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Historical Review

More than 80 years have passed since in 1919 the University Ljubljana in Slovenia was founded. Technical fields were joint in the School of Engineering that included the Geologic and Mining Division while the Metallurgy Division was established in 1939 only. Today the Departments of Geology, Mining and Geotechnology, Materials and Metallurgy are part of the Faculty of Natural Sciences and Engineering, University of Ljubljana.

Before War II the members of the Mining Section together with the Association of Yugoslav Mining and Metallurgy Engineers began to publish the summaries of their research and studies in their technical periodical Rudarski zbornik (Mining Proceedings). Three volumes of Rudarski zbornik (1937, 1938 and 1939) were published. The War interrupted the publication and not untill 1952 the first number of the new journal Rudarsko-metalurški zbornik - RMZ (Mining and Metallurgy Quarterly) has been published by the Division of Mining and Metallurgy, University of Ljubljana. Later the journal has been regularly published quarterly by the Departments of Geology, Mining and Geotechnology, Materials and Metallurgy, and the Institute for Mining, Geotechnology and Environment.

On the meeting of the Advisory and the Editorial Board on May 22nd 1998 Rudarsko-metalurški zbornik has been renamed into “RMZ - Materials and Geoenvironment (RMZ - Materiali in Geookolje)” or shortly RMZ - M&G.

RMZ - M&G is managed by an international advisory and editorial board and is exchanged with other world-known periodicals. All the papers are reviewed by the corresponding professionals and experts.

RMZ - M&G is the only scientific and professional periodical in Slovenia, which is published in the same form nearly 50 years. It incorporates the scientific and professional topics in geology, mining, and geotechnology, in materials and in metallurgy.

The wide range of topics inside the geosciences are wellcome to be published in the RMZ - Materials and Geoenvironment. Research results in geology, hydrogeology, mining, geotechnology, materials, metallurgy, natural and antropogenic pollution of environment, biogeochemistry are proposed fields of work which the journal will handle. RMZ - M&G is co-issued and co-financed by the Faculty of Natural Sciences and Engineering Ljubljana, and the Institute for Mining, Geotechnology and Environment Ljubljana. In addition it is financially suported also by the Ministry of Education Science and Sport of Slovenian Government.

Editor in chief

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Sorption of Zn and Mn ions from single and binary metal solutions by Kaolinite: *Influence of physico-chemical factors*

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Abstract: Batch equilibrium sorption studies of Zn and Mn in kaolinite under single and binary metal systems were carried out in order to assess the controlling experimental and physico-chemical conditions on the adsorption process. The experimental data show that the equilibrium isotherms of Mn and Zn onto kaolinite correlate well with both Langmuir and Freundlich models. Increase in the estimated maximum adsorption (M, mg/g) for Zn and Mn uptake/removal were observed with increasing pH from 2.5 to 8.5 under binary metal solution system while similar trend were only observed between pH 2.5 and pH 5.5 under single metal solution system. However, the observed influence of sorbent mass is appreciable at pH of 2.5 with >20% reduction in adsorption capacity (when solution-solid ratio was increased from 10ml/g to 20ml/g) for Zn and Mn under both single and binary metal solution systems. Also, increase in metal concentration from 50 to 100mg/l and from 100 to 200g/l resulted in about 10% reduction in adsorption capacity at pH of 2.5 and about 10-15% reduction at pH of 5.5 under both single and binary systems. However, the reduction of less than 2% at pH of 8.5 especially under binary system could be attributed to complementary co-precipitation of metal hydroxides. Further evaluation had shown that the adsorption mechanism of both metals is characterized by ion-exchange process most especially at pH of 2.5. Finally, based on the overall assessment, this study highlighted the potentials of clay materials as cheap sorbents for removal of trace/heavy metals from contaminant aqueous wastes.

Key words: Sorption, Kaolinite, Batch equilibrium test, single and binary metal solution.

INTRODUCTION

Over the last century, there have been increasing environmental contamination/pollution problems associated with exponential growth of the world's population on one hand and with the corresponding increase in exploitation of the earth's raw mineral materials on the other hand. These had undoubted led to build-up of waste products, of which trace/heavy metals are of particular environmental concern. Usually soils serve as important sinks for contaminant metals, however clay and organic contents are important components that control the sorption/retention capacity of soils in respect of the contaminant trace metals. Nonetheless, the nature of heavy metal retention depends on the species and concentration of the respective heavy metal, soil constituents, pH, redox conditions, and other physico-chemical characteristics of the solid–solution system. Furthermore, the

Scientific paper

overall behavior of heavy metals in a soil is said to be governed largely by their sorption and desorption reactions with different soil constituents, most especially the clay components (APPEL AND MA, 2002).

Hence understanding mechanisms of metal sorption in soils is important as these reactions dictate the strength of the metal–soil surface interaction. The stronger the interaction with the soil surface, the less is the likelihood of environmental contamination. On a relative basis, exchange reactions (i.e. reversible electrostatic or outer-sphere reactions) are said to render metals most labile. However, inner sphere complex formation and co-precipitation with soil surfaces (i.e., bond formation between contaminant metal and soil surface) cause metals to be retained strongly and in most cases nearly irreversibly (MCBRIDE, 1994). Consequently, metal immobilization through precipitation and adsorption processes is considered a common mechanism to decrease the hazards of heavy metal in contaminated soils (MA ET AL., 1993; MALAKUL ET AL., 1998). However, a number of available common methods for removing metals in contaminated soils are said to be economically unfavorable (e.g. conventional ion exchange, electrolyte or liquid extraction, electrodialysis) or technically complicated (e.g. precipitation, cementation, reverse osmosis) (HORACEK ET AL., 1994, BROWN ET AL, 2000). In addition to these constraints, most of the modern remediation and removal methods are not always available in typical developing countries. Hence, the need to look at clay materials as effective and alternative low cost, natural adsorbents for the removal of metal ions from polluted aqueous wastes in developing countries. Clay materials, besides serving as excellent hydraulic barriers, can attenuate contaminant migration via geochemical processes such as adsorption, precipitation, and co-precipitation (LIM ET AL., 2002 AND SEZER ET AL., 2003). The effectiveness of clay / clay minerals (e.g. smectite, illite and kaolinite) as well as artificial commercial adsorbents (e.g. activated carbon and zeolite) as adsorption and/or ion-exchange media for dissolved metal ions has been known and studied extensively (GRIFFIN AND AU, 1977; YONG ET AL., 1990 AND 1993; SPARK ET AL., 1995; LOTHENBACH ET AL., 1998; KRAEPIEL ET AL., 1999).

However this study focus on the influence of pH, solution-solid ratio (SSR) and initial metal concentrations on the adsorption characteristics of kaolinite clays in single and in binary metal system and to assess possible metal interference on adsorption using batch equilibrium sorption tests. Furthermore, the abundance of weathered clay in tropical environment that characterized most of the developing regions warrants renewed investigation into the heavy metal immobilization potential of clay materials as cheap natural adsorbent in contaminated sites as well as in application as barrier fills in waste disposal systems.

STUDY CONCEPT

Background to the Study Approach: Equilibrium adsorption isotherms, or capacity studies are of fundamental importance in the design of adsorption systems since they indicate how the metal ions partition themselves between the media and liquid phase with increasing concentration at equilibrium. Usually, the batch equilibrium test (BET) is used to determine such adsorption characteristics in clay materials. However, the metal uptake process is complex and dependent on the chemistry of the metal ions, specific surface properties of the clays and the physicochemical influence like pH, temperature, and metal concentration (Goyal et al., 2003). From the experimental results of BET, the amount of respective metals (in this case, Mn and Zn) removed from the solution per gram of clay (soil) sample (mg/g) at specific pH and test/reaction period of about 12-24 h can be calculated using the equation below:

$$q = \{(C_i - C_e)*V\}/(M*1000) \qquad (1)$$

where:

q = Amount of metal contaminant removed from solution or sorbed per unit mass of soil material (mg/g or ug/g)

C_i = Initial concentration of metal contaminant in the solution before the experiment (mg/l or ug/l)

C_e = Concentration of the metal contaminant left in the solution after the BET experiment (mg/l or ug/l)

V = Volume of solution used in the BET experiment (ml)

M = Mass of soil or clay material used in the in BET experiment (g)

Hence, the above equation represents the fundamental quantification of the sorption potentials of the clay sorbent and forms the basis of further evaluation and assessment employed in this study.

MATERIALS AND METHODS

The sorbents selected for this study was mainly kaolinite clay. The dry clay samples were grounded and pulverized into fine powder and stored in sealed polyethylene sample bags prior to the laboratory experiments. Mineralogical composition and characters of the kaolinite clay was determined on duplicate samples via X-ray diffraction (XRD) analysis using CuKα radiation with the aid of computer controlled MAC-Science XRD machine (model M18XHF). An example of the X-ray diffractogram of the kaolinite, which was scanned between 2 to 50° at 2°θ/min on glass plate, is pesented in Figure 1.

Prior to the experiment, all the laboratory wares used for the experiments were thoroughly washed and double rinsed with

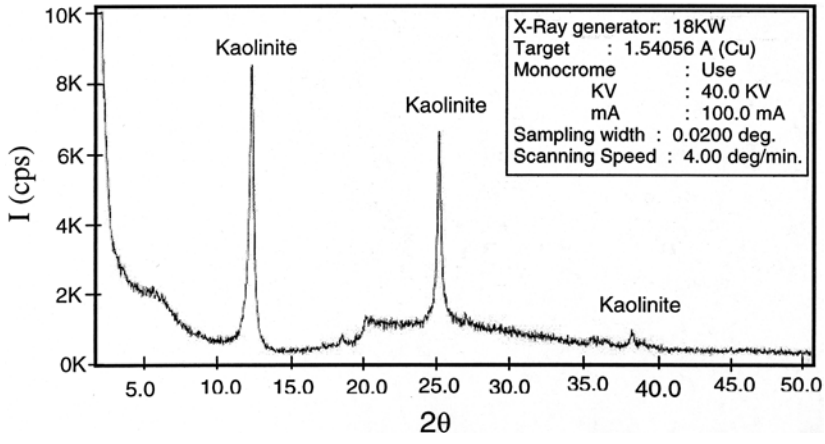

Figure 1. XRD Diffractogram of the analyzed Kaolinite sample used for the BET tests.

Table 1. Characteristics of metals and sorbates

Metal	Valency	***Ionic radius**	***IP**	**Atomic Weight**	**Salt Formula**	**Molecular Weight (salt)**	**% Purity**
Zn	2+	0.83	2.4	65.37	$ZnCl_2$	136.28	98.0
Mn	2+	0.92	2.2	54.94	$MnCl_2.4H_2O$	197.91	99.0

*IP = Ionic potencial
*Source = TAYLOR & EGGLETON, 2001

distilled and MilliQ water. The test stock solutions were prepared by dissolving the analytical grade chloride salts of the respective metals in MilliQ water; stock solution of Zn was obtained by dissolving 1.020g of dried $ZnCl_2$ salt (98 % purity) in 1 litre of MilliQ water, while that of Mn solution was prepared by dissolving 1.010 g of crystallized $MnCl_2.4H_2O$ salt (99 % purity) in 1litre of MilliQ water, given a corresponding concentration of 480mg/l Zn and 278mg/l Mn respectively. The stock solutions were then refrigerated at 4°C and subsequently used to make the various dilutions; single–metal component and binary–metal component systems with concentrations of 50, 100 and 200 mg/l used for the experiments. The characteristics of the metals and their salts are presented in Table 1.

