA), European Association for the Conservation of the Geological Heritage (ProGeo), European Mineralogical Union (EMU) in International Mineral Association (IMA). Včlanjeni smo tudi v Slovensko inženirsko zvezo (SIZ).

Na poziv *European Federation of Geologists (EFG)* smo posredovali seznam nacionalnih ekspertov za 9 področij geologije. Podpisali smo dogovor o sodelovanju v dveh evropskih (Horizon 2020) projektih (INTRAW in KINDRA) kot pridruženi partner EFG, ki je vodilni partner. Odgovorni osebi SGD za izvedbo projektov sta Snježana Miletić za INTRAW – *International Cooperation on Raw materials* in Mihael Brenčič za KINDRA – *Knowledge Inventory for Hydrogeology Research*.

Marko Komac je maja 2015 postal prvi slovenski geolog, ki mu je bil uradno podeljen naziv Evrogeolog.

Konec leta 2015 smo prejeli povabilo EFG, da sodelujemo kot njihovi pridruženi partnerji še v dveh evropskih (Horizon 2020) projektih: UNEXMIN – *An Autonomous Underwater Explorer for Flooded Mines* in CHPM 2030 – *Combined Heat, Power and Metal extraction from ultra-deep ore bodies*. Odločili smo se, da podpišemo dogovor o sodelovanju za oba projekta.

Sodelovali smo kot soorganizator *4. znanstvenega srečanja INQUA* z naslovom »*Quaternary Geology in Croatia and Slovenia*«, ki je bilo v Zagrebu 25.–26. marca 2015. V okviru srečanja je bila 27. marca organizirana *ekskurzija v Ljubljansko kotlino*. Tema ekskurzije je bila kvartarna dinamika Ljubljanske kotline (aktivna tektonika, razvoj kotline, poledenitve in pobočni procesi). Ekskurzijo so vodili člani našega nacionalnega odbora v INQUA, Petra Jamšek Rupnik, Tomislav Popit, Miloš Bavec, Tina Peternel in Jernej Jež. Izdan je bil vodič za to ekskurzijo.

Drugi dogodki

V mesecu maju 2015 so vaščani vasi Dešen pri Kresnicah zaprosili Zavod RS za varstvo narave, Oddelek za geologijo NTF in SGD za pomoč pri predstavitvi zanimive geologije kamnoloma nad omenjeno vasjo in za donacijo za postavitev informativne table. SGD je obema prošnjama ustreglo in maja 2016 bo *v Dešnu postavljena interpretacijska točka*.

SGD je 12. junija 2015 sodelovalo na dogodku *BioBlitz – 24 ur z reko Muro* v organizaciji Zavoda RS za varstvo narave, Območne enote Maribor. Na dogodku smo se predstavili na stojnici skupaj z Geološkim zavodom Slovenije in Oddelkom za geologijo NTF. Na stojnici smo predstavili značilne geološke primerke in model vodonosnika, kot jih najdemo na območju SV Slovenije, omogočili izdelavo in barvanje modelčkov fosilov, izdelavo peščenih slik z geološko vsebino in predstavljali poljudne in strokovne publikacije omenjenih inštitucij.

Rmanova in Novak sta na BioBlitzu izvedla še *Geološko delavnico o kamninah, mineralih in fosilih* za učence prve in druge triade, ter vodeni sprehod z naslovom *Kakšna voda se skriva v Veržeju?* za učence druge in tretje triade OŠ in SŠ. Obeh aktivnosti se je skupaj udeležilo 46 otrok.

Vsakoletna *delovna akcija čiščenja zarasti geološkega profila* v sodelovanju z Zavodom RS za varstvo narave (ZRSVN), ki je bila predvidena v kamnolomu Lastivnica (Anhovo) v soboto, 7. novembra, je zaradi neizvedenih pripravljalnih del v kamnolomu (sečnja večjih dreves) odpadla in je prestavljena na leto 2016.

V letu 2016 so načrtovane in delno že izvedene naslednje dejavnosti društva:

Strokovna predavanja

Predavanje Sarah Halvorson (Oddelek za geografijo Univ. v Montani, ZDA) z naslovom »*Large -Scale Environmental Transformations in Western Montana: From Glacial Lake Missoula to 21st Century Restoration Science*« je bilo že izvedeno 10. marca 2016 ob 17. uri v Ljubljani v dvorani Zemljepisnega muzeja Geografskega inštituta Antona Melika ZRC SAZU, Gosposka 16. Predavanje je bilo izvedeno v soorganizaciji z Geomorfološkim društvom Slovenije.