Experimental equilibrium adsorption studies were performed to determine the relationship between capacity of the kaolinitic clay media for the metal ions and equilibrium metal ion concentration under different pH (2.5, 5.5 and 8.5) and initial solution concentrations. For the adsorption capacity studies, solutions with concentrations of 50, 100 and 200 mg/l of Zn and Mn in single-component and binary-component systems were prepared from stock solution. Prior to mixing with the clay materials, the pH of each test solutions were adjusted to the required value using 0.1 M HNO_3 and 0.1M of NaOH depending on the situation. Forty milliliters (40 ml) of each concentration were mixed separately with 2g and 4g of kaolinite clay in conical flasks sealed with parafilm. These were shaken for 18-hours at about 180rev/min on a platform rotary shaker (Model TAITEC-R20 mini) at room temperature (25° +/-3°C). After equilibration, the samples were centrifuged using a centrifuge machine (model KUBOTA KN-70) and the supernatant were collected and refrigerated (4°C) prior to analyses of trace metals. Subsequent analyses were performed using Inductively Coupled Plasma - Atomic Emission Spectrophotometer (ICP-AES; Perkin Elmer Model OPTIMA 3000). To ensure precision and accuracy of the ICP-AES, a series of check standards were analyzed 3 times in the course of each analysis operation to ensure that drift do not occur. Each sample was analyzed three times by the ICP-AES and a mean concentration calculated by averaging. The relative standard deviation (RSD) for each sample was estimated on percent basis while RSD greater than 10 % were excluded from the subsequent data evaluation.

Data evaluation

Subsequent to the experimental phase and estimation of the amount of metal sorbed from the difference between the initial concentration and the portion remaining in solution after equilibration using Equation (1), the following data evaluations were carried on in order to adequately assess and discuss Mn and Zn adsorption on kaolinite under the varied experimental conditions used in this study. Adsorption isotherms provide the adsorption behavior of soil or clay suspension at equilibrium with the contaminant solutions. In this study, adsorption isotherms were obtained by plotting the amounts of heavy metal species removed from solution (q in mg/g or ug/g of the clay sample) as a function of the equilibrium ion concentration in the filtrate solution (C_e in mg/l or ug/l). Naturally, different soils materials will show different capacities to adsorb heavy metals in response to their respective physico-chemical characteristics.

In adsorption-desorption studies, three major adsorption isotherm equations, which describe the relationship between the solution concentration and species adsorbed, are available from the literature, namely: the constant linear model, the Freundlich model and the Langmuir model (Griffin and Shimp 1978; Yong et al., 1992; Majone et al., 1993; Mohamed et al., 1994). However, the Langmuir model is often preferred according to Farrah et al., (1980), as it allows the calculation of capacity values and the constant, which is considered to reflect the relative bonding strength.

The Langmuir model used in this study are given by the following equations:

$$q = K_LM/(1+KC_e) \qquad (2)$$

Langmuir Model

where q and C_e are as explained earlier; a and b are linear constants, M and K_L are the Langmuir model constants. The Langmuir equation (Equation 2) can be linearized as shown in Equation (3) below by plotting C_e/q as a function of C_e (Lamgmuir model):

$$C_e/q = C_e/M + 1/K_LM \qquad (3)$$

For the Langmuir model, constants M, as the adsorption maximum and K_L as a constant related to bonding energy of the adsorption to the adsorbent can be obtained from the intercept and slope of the linear graph respectively.

Results and discussion

Equilibrium Isotherms and Adsorption Capacities: Figure 2a and Figure 2b shows adsorption isotherm plots for Mn and Zn in

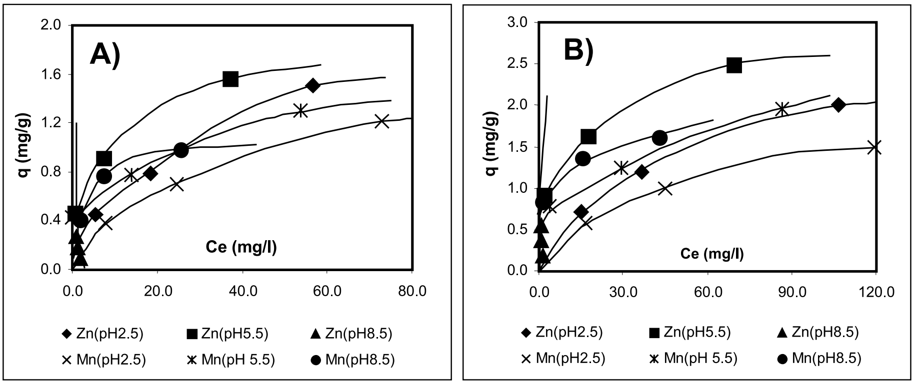

Figure 2. Sorption isotherms of Mn and Zn at SSR of 10ml/g (a) and SSR of 20ml/g (b) under single metal solution system.

single metal system at varied initial pH and under varied solution-solid ratio of 10 and 20 ml/g respectively, while Figure 3a and Figure 3b presents data for binary metal system under similar operating conditions.

As shown in Figure 2 and Figure 3, both Mn and Zn revealed similar adsorption characteristic under both single and binary metal systems.

The curves revealed more or less a two-stage trend as also recognized by KAN ET AL., 1994 in sorption of organic contaminants, involving a relatively fast initial adsorption followed by a gradual slower adsorption phase.

The first stage is characterized by physical adsorption (i.e. ion exchange) at the surface of the kaolinite functional group, which in this study accounts for about 70% and 80% adsorption of Mn and Zn respectively by the kaolinite samples. Such adsorption process is characterized by substitution of hydrogen ion in the outer sheet of the hydroxil group of kaolinite as well as the negatively charged kaolinite surface as represented below:

$$nSi\text{-}OH + Me^{n+} \rightarrow (Si\text{-}O)n\text{-}Me + nH^{+} \quad (6)$$

$$nSiO^{-} + Me^{n+} \rightarrow (Si\text{-}O)n\text{-}Me \quad (7)$$

Kaolinite is a layered alumino-silicate mineral with the tetrahedral and octahedral sheets dominated by Si and Al respectively in a 1:1 ratio. Consequently, adsorption of metal cations seems to take place at the proton-bearing surface of the functional group (silanols and aluminols) exposed at the edge of the kaolinite sheets. This adsorption process/ mechanism is said to be favour by the low permanent structural charge and low CEC i.e. low base saturation (40 meq/kg) of kaolinite (DREVER, 1988, YAVUZ ET AL., 2003).

Nonetheless, the adsorption capacity (in mg/g) is much higher at SSR of 20ml/g compared to SSR of 10ml/g for both metals on one hand

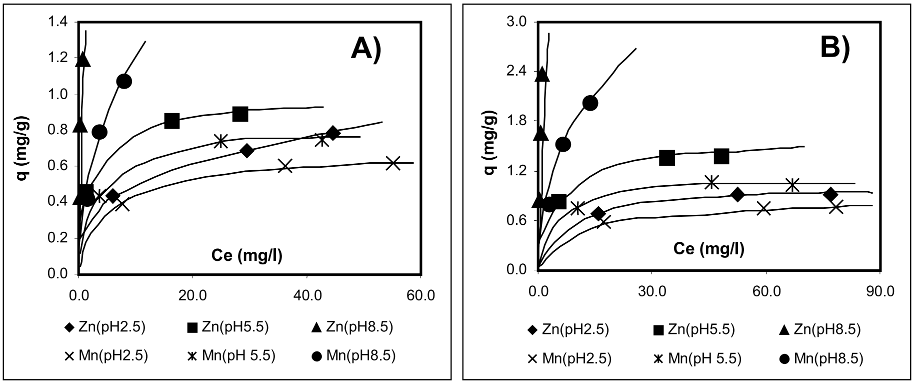

Figure 3. Sorption isotherms of Mn and Zn at SSR of 10ml/g (a) and SSR of 20 ml/g (b) under binary metal solution system.

Table 2. Profiles of the Langmuir constants with respect to pH and SSR variations

Experiment Condition			Kaolinite-Single Metal System				Kaolinite-Binary Metal System			
System	pH	SSR	M(mg/g)	M(mmol/g)	K(l/mg)	R^2	M(mg/g)	M(mmol/g)	K(l/mg)	R^2
Mn	2.5	10	1.70	0.031	0.03	0.98	0.68	0.012	0.18	0.99
Mn	5.5	10	1.38	0.025	0.22	0.96	0.75	0.014	0.52	0.99
Mn	8.5	10	1.10	0.020	0.32	1.00	1.59	0.029	0.26	0.99
Mn	2.5	20	2.25	0.041	0.02	0.99	0.84	0.015	0.13	1.00
Mn	5.5	20	2.11	0.038	0.08	0.97	0.98	0.018	0.65	0.98
Mn	8.5	20	1.67	0.030	0.44	0.99	3.41	0.062	0.11	0.98
Zn	2.5	10	2.15	0.033	0.04	0.95	0.89	0.014	0.14	0.99
Zn	5.5	10	1.71	0.026	0.26	0.99	0.93	0.014	0.74	1.00
Zn	8.5	10	0.05	0.001	-1.25	0.98	4.55	0.070	0.51	0.39
Zn	2.5	20	2.96	0.045	0.02	0.99	1.00	0.015	0.14	0.99
Zn	5.5	20	2.69	0.041	0.14	0.99	1.51	0.023	0.23	1.00
Zn	8.5	20	0.07	0.001	-1.18	0.79	14.68	0.225	0.18	0.24

and it is also higher for Zn compared to that of Mn on the other hand. While the former scenario could be attributed to quantity effect, characterized by saturation of the most active sites at high SSR, the latter could be attributed to differences in ionic radius as well as ionic potential of the two metals (see Table 1). Zinc is readily more adsorbed compared to Mn because of its smaller ionic radius and thus able to be more competitively fix into the pores of the kaolinite clay.

Generally the results of experimental adsorption measurements are usually expressed in the form of one or more equilibrium adsorption isotherm models. The Langmuir isotherm model was tested in this study due to its wider application in contaminant sorbent investigations. The Langmuir (1916 and 1918) isotherm theory assumes a mono-layer adsorption and that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in solution is constant at different solution concentrations.

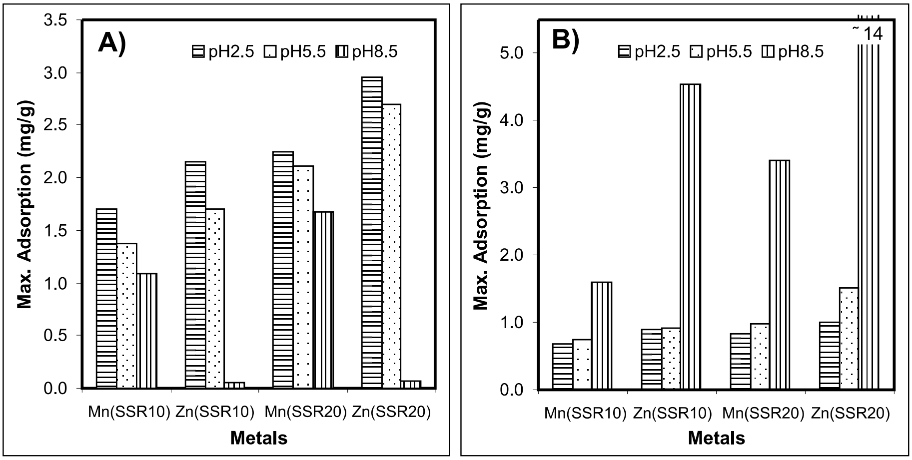

Figure 4. Estimated Langmuir maximum adsorption capacity (M, mg/l) for Mn and Zn at different SSR under (a) Single metal solution system and (b) binary metal solution system.

To quantify the adsorption capacity of the kaolinite for removal of Zn and Mn, typical Langmuir model was applied to the experimental data using to Equation 3, while the estimated Langmuir constants (M and K_L) there-from, are presented in Table 2 (above).

The correlation coefficients (R^2) for the linear regression were >0.90, which is an indication that the experimental data for both metals can be fitted into both Langmuir equation. As indicated in Table 2, sorption parameters for kaolinitic clay show variability between Mn and Zn ions, as reflected by their sorption maximum, Langmuir affinity constants. It can be seen that the maximum adsorption (M, mg/g) generally decreases with increasing pH for both Zn and Mn in single metal solution system, while increasing maximum adsorption with increasing pH is observed in the case of binary system (see Figure 4a and Figure 4b above).

The latter trend for the binary system can be attributed to the fact that the aluminol and silanol groups are more protonated at low pH and hence less available to retain or adsorb the metals. However, the trend in the single metal solution system can be attributed to the interplay of proton input at low pH, which causes hydrolysis of the exchangeable silicate base of the kaolinite (mostly Al in this case) on one hand and cation exchange reaction and in other words the removal of Zn and Mn from solution on the other hand. Therefore, it can be concluded that while hydrolysis and surface adsorption reaction characterized the adsorption mechanism in the single metal system, cation exchange with functional group characterized the adsorption process in the binary metal solution system.

Sorption of Zn and Mn as a function of pH: In soil/clay material pH plays a major role in the sorption of heavy metals as it directly controls the solubilities of metal hydroxides (APPEL AND MA, 2002) while increasing pH is said to increases cationic heavy metal retention to clay/soil surfaces via adsorption, inner-sphere surface complexation, and/or precipitation type reactions (MCBRIDE, 1994; SPARKS, 1995; ZUHAIRI, 2003). However, the

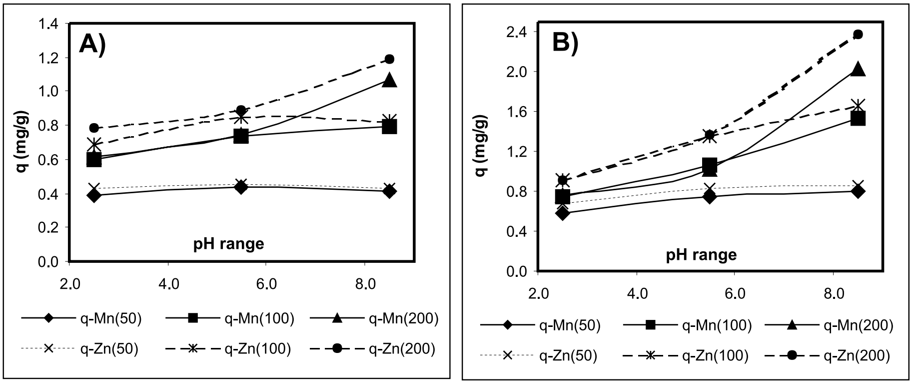

Figure 5. Variation of metal adsorption (q, mg/g) against pH for Mn and Zn at (a) SSR of 10 and (b) SSR of 20 under binary metal solution system.

effects of pH on the adsorption capacity of clay materials are said to depend on the respective isoelectric points (e.g. roughly 3.5 for kaolinite). This is due to the fact that at pH above the isoelectric point, the net negative charge and the ionic states of active sites and hydroxyl groups do promote exchange reactions (Drever, 1988). For this study, the adsorption of Zn and Mn followed the expected trend of increasing metal uptake/ removal with increasing pH from 2.5 to 8.5, most especially under binary metal system (see Figure 5a and Figure 5b above).

However this trend is observable under single metal system only between pH 2.5 and pH 5.5 and at low initial concentration (50mg/l) for both metals while the sorption capacities are greatly reduced at higher pH of 8.5 with higher metal concentration of 100 and 200 mg/l most especially for Zn (Figure 6a and Figure 6b).

This could be attributed to the co-precipitation of the metal hydroxides at higher pH (>6.5 for Zn and >8.0 for Mn), which implies that most of the metal ions rather than participated in the exchange adsorption were precipitated from the solution as hydroxide at operating pH of 8.5 as represented below:

$$Me^{2+} + OH^- = Me(OH)^+ + OH^- = Me(OH)_2 \qquad (8)$$

The above assertion is supported by the fact that metal concentrations in solutions are said to be unstable at higher pH due to precipitation of metal hydroxides (Plassard et al., 2000). Hence, the estimated percentage adsorption are >90% (at pH 8.5 for both metal) as presented in Table 3 imply a combination of those actually adsorbed and those precipitated directly out of the solution.

Therefore it can be concluded that the increasing adsorption capacity with pH under binary system is related to the influence of silanol and aluminol groups that are less protonated with increasing pH and thus more available for the adsorption of the metal ions. This is also supported by the fact that at higher pH active sites on the clay surface are more or less negatively charged and thus

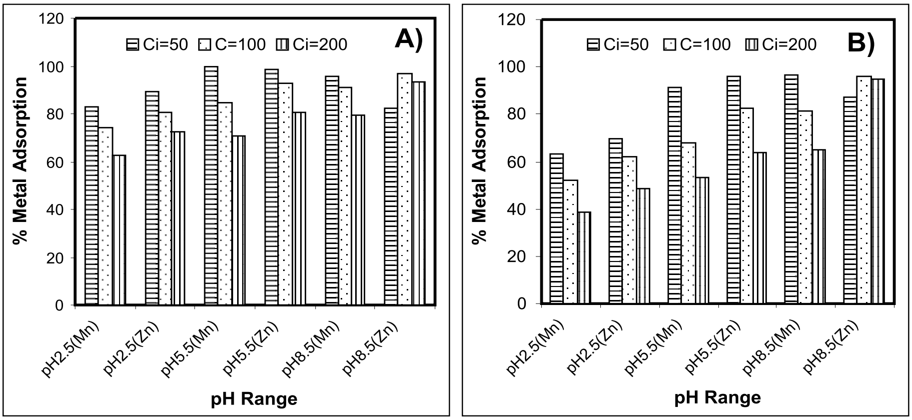

Figure 6. Variation of metal adsorption (q, mg/g) against pH for Mn and Zn at (a) SSR of 10 and (b) SSR of 20 under single metal solution system.

Table 3. Estimated percentage adsorption under varied metal concentration, pH and SSR

System	Ci	SSR	% Adsorption of Mn			% Adsorption of Zn		
Single System			**pH=2.5**	**pH=5.5**	**pH=8.5**	**pH=2.5**	**pH=5.5**	**pH=8.5**
	50	10	83.1	99.9	95.7	89.0	98.6	82.3
	50	20	63.3	91.1	96.8	69.8	96.2	87.1
	100	10	74.0	84.8	91.2	80.8	92.5	96.8
	100	20	52.3	68.1	81.2	61.9	82.4	96.0
	200	10	62.5	70.8	79.3	72.7	80.8	93.4
	200	20	38.5	53.1	65.1	48.5	64.1	94.8
Binary System			**pH=2.5**	**pH=5.5**	**pH=8.5**	**pH=2.5**	**pH=5.5**	**pH=8.5**
	50	10	83.5	92.2	96.8	87.7	97.3	99.5
	50	20	62.5	78.2	93.2	68.2	88.3	99.1
	100	10	62.4	74.7	95.6	69.9	83.8	99.6
	100	20	38.4	53.6	92.1	46.4	66.7	99.3
	200	10	52.7	62.2	93.1	63.7	75.8	99.4
	200	20	32.8	40.7	88.2	37.1	58.8	99.1

promote cation exchange reactions. However, the reduced capacity at pH of 8.5 under single metal system can be related to the instability of the respective metal ions in the reacting solution at such high pH. That is to say that at pH of ≥6.5 (for Zn) and ≥8.0 (for Mn), the respective metal ion species are in hydroxide form [$Zn(OH)_2$ and $Mn(OH)_2$], which are not readily available for adsorption/exchange process, hence the reduction in capacity at pH of 8.5 for both metals under the single metal solution system.

Sorption of Zn and Mn as a function SSR: The results of assessment of the influence of quantity of sorbent (kaolinite) on the adsorption capacities of kaolinite with respect to Mn and Zn are presented in Table 3. The observed general trend is decrease in adsorption capacity with increasing SSR, which implies considerable influence of sorbent mass due to surface area effect. Increase in SSR from 10ml/g to 20ml/g is accompanied by about 20-25%, 10-20% and <5% decrease in adsorption capacities at operating pH of 2.5, 5.5 and 8.5 respectively for both Zn and Mn and under both single and binary metal systems. However, a closer look at Table 3 shows that the influence of sorbent mass is appreciable at pH of 2.5 with decrease in adsorption capacity of >20% for both metals and under both single and binary metal systems (when SSR was increased from 10ml/g to 20 ml/g). At pH of 5.5 there are relatively lower capacity reduction of about 10-20 % for both metals while at pH of 8.5 there are much smaller influence of <10 % and <5 % capacity reduction for Mn and Zn respectively. For Zn, this can be attribute to complementary co-precipitation of hydroxides at such alkaline pH of 8.5. Furthermore the above trend is supported by graphical presentation in Fig. 4a and b above, which indicates that the estimated maximum adsorption (M, mg/g) generally increases with decreasing sorbent mass for both metals and under both single and binary systems. This implies that smaller sorbent mass get saturated faster with respect to the adsorbed metal. In summary, it can be concluded that while there is obvious decrease in adsorption capacity with increasing SSR, a situation attributed to surface area effect, the influence is appreciable only at pH of less than 6.