Predavanje Micheleja Morsillija (Univ. v Ferrari) z naslovom »*Internal waves: their impact on sedimentary systems and benthic communities*« je bilo izvedeno 22. marca 2016 ob 17. uri v Ljubljani na Oddelku za geologijo NTF, Privoz 11.

Predavanje Mihaela Brenčiča (NTF, GeoZS) z naslovom *Popotovanje po moskovskih geoloških muzejih* je bilo 7. aprila 2016 ob 17. uri v Ljubljani na Oddelku za geologijo NTF, Privoz. Predavanje je bilo izvedeno v soorganizaciji s Prirodoslovnim društvom Slovenije.

Predavanje Mihaela Brenčiča (NTF, GeoZS) z naslovom *Ob dvestoletnici rojstva prvega šolanega slovenskega geologa Marka Vincenca Lipolda* bo izvedeno v jeseni 2016.

Predavanje Mirijam Vrabec z naslovom *Sveže novice s pohorske golice* o rezultatih geoloških raziskav v zadnjih 6 letih na območju Pohorja je predvideno v oktobru 2016.

Strokovne ekskurzije

SGD bo sodelovalo pri organizaciji terenske delavnice »*27th European Dendroecological Fieldweek*«, ki bo septembra potekala med 12. in 18. septembrom 2016 v Kranjski gori in dolini Tamar. Delavnico organizira Švicarski gozdarski inštitut (WSL) v sodelovanju z Naravoslovnotehniško fakulteto UL in Gozdarskim inštitutom Slovenije.

V oktobru 2016 je predvidena *strokovna ekskurzija na Pohorje* pod vodstvom Mirijam Vrabec. Tema ekskurzije bo predstavitev novih dognanj o sestavi magmatskih in metamorfnih kamnin Pohorja.

Za pozno jesen je načrtovana ekskurzija v Devin na ogled razstave o hadrozavru Antoniju in na predavanje in ogled nihala (sinhrotrona) v Briški jami. Ekskurzija bo izvedena v soorganizaciji z Društvom študentov geologije.

Drugi dogodki

Jeseni ali pozimi 2016 nameravamo izvesti delavnico *Rišem in fotografiram geološko* za študente, zbiralce in raziskovalce. Delavnico o fotografiranju v studiu in tehnikah risanja bo vodil Matija Križnar s sodelovanjem z Društvom prijateljev mineralov in fosilov Slovenije (Rok Gašparič) in Društvom študentov geologije.

Slovensko geološko društvo bo tudi v letu 2016, 10. in 11. junija, sodelovalo na dogodku *BioBlitz – 24 ur z reko Muro* v Veržeju v organizaciji Zavoda RS za varstvo narave, Območne enote Maribor. Izvedeni bosta geološka in hidrogeološka delavnica in predstavitev na stojnici skupaj z Geološkim zavodom Slovenije in Oddelkom za geologijo Naravoslovnotehniške fakultete.

Sporočilo članom Slovenskega geološkega društva

Ker jedro društva tvorijo njegovi člani, pozivam vse k večji aktivnosti, izvedbi predavanj in ekskurzij ter seveda k spodbujanju debat in reševanju odprtih problemov slovenske geologije.

Redni član društva lahko postane vsak, ki se poklicno ali kako drugače ukvarja z vsaj eno od vej geološke vede in s svojim raziskovalnim, strokovnim, pedagoškim ali ljubiteljskim delom prispeva k razvoju vede in z njo povezanih strok. Častni član lahko postane posameznik, ki je pomembno prispeval k razvoju geološke vede v Sloveniji in v mednarodnem prostoru. Častni člani ne plačujejo članarine. Pridruženi člani so fizične osebe, ki se ljubiteljsko ukvarjajo z zbiranjem mineralov in fosilov ali se drugače zanimajo za geologijo. Podporni člani so fizične in pravne osebe, ki finančno podpirajo delovanje društva, lahko sodelujejo na sejah skupščine, vendar nimajo pravice odločanja. Za včlanitev v društvo je treba predložiti pisno pristopnico (dostopna na spletni strani www.geoloskodrustvo.si), s katero se posameznik zaveže, da bo deloval v skladu s statutom in plačeval članarino.