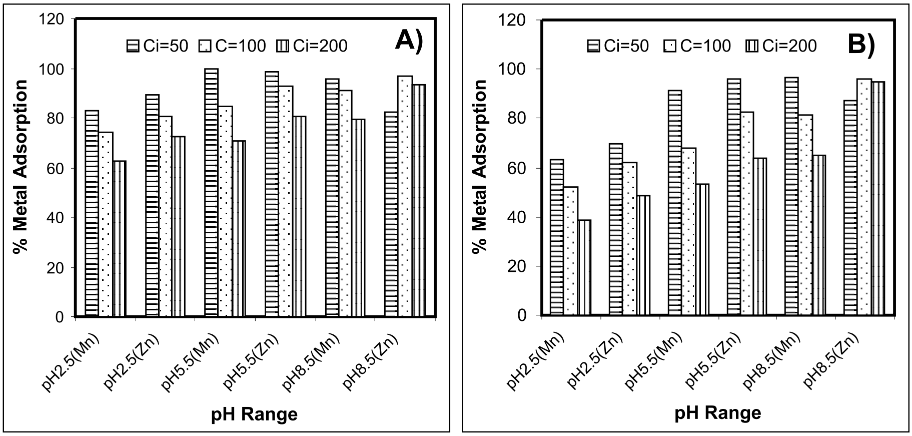

Figure 7. Variation of percentage metal adsorption with metal concentrations and pH for Mn and Zn at (a) SSR of 10 and (b) SSR of 20 under single metal solution system.

Effects of initial metal solution concentration: The results presented in Table 3 also revealed the effects of initial metal concentration on the uptake or adsorption of Zn and Mn at different pH by kaolinite under both single and binary systems. From the results, it is clearly evident that adsorption capacity decreases with increasing initial metal concentrations. That is to say, higher percentage adsorptions were obtained at lower initial metal concentrations (50 mg/l) irrespective of the operating conditions under both single and binary systems (see Figure 7 and Figure 8).

On the average, the overall results show that increase in metal concentration from 50 to 100 mg/l and from 100 mg/l to 200 mg/l resulted in about 10 % reduction in adsorption capacity at pH of 2.5 and about 10-15 % reduction for pH of 5.5 under both single and binary systems.

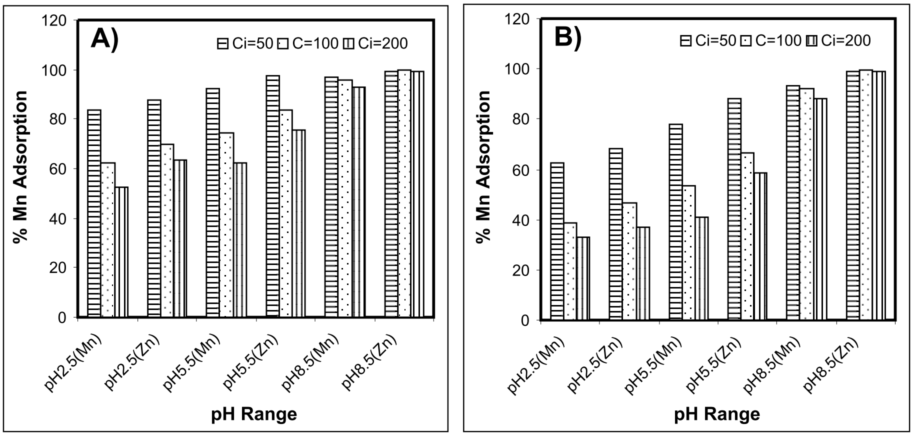

Figure 8: Variation of percentage metal adsorption with metal concentrations and pH for Mn and Zn at (a) SSR of 10 and (b) SSR of 20 under binary metal solution system.

However, reduction of less than 2 % for pH of 8.5 especially under binary system is a confirmation of the fact that adsorption process at such higher pH range is a combination of exchange process and co-precipitation of metal hydroxides. Hence it can be concluded that at low concentrations metals are adsorbed by specific adsorption sites, while at higher concentrations, the specific sites are saturated and the exchange sites filled, resulting in lower effective adsorption. Nonetheless, the trend is clearly observable only for pH of 2.5 and 5.5 while at pH of 8.5 there was apparently very little or no influence on the adsorption of Zn and Mn and more especially under binary system.

CONCLUSIONS

In this study, experimental data of Zn and Mn adsorption on kaolinite at different metal concentration, varied pH and solution-solid ratio were studied. The equilibrium data correlated well with Langmuir isotherm model indicating positive influence of pH on the metal removal by kaolinite, while the estimated maximum adsorption (M, mg/g) generally increases with decreasing sorbent mass for both metals and under both single and binary systems which implies that smaller sorbent mass get saturated with respect to the adsorbed metal faster. However, increasing adsorption capacity with pH under binary system is related to the influence of silanol and aluminol groups that are less protonated with increasing pH and thus more available for the adsorption of the metal ions on one hand. On the other hand the reduced capacity at pH of 8.5 under single system can be related to the instability of the respective metal ions, whereby at pH of ≥6.5 (for Zn) and ≥8.0 (for Mn) the respective metal ion species are in hydroxide form [$Zn(OH)_2$ and $Mn(OH)_2$] which are not readily available for adsorption/exchange process.

The overall evaluation and assessment of the data had shown that pH, solution-solid ratio, initial metal concentrations are critical factors in respect of Mn and Zn adsorption on kaolinite especially under the single metal solution system. However, in the binary metal system, physico-chemical characteristics of respective metals (i.e. ionic potential, ionic radius, ionic stability limit) seems to be exert some additional influence on the competitive preferential adsorption on metals on the sorbent kaolinite. In addition there is obvious decrease in adsorption capacity with increasing SSR, a situation attributed to surface area effect, however, this influence is appreciable only at pH of less than 6 with capacity reduction of about 10-20 % for both metals while at pH of 8.5 there is a much smaller influence of <10 % and <5 % capacity reduction for Mn and Zn respectively.

Furthermore, the higher percentage adsorptions at lower metal concentrations especially at pH of 2.5 and 5.5 under both single and binary systems imply that at low concentrations metals are adsorbed by specific adsorption sites, while at higher concentrations, the specific sites are saturated and exchange sites filled resulting in lower effective adsorption. On the average, the overall results show that increase in metal concentration from 50 to 100mg/l and from 100 to 200g/l resulted in about 10 % reduction in adsorption capacity at pH of 2.5 and about 10-15 % reduction for pH of 5.5 under both single and binary systems.

However, reduction of less than 2 % for pH of 8.5 especially under binary system is a confirmation of the fact that adsorption process at such higher pH range is a combination of exchange process and co-precipitation of metal hydroxides.

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The distribution of rare earth elements (REEs) in paddy soil and rice seeds from Kočani Field (eastern Macedonia)

Razporeditev REE (redkih zemelj) v tleh riževih polj in rižu na območju Kočanskega polja (vzhodna Makedonija)

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Abstract: The concentrations of rare-earth elements (REEs) were analysed in paddy soil and rice grains collected from Kočani Field in eastern Macedonia. The results showed that the paddy soil originated from composite material mostly derived from igneous, volcanic, metamorphic and sedimentary rocks transported by the Bregalnica River and its tributaries and deposited in the Kočani depression. The elevated concentrations of heavy REEs (HREE) could be explained by the contribution of the mafic and ultramafic lithologies to the soil formation. The concentrations of REEs in unpolished rice from Kočani Field exhibited a similarly elevated HREE pattern, like paddy soils, with up to 6.6×10^3 times lower values compared to those in the soil. The very similar accumulation coefficients (La - Sm) indicated no preferential fractionation of La-Sm in the rice-paddy soil system of Kočani Field.

Povzetek: V članku so podani izsledki geokemičnih raziskav vsebnosti redkih zemelj (REE) v tleh riževih polj in v oluščenem rižu z območja Kočanskega polja v vzhodni Makedoniji. Rezultati kažejo, da predstavljajo izvorne kamnine, ki so dale material za tamkajšnja tla v glavnem magmatske, metamorfne in sedimentne kamnine, katerih preperino so odložili v Kočansko depresijo reka Bregalnica in njeni pritoki. Povišane vsebnosti HREE kažejo tudi na prisotnost mafične in ultramafične komponente v materialu iz katerega so nastala tla. Vsebnost REE v neoluščenem rižu kaže podobno obogatitev s HREE kot tla, le da so njihove koncentacije do $6,6 \times 10^3$ manjše kot v tleh. Na podlagi zelo podobnih koeficientov akumulacije za La-Sm sklepamo, da v sistemu tla - riž ni prišlo do bistvene frakcionacije omenjenih prvin.

Key words: Rare-earth elements (REEs), paddy soil, unpolished rice, Kočani Field, Macedonia

Ključne besede: Redke zemlje (REE), tla, nepoliran riž, Kočansko polje, Makedonija

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Scientific paper

INTRODUCTION

The rare-earth elements (REEs) are a group of 15 elements, of which one, promethium (Pm), does not occur naturally in the earth's crust, while the others occur in all rocks (KABATA-PENDIAS & PENDIAS, 2001). They are fractionated during the crystallization of minerals from magma and during the regional metamorphism of volcano-sedimentary rocks (LIPIN & MCKAY, 1989). REEs have very similar chemical properties and tend to be present naturally as a group rather than existing alone, which makes them very useful tracers in geochemical studies (HENDERSON, 1984). REE data, however, might also be useful in the provenance determination of coarse and fine-grained sedimentary rocks or even in soil genesis (CULLERS ET AL., 1987; EGASHIRA ET AL., 1997; YOSHIDA ET AL., 1998). However the application of REEs to these problems has been hampered by the lack of a complete understanding of how they behave in aqueous solutions and size-fractions during weathering, transportation, deposition and soil-forming processes. The potential for chemical fractionation of the REEs in solution in natural waters is the energies of the formation of the common ionic species, which may cause certain elements of this series to be removed from solution by preferential sorption to colloidal particles (FAURE, 1998). For example, the chemical fractionation of trace elements, including REEs by sorption to ferric hydroxide particles was reported by CENTENO et al. (2004). YOSHIDA et al. (1998) found that REEs were rather resistant during soil-formation processes, because their concentrations and the chondrite-normalized patterns are not so far from those of the possible parent material. Therefore, a knowledge of REE concentrations in soils is required as background data for estimating soil contamination due to anthropogenic sources. Elevated concentrations of some REEs, such as La, Ce, Sm, Eu and Tb, have been found in the environments of industrial and urban areas (YOSHIDA, et al., 1998). These elements are likely to be released into the environment, mainly from coal-burning and nuclear energy material processing (KABATA-PENDIAS & PENDIAS, 2001). Phosphatic fertilizers added to agricultural soils can also be sources of REEs (TSUMURA & YAMASAKI, 1993). Brown et al. (1990) have demonstrated that the REEs could stimulate the plant growth of cereals, vegetables, fruits and tea. Inorganic compounds of REEs, such as $REE(NO_3)_2$, which act as microelement fertilizer, have been entered the environment and accumulated in the ecosystem (DING, et al., 2006). Special attention should thus be paid to the concentrations of trace elements such as REEs in agricultural soils, because of their potential to transfer to plants and the resultant internal exposure through ingestion, which could endanger public health (CHUA, 1998; VOLOKH, et al., 1990).