Navodila avtorjem

GEOLOGIJA objavlja znanstvene in strokovne članke s področja geologije in sorodnih ved. Revija od leta 2000 izhaja dvakrat letno. Članke recenzirajo domači in tuji strokovnjaki z obravnavanega področja. Ob oddaji člankov avtorji predlagajo **tri recenzente**, vendar pa si uredništvo pridržuje pravico do izbire recenzentov po lastni presoji. Avtorji morajo članek popraviti v skladu z recenzentskimi pripombami ali utemeljiti zakaj se z njimi ne strinjajo.

Avtorstvo: Za izvirnost podatkov, predvsem pa mnenj, idej, sklepov in citirano literaturo so odgovorni avtorji. Z objavo v GEOLOGIJI se tudi obvežejo, da ne bodo drugje objavili prispevka z isto vsebino.

Jezik: Članki naj bodo napisani v angleškem, izjemoma v slovenskem jeziku, vsi pa morajo imeti slovenski in angleški izvleček. Za prevod poskrbijo avtorji prispevkov sami.

Vrste prispevkov:

Izvirni znanstveni članek
Izvirni znanstveni članek je prva objava originalnih raziskovalnih rezultatov v takšni obliki, da se raziskava lahko ponovi, ugotovitve pa preverijo. Praviloma je organiziran po shemi IMRAD (**I**ntroduction, **M**ethods, **R**esults, **A**nd **D**iscussion).

Pregledni znanstveni članek
Pregledni znanstveni članek je pregled najnovejših del o določenem predmetnem področju, del posameznega raziskovalca ali skupine raziskovalcev z namenom povzemati, analizirati, evalvirati ali sintetizirati informacije, ki so že bile publicirane. Prinaša nove sinteze, ki vključujejo tudi rezultate lastnega raziskovanja avtorja.

Strokovni članek
Strokovni članek je predstavitev že znanega, s poudarkom na uporabnosti rezultatov izvirnih raziskav in širjenju znanja.

Diskusija in polemika
Prispevek, v katerem avtor ocenjuje ali dokazuje pravilnost nekega dela, objavljenega v Geologiji, ali z avtorjem strokovno polemizira.

Recenzija, prikaz knjige
Prispevek, v katerem avtor predstavlja vsebino nove knjige.

Oblika prispevka: Besedilo pripravite v urejevalniku Microsoft Word. Prispevki naj praviloma ne bodo daljši od 20 strani formata A4, v kar so vštete tudi slike, tabele in table. Le v izjemnih primerih je možno, ob predhodnem dogovoru z uredništvom, tiskati tudi daljše prispevke.

Članek oddajte uredništvu vključno z vsemi slikami, tabelami in tablami v elektronski obliki po naslednjem sistemu:
- *Naslov članka (do 12 besed)*
- *Avtorji (ime in priimek, naslov, e-mail naslov)*
- *Ključne besede (do 7 besed)*
- *Izvleček (do 300 besed)*
- *Besedilo*
- *Literatura*
- *Podnaslovi k slikam in tabelam*
- *Tabele, Slike, Table*

Citiranje: V literaturi naj avtorji prispevkov praviloma upoštevajo le tiskane vire. Poročila in rokopise naj navajajo le v izjemnih primerih, z navedbo kje so shranjeni. V seznamu literature naj bodo navedena samo v članku omenjena dela. Citirana dela, ki imajo DOI identifikator, morajo imeti ta identifikator izpisan na koncu citata. Za citiranje revije uporabljamo standardno okrajšavo naslova revije. Med besedilom prispevka citirajte samo avtorjev priimek, v oklepaju pa navajajte letnico izida navedenega dela in po potrebi tudi stran. Če navajate delo dveh avtorjev, izpišite med tekstom prispevka oba priimka (npr. Pleničar & Buser, 1967), pri treh ali več avtorjih pa napišite samo prvo ime in dodajte et al. z letnico (npr. Mlakar et al., 1992). Citiranje virov z medmrežja v primeru, kjer avtor ni poznan, zapišemo (Internet 1). V seznamu literaturo navajajte po abecednem redu avtorjev.

Imena fosilov (rod in vrsta) naj bodo napisana poševno, imena višjih taksonomskih enot (družina, razred, itn.) pa normalno. Imena avtorjev taksonov naj bodo prav tako napisana normalno, npr. *Clypeaster pyramidalis* Michelin, *Galeanella tollmanni* (Kristan), Echinoidea.