The objective of the present study was:

1. to estimate the contents and distribution patterns of REEs in the paddy soil of Kočani Field and unpolished rice grown on this area,
2. to reveal the possible fractionation of REE in the paddy-soil rice-grain system.

MATERIALS AND METHODS

Study area

The study area of the Kočani paddy fields is located in eastern Macedonia, about 32 km from the city of Štip. It is situated in the valley of the Bregalnica River between the Osogovo Mountains in the north and the Plačkovica Mountains in the south (1). Its average length is 35 km and its width is about 5 km. Previous investigations revealed the heavy metal contamination of the paddy soil, especially those areas from the western part of Kočani Field, due to the irrigation with riverine water impacted by heavy metals originating from mining activities and acid mine drainage from the Zletovo-Kratovo and Sasa-Toranica base-metal ore districts (Dolenec, et al., 2006).

Soil sampling and preparation

The objective of the field sampling programme performed in 2004-2005 was also to provide a characterization of the REEs in the paddy soil and the rice of Kočani Field. For this purpose paddy soil samples, as previously reported (Dolenec, et al., 2006), were collected at 38 locations from 7 profiles across Kočani Field, as shown in Figure 2. Near-surface paddy soils (0-20 cm in depth) were sampled using aplastic spade to avoid any heavy metal contamination. Each soil

Figure 1. Map of the study area showing the drainage system of the Bregalnica River and its tributaries

Slika 1. Geografska karta Kočanskega polja z drenažnom sistemom Bregalnice in njenih pritokov

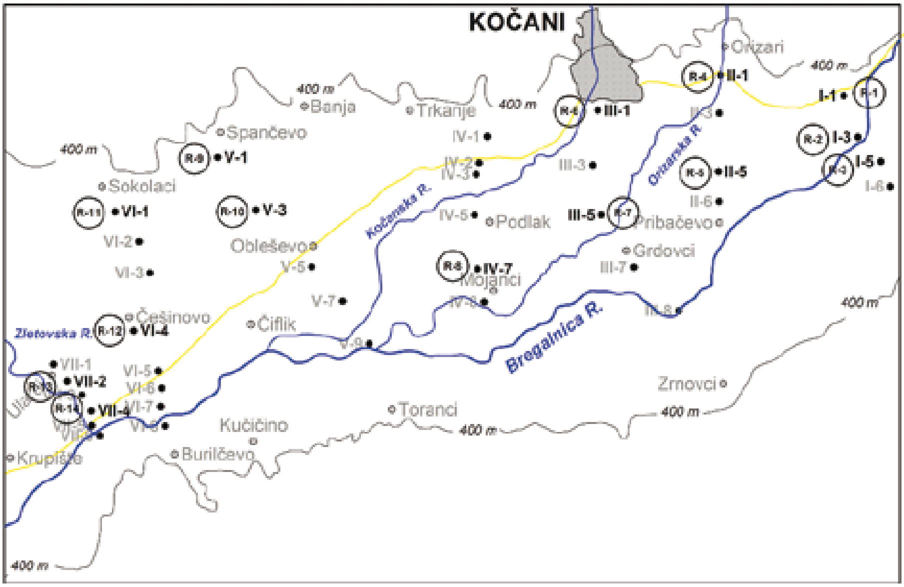

Figure 2. Sampling location map of the study area: (I - VII) soil samples®, unpolished rice samples
Slika 2. Geografski položaj vzorčnih točk (I - VII vzorčne točke tal®, vzorčne točke riža)

sample comprised a composite of 5 subsamples taken within a 1×1 square. The soil samples were air dried at 20 °C for one week and sieved through a 2 mm polyethylene sieve to remove the plant debris, the pebbles and the stones. They were ground in a mechanical agate grinder to a fine powder for a subsequent geochemical analyses.

Rice sampling and preparation

Rice grain samples with a hull were collected in October 2005 at physiological maturity from 14 sampling sites over Kočani Field (Figure 2). At each sampling site, rice grains were taken over an area of 10x10 m to get a final composite sample of about 1 kg. Each composite rice sample was collected from approximately the same location as the corresponding soil samples for further studies of heavy metal mobility and bioavailability. All the samples were collected and stored in polythene and brought to the laboratory for further preparation and treatment. In the laboratory, rice grains with a hull were thoroughly washed three times with deionised water to remove the soil particles and dust, and after that they were oven dried to a constant weight at 75 °C for 72 hours. The rice was de-hulled with a ceramic pestle and mortar and the de-hulled rice grains were ground in an agate mortar to a fine powder. The powdered samples were packed in clean, dry, stoppered-glass containers and stored in a refrigerator before being analyzed.

Determination of the REEs

All the paddy soil and rice samples were analyzed for their REE concentrations in a certified commercial Canadian laboratory (Acme Analytical Laboratories, Ltd) using different analytical methods. According to the reports, the REEs in the soil samples were determined after fusion with a mixture of lithium/tetraborate and dissolution in nitric acid by ICP-MS. The rice samples were dissolved in environmental-grade nitric acid and then also analysed by ICP-MS. The accuracy and precision of the REE soil analyses were assessed by using international reference material such as USGS G-1 (granite) and CCRMP SO-1 (soil). Quality checks of the rice analyses included analyses of certified reference material (rice flour SRM 1568) from the National Bureau of Standards (NBS). The analytical precision and accuracy were better than ± 8 %. This was indicated by the results of duplicate measurements on 10 soil and 3 rice samples as well as duplicate measurements of the G-1, SO-1 and SRM 1568 standards.

Statistical analyses

The calculations for mean, medium, minimum and maximum concentration values for analyzed elements in the soil and rice samples together with the variance and standard deviation (S. D.) data were obtained with the statistical package Statistica version 6.

RESULTS AND DISCUSSION

The REE concentrations in paddy soil

The concentrations of REEs in the paddy soil from Kočani Field are presented in Table 1 together with the concentrations of REEs in the upper continental crust (TAYLOR & MCLENNAN, 1995; WEDEPOHL, 1995) and the mean concentrations of the lanthanides in soils, given by URE AND BACON (1979) and YOSHIDA et al. (1998) used for a comparison with REE contents in the Kočani paddy soil. Table 2 shows a synthesis of the main statistical parameters (mean, median, range and standard deviation - S. D.).

The mean REE levels in the paddy soil were slightly higher than those reported for the mean concentrations of the average upper crust and for the soils. Their content also exceeded the values reported by YOSHIDA et al. (1998) for the Japanese soils; however, the median content of Ce and the light rare earth elements (LREEs) were also elevated in comparision with the mean concentrations of lanthanides in the soil (Table 1 and Table 2). The sum of REEs in the paddy soil measured during this study ranged from 106.4 to 244.4 µg/g, with a median of 171.7 µg/g (Table 1). The relatively high amounts of REEs could be attributed to the predominantly granitic lithologies exposed in the drainage area of the Bregalnica and Zletovska Rivers as well as in the surroundings of Kočani Field. It is well known that granitic rocks contain a larger amount of light rare-earth elements (LREE: La-Sm) compared to other igneous rocks, such as basalts and andesites (HERMAN, 1970; REIMAN & CARITAT, 1998 and references therin). Among the essential minerals, salic minerals preferentially concentrate the LREE and the femic minerals concentrate the heavy rare-earth elements (HREE: Gd-Lu). The REEs in the paddy soil seem to be realised mainly from parent material during the weathering and soil formation. Due to their low solubility and relative immobility in the upper crust the REEs are very useful for studying sedimentary environments, because sediments inherit the REE composition of their source rocks and, therefore, carry information about the origin of those

Table 1. Total REE concentrations in the paddy soil of Kočani Field. 1) upper continental crust (TAYLOR & MCLENNAN, 1995; WEDEPOHL, 1995); 2) URE and BACON (1979) and 3) YOSHIDA et al. (1998)

Tabela 1. Vsebnosti REE v tleh riževih polj Kočanskega polja. 1) zemeljska skorja - zgornji del (TAYLOR & MCLENNAN, 1995; WEDEPOHL, 1995); 2) URE and BACON (1979) and 3) YOSHIDA et al. (1998)