Primeri citiranja članka:

Mali, N., Urbanc, J. & Leis, A. 2007: Tracing of water movement through the unsaturated zone of a coarse gravel aquifer by means of dye and deuterated water. Environ. geol., 51/8: 1401–1412, doi:10.1007/s00254-006-0437-4.

Pleničar, M. 1993: *Apricardia pachiniana* Sirna from lower part of Liburnian beds at Divača (Triest-Komen Plateau). Geologija, 35: 65–68.

Primer citirane knjige:

Flügel, E. 2004: Mikrofacies of Carbonate Rocks. Springer Verlag, Berlin: 976 p.

Jurkovšek, B., Toman, M., Ogorelec, B., Šribar, L., Drobne, K., Poljak, M. & Šribar, Lj. 1996: Formacijska geološka karta južnega dela Tržaško-komenske planote – Kredne in paleogenske kamnine 1: 50.000 = Geological map of the southern part of the Trieste-Komen plateau – Cretaceous and Paleogene carbonate rocks. Geološki zavod Slovenije, Ljubljana: 143 p., incl. Pls. 23, 1 geol. map.

Primer citiranja poglavja iz knjige:

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Čarman, M. 2009: Priporočila lastnikom objektov, zgrajenih na nestabilnih območjih. Internet: http://www.geo-zs.si/UserFiles/1/File/Nasveti_lastnikom_objektov_na_nestabilnih_tleh.pdf (17. 1. 2010)

Če avtor ni poznan zapišemo tako:
Internet: http://www.geo-zs.si/ (22. 10. 2009)

Če se navaja več enot z medmrežja, jim dodamo še številko
Internet 1: http://www.geo-zs.si/ (15. 11. 2000)
Internet 2: http://www.geo-zs.si/ (10. 12. 2009)

Slike, tabele in table: Slike (ilustracije in fotografije), tabele in table morajo biti zaporedno oštevilčene in označene kot sl. 1, sl. 2 itn., oddane v formatu TIFF, JPG ali EPS z ločljivostjo 300 dpi. Le izjemoma je možno objaviti tudi barvne slike, vendar samo po predhodnem dogovoru z uredništvom. Obvezno je treba upoštevati zrcalo revije **172 x 235 mm**. Večjih formatov od omenjenega zrcala GEOLOGIJE ne tiskamo na zgib, je pa možno, da večje oziroma daljše slike natisnemo na dveh straneh (skupaj na levi in desni strani) z vmesnim »rezom«. V besedilu prispevka morate omeniti vsako sliko po številčnem vrstnem redu. Dovoljenja za objavo slikovnega gradiva iz drugih revij publikacij in knjig, si pridobijo avtorji sami. Table pripravite v formatu zrcala naše revije.

Če je članek napisan v slovenskem jeziku mora imeti celotno besedilo, ki je na slikah in tabelah tudi v angleškem jeziku. Podnaslovi naj bodo čim krajši.

Korekture: Te opravijo avtorji člankov, ki pa lahko popravijo samo tiskarske napake. Krajši dodatki ali spremembe pri korekturah so možne samo na avtorjeve stroške.

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Geološki zavod Slovenije
Dimičeva ulica 14, 1000 Ljubljana
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Uredništvo Geologije

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Scope of the journal: GEOLOGIJA publishes scientific papers which contribute to understanding of the geology of Slovenia or to general understanding of all fields of geology. Some shorter contributions on technical or conceptual issues are also welcome. Occasionally, a collection of symposia papers is also published.
All submitted manuscripts are peer-reviewed by at least two specialists. When submitting their paper, authors should recommend at least **three reviewers**. Note that the editorial office retains the sole right to decide whether or not the suggested reviewers are used. Authors should correct their papers according to the instructions given by the reviewers. Should you disagree with any part of the reviews, please explain why. Revised manuscript will be reconsidered for publication.

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In an original scientific paper, original research results are published for the first time and in such a form that the research can be repeated and the results checked. It should be organised according to the IMRAD scheme (**I**ntroduction, **M**ethods, **R**esults, **A**nd **D**iscussion).

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Pleničar, M. 1993: *Apricardia pachiniana* Sirna from lower part of Liburnian beds at Divača (Triest-Komen Plateau). Geologija, 35: 65–68.

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GEOLOGIJA
št.: 59/1, 2016
www.geologija-revija.si

ISSN 0016-7789
9 770016 778002

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Geološki zavod Slovenije