Element		**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**ΣREE**
Units		µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Location	Sample															
I-1	1	31.6	65.4	7.6	30.1	6.0	1.14	5.80	0.98	5.93	1.16	3.44	0.53	3.32	0.51	163.51
I-3	2	48.3	99.2	11.3	45.6	8.7	1.77	7.84	1.47	7.86	1.52	4.30	0.69	4.20	0.65	243.40
I-5	3	32.7	67.6	7.8	30.6	6.1	1.29	5.44	0.94	5.30	1.03	3.03	0.48	3.11	0.44	165.86
I-6	4	20.9	47.0	5.3	23.7	5.3	1.29	5.09	0.93	5.21	1.10	3.16	0.50	3.02	0.49	122.99
II-1	5	39.6	84.9	9.3	39.3	7.9	1.50	6.58	1.13	5.97	1.24	3.32	0.53	3.41	0.53	205.21
II-3	6	38.9	84.3	8.9	37.6	7.1	1.46	5.85	1.03	5.62	1.21	3.27	0.49	3.12	0.50	199.35
II-5	7	35.3	74.9	8.4	35.7	6.7	1.31	5.21	0.98	5.05	1.13	3.04	0.49	3.05	0.46	181.72
II-6	8	38.1	83.6	9.3	40.2	7.9	1.58	6.78	1.24	6.66	1.36	3.94	0.65	4.10	0.59	206.00
III-1	9	31.9	70.2	8.1	35.0	7.0	1.49	6.99	1.25	6.95	1.42	4.24	0.65	4.00	0.62	179.81
III-3	10	34.9	74.1	8.5	37.2	6.9	1.46	6.76	1.17	6.52	1.33	3.80	0.57	3.78	0.59	187.58
III-5	11	49.8	103.1	11.5	45.9	8.6	1.63	7.00	1.26	6.45	1.26	3.51	0.56	3.33	0.49	244.39
III-7	12	30.6	64.3	7.3	30.1	5.5	1.27	5.23	0.90	5.25	1.03	3.11	0.52	3.27	0.52	158.90
III-8	13	18.4	41.2	4.8	21.0	4.3	1.00	4.04	0.67	4.28	0.83	2.45	0.40	2.64	0.39	106.40
IV-1	14	29.7	65.7	7.6	34.3	7.0	1.91	7.44	1.22	7.13	1.40	4.16	0.63	3.90	0.58	172.67
IV-2	15	28.3	63.6	7.4	34.1	7.0	1.77	7.34	1.23	6.84	1.39	3.95	0.60	3.60	0.57	167.69
IV-3	16	30.2	67.3	7.9	33.6	6.7	1.73	7.23	1.28	7.34	1.35	4.02	0.60	3.68	0.56	173.49
IV-5	17	32.3	71.0	7.6	32.3	6.1	1.31	5.63	1.01	5.91	1.06	3.28	0.51	3.29	0.50	171.80
IV-7	18	36.5	86.7	8.7	37.1	7.0	1.37	6.34	1.08	6.12	1.11	3.48	0.51	3.37	0.54	199.92
IV-8	19	42.0	87.0	10.1	41.6	7.4	1.43	6.78	1.10	6.28	1.19	3.45	0.52	3.37	0.51	212.73
V-1	20	39.2	79.1	8.7	35.0	6.2	1.39	4.84	0.81	4.48	0.85	2.43	0.37	2.51	0.34	186.22
V-3	21	39.6	83.6	9.1	37.2	6.4	1.45	5.32	0.81	4.47	0.87	2.61	0.38	2.45	0.36	194.62
V-5	22	31.6	65.8	7.3	31.0	5.8	1.26	5.46	0.95	5.25	0.98	2.92	0.47	2.98	0.44	162.21
V-7	23	26.4	56.9	6.7	28.6	5.6	1.25	5.31	0.94	5.48	1.11	3.26	0.49	3.24	0.55	145.83
V-9	24	27.1	58.7	6.7	28.4	5.6	1.20	5.09	0.87	5.19	1.05	3.01	0.49	3.06	0.47	146.93
VI-1	25	36.4	76.7	8.5	33.5	6.0	1.34	4.89	0.81	3.97	0.76	2.25	0.38	2.22	0.32	178.04
VI-2	26	40.5	88.0	9.1	36.7	6.8	1.62	5.35	0.91	4.67	0.90	2.68	0.41	2.34	0.43	200.41
VI-3	27	36.1	73.5	8.5	34.1	6.4	1.38	5.55	0.91	5.01	0.92	2.77	0.43	2.58	0.42	178.57
VI-4	28	31.5	69.0	8.0	33.4	6.4	1.35	5.98	1.02	5.84	1.15	3.46	0.52	3.52	0.50	171.64
VI-5	29	30.8	65.7	7.5	30.8	6.0	1.43	5.70	1.04	5.70	1.16	3.28	0.55	3.31	0.52	163.49
VI-6	30	30.8	67.0	7.7	32.4	6.3	1.34	5.80	0.98	5.66	1.15	3.35	0.52	3.30	0.47	166.77
VI-7	31	22.4	50.2	5.7	23.8	4.9	1.17	4.70	0.88	4.90	0.98	2.98	0.52	3.16	0.49	126.78
VI-8	32	28.6	61.3	7.0	29.7	6.0	1.38	5.65	1.00	5.66	1.07	3.25	0.50	2.99	0.48	154.58
VII-1	33	27.1	56.9	6.3	25.6	4.7	1.16	4.53	0.76	4.02	0.80	2.31	0.40	2.50	0.39	137.47
VII-2	34	31.9	66.1	7.3	31.5	5.7	1.34	5.02	0.77	4.73	0.85	2.58	0.40	2.48	0.40	161.07
VII-3	35	33.2	70.2	7.6	30.6	5.5	1.42	5.01	0.84	4.66	0.90	2.66	0.39	2.65	0.38	166.01
VII-4	36	30.7	65.5	7.1	28.2	5.4	1.33	4.76	0.86	4.66	0.88	2.60	0.41	2.56	0.38	155.34
VII-5	37	29.4	60.7	6.7	27.6	4.8	1.20	4.70	0.76	4.18	0.80	2.35	0.39	2.34	0.37	146.29
VII-6	38	35.7	75.9	8.7	36.7	6.9	1.55	6.57	1.07	6.38	1.22	3.64	0.55	3.43	0.58	188.89
	1	32.3/30	65.7/64	6.3/7.1	25.9/26	4.7/4.5	0.95/0.9	2.8/3.8	0.5/0.44	2.9/3.5	0.62/0.8	-/2.3	-/0.33	1.5/2.2	0.27/0.3	
	2	33.5	48.5	7.7	33.0	6.1	1.9	3.0	0.63	3.8	0.38	2.0	0.16	2.3	0.34	
	3	18.0	40	4.5	18.0	3.7	0.96	3.7	0.56	3.3	0.68	2.0	0.29	2.0	0.39	

Table 2. Descriptive basic statistic of the REE contents in the paddy soil of Kočani Field

Tabela 2. Osnovna statistika za vsebnosti REE v tleh riževih polj Kočanskega polja

Element	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**
Units	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**
Mean	33	71	7.93	33.2	6.33	1.40	5.78	1.00
Median	32	68	7.71	33.5	6.25	1.38	5.59	0.98
Minimum	18	41	4.75	21.0	4.30	1.00	4.04	0.67
Maximum	50	103	11.50	45.9	8.70	1.91	7.84	1.47
S.D.	7	13	1.40	5.5	1.00	0.19	0.94	0.18

Element	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**ΣREE**
Units	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**	**µg/g**
Mean	5.57	1.09	3.19	0.50	3.14	0.48	173.542
Median	5.55	1.11	3.26	0.51	3.20	0.49	171.720
Minimum	3.97	0.76	2.25	0.37	2.22	0.32	106.400
Maximum	7.86	1.52	4.30	0.69	4.20	0.65	244.390
S.D.	0.97	0.20	0.56	0.08	0.52	0.08	29.006

rocks (Ross, et al., 1995). The fraction and mobilization of the REEs during weathering could be related to geochemical reactions that involve changes in the pH values in the soil and waters (Duddy, 1980; Ross, et al., 1995).

Chondrite normalized patterns of the paddy soil and those of selected granitic rocks from the Osogovo Mountains did not differ appreciably from each other and are similar to that of the mean REE concentrations for the average upper crust (Figure 3). The REE normalised patterns of paddy soil are characterized by a similar concentration of LREEs, a prominent Eu anomaly and a higher HREE content relative to the original material of the soil. The elevated levels of HREEs could be explained by the contribution of the mafic and ultramafic lithologies to the soil formation. The preferential decomposition of femic minerals and calcic plagioclases relative to the more resistant sodic and potassium feldspars during weathering of the exposed lithologies in the drainage area of the Bregalnica River and its tributaries seems to result in HREE enrichment of the paddy soil. This could be related to the irrigation of the paddy fields with water from the Bregalnica River. Another source of HREE is thought to be the amphiboles and pyroxenes present in the paddy soil (Dolenec, et al., 2006).

A study of lateritic soils has shown that there is a preferential retention of LREEs in the solid phases and a preferential transport of the HREEs in the solution phase (Sholkowitz, 1992). REEs can also be enriched during the soil-formation processes, even if the source material is not granitic rock (Yoshida, et al., 1998). In addition, REEs are used as fertilizer additives for the stimulation of the plant growth of cereals, vegetables, fruits and tea (Brown, et al., 1990; Yuan, et al., 2001). Phosphatic fertilizer added to agricultural soils could thus be a source of REE as well as U and Th (Tsumura & Yamasaki, 1993; Yoshida, et al., 1998). Although the data for REE concentrations in soils are limited, compared with those in rocks and meteorites (Yoshida,

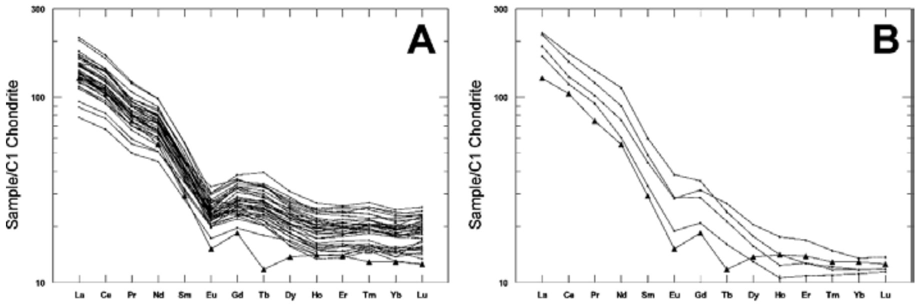

Figure 3. Rare-earth element patterns normalized to C1 chondrite for the paddy soil of Kočani Field (A) and granitic rocks (dacites, trahidacites) (B) from the Osogovo Mountains (REE content of volcanites is taken from Serafimovski et al., (2005). ▲ - Upper crust (Taylor & McLennan, 1995)

Slika 3. Vzorec redkih zemelj (REE) za tla riževih polj Kočanskega polja normaliziran na C1 hondrit (A) in normalizirane vrednosti REE za granitoide (daciti, trahidaciti) Osogovskih planin (B) - vsebnosti REE v vulkanitih so po Serafimovskem et al. (2005), ▲ zemeljska skorja - zgornji del (Taylor & McLennan, 1995) et al., 1998), we suppose that the observed concentrations of REEs in the paddy soil are generally attributed to the concentrations of these elements in predominantly acidic and intermediate igneous rocks, which are the main source materials for the paddy soil of Kočani Field. The possible contribution of REEs due to the application of phosphate fertilizers seems to be negligible.

The REE concentrations in unpolished rice

The concentrations of the REE in unpolished rice from Kočani Field are presented in Table 3, while Table 4 shows the synthesis of the main statistical parameters (mean, median, range and standard deviation - S. D.). Table 5 lists the accumulation coefficients for La, Ce, Pr, Nd and Sm. A synthesis of the main statistical parameters for the accumulation coefficients (mean, median, range and standard deviation-S.D.) is shown in Table 6. The contents of Eu, Gd, Tb, Ho, Er, Tm, Yb, and Lu were lower than the detection limit of the ICP-MS. Therefore, these elements were not taken into consideration during this study.

The concentrations of REEs in plants vary within a broad range from below 0.001 to above 15µg/g (Kabata-Pendias & Pendias, 2001). In rice the sum of the REEs was found to be 0.6 µg/g (Liu, 1988). The sum of the REEs in unpolished rice found during this study ranged from 0.037 to 0.155 µg/g, with a median of 0.066 µg/g, which is about nine times lower than the value reported by Liu (1988). This could be explained by the different REE content of the paddy soils. Plants grown on REE enriched soils showed very high concentrations of these elements (Miekeley, et al., 1994), although the concentrations of the individual REEs were not a function either of their total content or their soluble forms in soils (Wyttenbach, et al., 1997). The concentrations of REEs

Table 3. Total REE (La - Sm) concentrations in the unpolished rice of Kočani Field
Tabela 3. Vsebnosti REE (La - Sm) v oluščenem (nepoliranem) rižu iz Kočanskega polja

Sample ID:		La	Ce	Pr	Nd	Sm	ΣREE
Units		µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
I-1	R-1	0.0141	0.0286	0.0036	0.0117	0.0023	0.060
I-3	R-2	0.0141	0.0329	0.0035	0.0110	0.0023	0.064
I-5	R-3	0.0155	0.0330	0.0037	0.0131	0.0031	0.068
II-1	R-4	0.0255	0.0546	0.0059	0.0235	0.0047	0.114
II-5	R-5	0.0129	0.0273	0.0032	0.0111	0.0025	0.057
III-1	R-6	0.0115	0.0240	0.0028	0.0096	0.0018	0.050
III-5	R-7	0.0173	0.0383	0.0041	0.0152	0.0036	0.079
IV-7	R-8	0.0119	0.0270	0.0031	0.0108	0.0022	0.055
V-1	R-9	0.0145	0.0326	0.0033	0.0141	0.0031	0.068
V-3	R-10	0.0089	0.0173	0.0015	0.0079	0.0016	0.037
VI-1	R-11	0.0348	0.0778	0.0081	0.0287	0.0056	0.155
VI-4	R-12	0.0157	0.0326	0.0041	0.0137	0.0025	0.069
VII-2	R-13	0.0092	0.0197	0.0025	0.0081	0.0019	0.041
VII-4	R-14	0.0263	0.0587	0.0063	0.0232	0.0057	0.120

Table 4. Descriptive basic statistic of the REE contents in the unpolished rice of Kočani Field
Table 4. Osnovna statistika za vsebnosti REE v oluščenem rižu iz Kočanskega polja

	La	Ce	Pr	Nd	Sm	ΣREE
Units	μg/g	μg/g	μg/g	μg/g	μg/g	μg/g
Mean	0.016586	0.036029	0.003979	0.014407	0.003064	0.074
Median	0.014300	0.032600	0.003550	0.012400	0.002500	0.066
Minimum	0.008900	0.017300	0.001500	0.007900	0.001600	0.037
Maximum	0.034800	0.077800	0.008100	0.028700	0.005700	0.155
Std.Dev.	0.007337	0.016702	0.001712	0.006296	0.001359	0.033

Table 5. The accumulation coefficients (La - Sm)×10^{-4} for unpolished rice from Kočani Field
Tabela 5. Koeficient akumulacije za (La - Sm)×10^{-4} za oluščen riž iz Kočanskega polja

Section	Sample	La2/La1	Ce2/Ce1	Pr2/Pr1	Nd2/Nd1	Sm2/Sm1
I-1	**R-1**	4.46	4.37	4.74	3.89	3.83
I-3	**R-2**	2.92	3.32	3.1	2.41	2.64
I-5	**R-3**	4.74	4.88	4.74	4.28	5.08
II-1	**R-4**	6.44	6.43	6.34	5.98	5.95
II-5	**R-5**	3.65	3.64	3.81	3.11	3.73
III-1	**R-6**	3.61	3.42	3.46	2.74	2.57
III-5	**R-7**	3.47	3.71	3.57	3.31	4.19
IV-7	**R-8**	3.26	3.11	3.56	2.91	3.14
V-1	**R-9**	3.7	4.12	3.79	4.03	5
V-3	**R-10**	2.25	2.07	1.65	2.12	2.5
VI-1	**R-11**	9.56	10.14	9.53	8.57	9.33
VI-4	**R-12**	4.98	4.72	5.13	4.1	3.91
VII-2	**R-13**	2.88	2.98	3.42	2.57	3.33
VII-4	**R-14**	8.57	8.96	8.87	8.23	10.56

Table 6. Descriptive basic statistic of the accumulation coefficients (La - Sm)×10^{-4} for unpolished rice from the Kočani Field
Tabela 6. Osnovna statistika za koeficient akumulacije z (La - Sm)×10^{-4} za oluščen riž iz Kočanskega polja

	La2/La1	Ce2/Ce1	Pr2/Pr1	Nd2/Nd1	Sm2/Sm1
Mean	4.61	4.71	4.69	4.16	4.7
Median	3.68	3.92	3.8	3.6	3.87
Minimum	2.25	2.07	1.65	2.12	2.5
Maximum	9.56	10.14	9.53	8.57	10.56
Std.Dev.	2.17	2.31	2.2	2.05	2.45

in plants seem to be extremely variable and dependent on the various species of plant and their corresponding habitat (Ichihashi, et al., 1992; Wyttenbach, et al., 1998). The REE content of different parts of the plants followed the order root > leaf > stem > grain (Li, et al., 1998; Xu, et al., 2002). In addition, enrichment with the HREEs relative to the LREEs in rice grains was also observed. This suggested that the rice grains had a greater ability to absorb the HREEs compared to the LREEs. Shi-Ming et al. (2006) also reported similar HREE enrichment for wheat grains.

To visualize REE abundance variations, accumulation coefficients, the soil normalized REE contents of rice grains were calculated according to Shi-Ming et al. (2006) by dividing the content of each REE in the rice grains by the content of the same REE in the soil. The accumulation coefficients (La - Sm) are shown in Table 5. From Table 5 it is clear that the accumulation coefficients for La, Ce, Pr, Nd, and Sm are very similar. Their median values were 3.7 x 10^{-4} (La2/la1), 3.9 x 10^{-4} (Ce2/Ce1), 3.8 x 10^{-4} (Pr2/Pr1), 3.8 x 10^{-4} (Nd2/Nd1), and 3.9 x 10^{-4} (Sm2/Sm1). Such values indicated a similar fractionation event of these elements in the paddy soil-rice system of Kočani Field. This is also suggested by the chondrite normalised pattern (La - Sm) (Figure 4), which is similar to that of the paddy soils.

CONCLUSIONS

The relatively high REE concentrations of the paddy soil from Kočani Field could be attributed predominantly to the granitic lithologies exposed in the drainage area of the Bregalnica River and its tributaries. This was confirmed by the REE normalised patterns of selected granitic rocks from the Osogovo Mountains, which did not differ appreciably from each other and are similar to those of the Kočani paddy soil. The elevated concentrations of HREEs could be explained by the contribution of the mafic and ultramafic lithologies, also exposed in the broader area of Kočani Field to the soil formation.

The concentrations of REEs in unpolished rice from Kočani Field exhibited a similarly elevated HREE pattern like the paddy soil, although their absolute values were up to

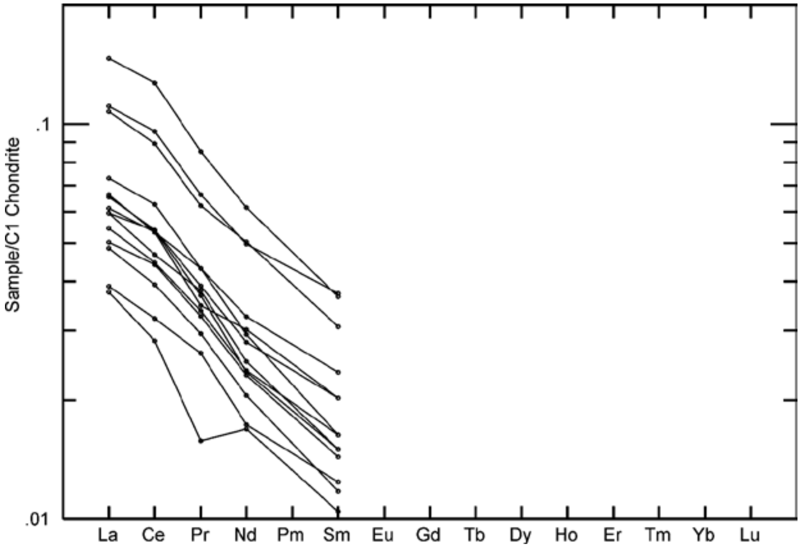

Figure 4. Rare-earth element patterns normalized to C1 chondrite for the unpolished rice from Kočani Field

Slika 4. Vzorec redkih zemelj (REE) za oluščen riž iz Kočanskega polja normaliziran na C1 hondrit

6.6 x 10^3 times lower than those in the soils. The very similar accumulation coefficients (La - Sm) indicated no preferential fractionation of La - Sm during their uptake by the rice plant.

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Actinolite-Phengite-Chlorite Metasomatites From The Toranica Pb-Zn Ore Deposit In Macedonia

Aktinolit-Phengit-Klorit metasomatiti v Pb - Zn rudišču Toranica v Makedoniji

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Abstract: In this investigation we focused on the contact metamorphic-metasomatic products in the Toranica Pb-Zn ore deposit. In the regionally metamorphed parts of the deposit we detected sericite-chlorite sub-facies, in the frame of the greenschist facies with its very common parageneses: chlorite+K-feldspar, chlorite+epidote+actinolite and chlorite+quartz. The presence of phengite indicated that the metamorphic-metasomatic processes took place under a pressure of about 5 kilobars and at a depth of 18 - 19 km. The absence of wollastonite, diopside, hedenbergite and hornblende suggested a low-temperature, < 420 ºC, character for these contact metasomatic processes.

Povzetek: Članek obravnava nekatere značilnosti kontaktno metamorfno-metasomatskih procesov v Pb - Zn rudišču Toranica. Mineralna parageneza in prisotnost phengita v kontaktno metamorfni coni rudišča kaže, da so kontaktno metamorfni procesi potekali pri pritisku približno 5 kilobarov in v globini približno 18-19 km. Temperatura njihovega nastanka, kakor tudi temperatura kristalizacije rudnih mineralov najverjetneje ni presegla 420 ºC. To potrjuje tudi odsotnost wolastonita, diopsida, hedenbergita in rogovače, ki so značilni za skarne nastale pri višji temperaturi.

Key words: contact metamorphism, metasomatites, skarns, Pb-Zn ore deposit Toranica, Macedonia

Ključne besede: kontaktna metamorfoza, metasomatiti, skarni, Pb-Zn rudišče Toranica, Makedonija

INTRODUCTION

The Toranica Pb-Zn ore district is situated in northeastern Macedonia. It belongs to the Sasa-Toranica ore zone and shows the metallogenic features that are characteristic of this zone. The Toranica ore field occupies an area of approximately 30 km^2 with a vertical extent of mineralization between 1300 and 1800 meters. The ore deposit was discovered in 1974 and the exploration period ended in 1981. After the preparation for the

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exploita tion, which lasted until 1988, the deposit began with trial production (BOGOJEVSKI & GATEOVSKI, 1990). The ore reserves were estimated to be 12.6 million tones, with 4.47 wt % of Pb, 2.93 wt % of Zn and 20 µg g^{-1} Ag (DOBROVOLSKAYA & STANKOVSKI, 1997). The mine was in operation untill the beginning of 2000, butthen in 2005 the mining activities began again. Although many researchers, including the first author of this paper, have extensively investigated the Torrance Pb-Zn ore deposit, only a few data on the alteration zones associated with the mineralization are available so far. Therefore, the purpose of this study was to assess the contact metamorfic metasomatic product related to the formation of the Toranica deposit and to provide useful information for a further study of the origin and evolution of the fluids and rocks involved in the contact metamorphism.

Geological setting

The Toranica lead-zinc deposit is located in the Sasa-Toranica mining district in the Osogovo Mountains, eastern Macedonia (Figure 1). The geology of the Toranica ore deposit comprises various rocks of metamorphic origin and igneous rocks of the Tertiary age. The most abundant lithologies in the area are believed to be closely associated with mineralization. The ore bodies of the Toranica deposit consist of peneconcordant tabular ore bodies that wedge out owing to the transition to non-mineralized metasomatites and lens-sheeted ore bodies. The most important economic mineralization is closely related to quartz-graphite schists. The ore consists mainly of galena, sphalerite, chalcopyrite and pyrite. In addition, a detailed study using transmitted and reflected light as well as X-ray diffractometry and both energy dispersive and wavelength dispersive systems revealed the more complex mineralogy of the deposit: galena, sphalerite, chalcopyrite, pyrite, pyrrhotite, magnetite, martite, bornite, enargite, tetrahedrite, marcasite, barite, native gold, cubanite and native bismuth. Geochemical analyses also showed very high concentrations of Cu, Bi, Sb, Ag, Au and Cd (BOGOJEVSKI, 1990; BOGOJEVSKI & GATEOVSKI, 1990; SERAFIMOVSKI & ALEKSANDROV, 1995; SERAFIMOVSKI, et al., 1997; SERAFIMOVSKI, et al., 1998; SERAFIMOVSKI, et al., 1992; STANKOVSKI, 1997).

The productive quartzgraphite schist series, which occupies the central part, hosted the main Pb-Zn mineralization, mostly related to the typical metasomatic skarns formed along the contact zone between the limestone marbles (cipolines) and the felsic intrusions. The overall occurrence of the skarns is concordant with that of the host rock. This lithological unit containing carbonate rocks was susceptible to metasomatic processes, the development of skarns and mineralization, which is genetically closely related to quartzlatite intrusions of the Tertiary age (24.5 Ma). The location of the Pb-Zn orebodies is controlled by bedding-parallel faults so that their shape and occurrences vary with the geometry of the faults, and is generally parallel to the bedding of the host rocks (Figure 2). Figure 2 shows the elongation and the depth of the productive series with three ore bodies and their contacts with gneiss and quartzlatite. The ore bodies can be followed below a level of 1400 m (see drill hole SD-86), which must be taken into account during the further exploitation.

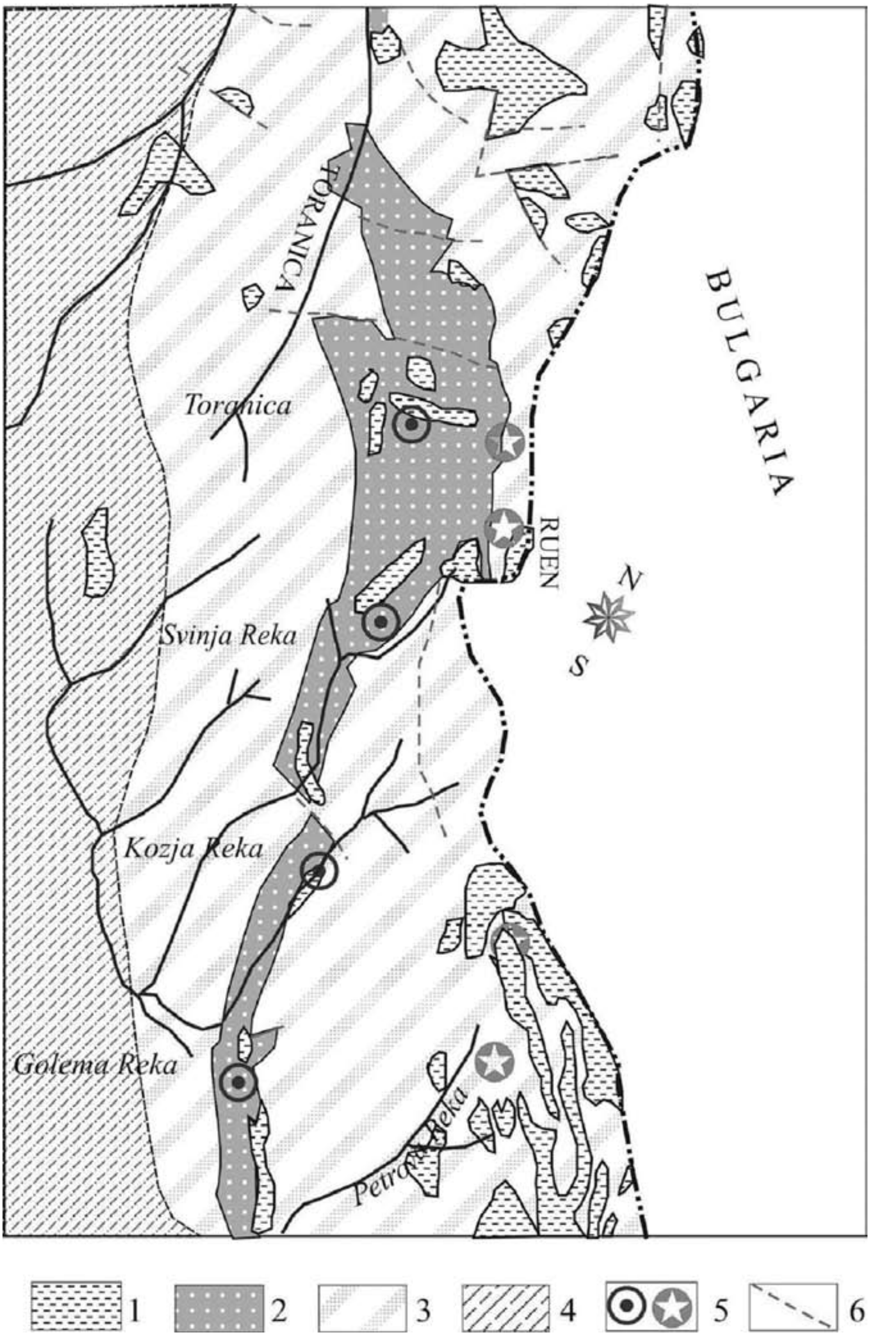

Figure 1. Geological map of the Sasa-Toranica mining district 1) Quartz-latite, 2) Quartz-graphite schist, 3) Sericite-chlorite schist, 4) Gneiss, 5) Pb-Zn deposits and mineralization, 6) Fault

Slika 1. Geološka zgradba rudonosnega območja Sasa-Toranica. 1) kremenovi latiti, 2) kremenovo-grafitni skrilavci, 3) sericitno-kloritni skrilavci, 4) gnajs, 5) svinčevo-cinkovo

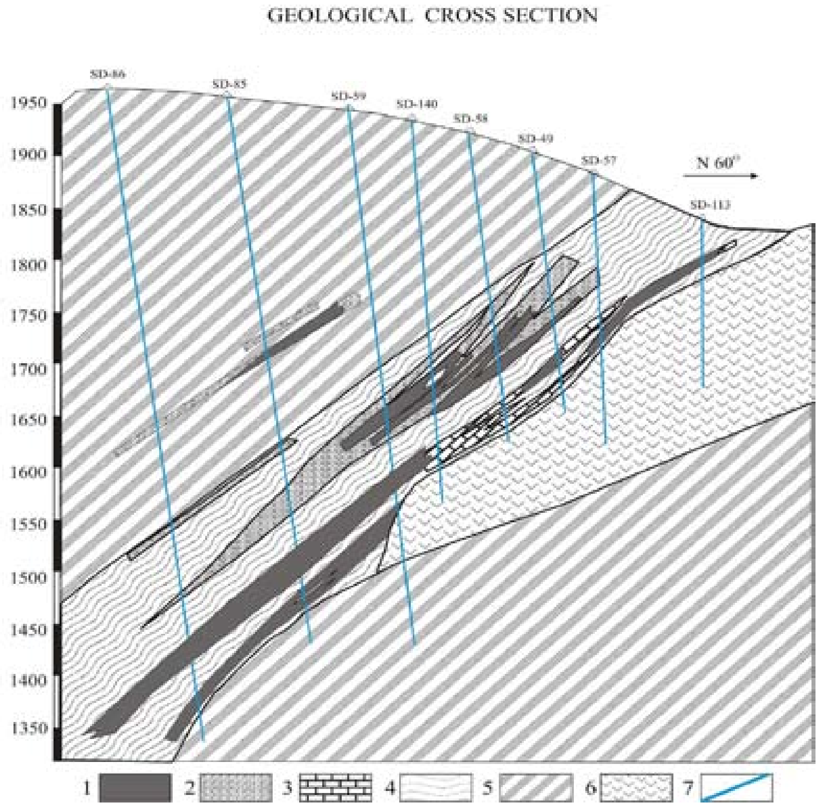

Figure 2. Geological section through the central part of the Toranica ore deposit 1) Ore body, 2) Pb-Zn mineralization, 3) Cipolino marble, 4. Quartzgraphite schist, 5) Gneiss, 6) Quartzlatite, 7 Drill hole

Slika 2. geološki profil skozi osrednji del rudišča Toranica 1) rudno telo, 2) Pb-Zn mineralizacija, 3) cipolinski marmorji, 4) kremenovo-grafitni skrilavci, 5) gnajsi, 6) kremenovi latiti, 7) vrtine

The determined contact-metamorphic-metasomatic products are also related with the schists and skarnoids series.

MATERIALS AND METHODS

In order to evaluate the contact-metasomathic phases related to Pb-Zn mineralization within the Toranica Pb-Zn deposit, 51 samples for petrographic and polished sections were collected during 2004 and 2005 at different levels in the Toranica mine. Most of the samples were taken at the 1600-m level, close to the contact of the quartz-latite dykes with quartz-graphite-schists, where the economically most important mineralization was located. Thirty-three samples were taken from the ore bodies, while 18 specimens sampled the rocks of the contact zone. All the samples were prepared for further analyses in the laboratory of the Faculty of Mining and Geology, Štip, Republic of Macedonia. After a detailed petrographic and ore microscopy study 12 samples of the host rocks and 6 polished samples were selected for further electron microprobe analyses. The electron-microprobe analyses were performed in the Laboratory of Petrology and Geochemistry, EUROTEST-CONTROL PLC, Sofia, Bulgaria. Quantitative X-ray spectral micro-analyses and second-electron photographs with a COMPO regime and the distribution of the elements within the minerals were performed with a Super probe 733 (JEOL, Japan). The following standards were used: for Bi, synthetic Bi_3S_3; for Cu, Fe and S, synthetic $CuFeS_2$; for Se, synthetic PbSe; and for Pb, synthetic PbS (I = 0.8 A, U = 25kV). A TUR-M-60 device connected to a RKD-57 camera was used to make the X-ray structural analyses of the individual minerals.

RESULTS AND DISCUSSIONS

The contact metamorphic processes in the Toranica ore deposit, as well as the alteration related to the ore mineralization, has been very rarely reported in the literature. There were practically no data concerning the processes of contact metamorphism and the relations between the newly formed metasomatites as a direct consequence of the contact-metamorphic-metasomatic processes and reactions that took place along the contacts between the different lithological units. For example, between the sub-volcanic intrusions and various schists, gneisses, as well as gneiss-schist, gneiss-volcanite, gneiss-carbonate and schist-carbonate where crystallized various rare minerals and mineral phases. The study of such processes and reactions is important for a better understanding of the multistage evolution of the metamorphic complexes and ore genesis in the broader area of the Osogovo Mountains.

The results of our preliminary study showed that the mineral assemblages of quartz-graphite schist and gneiss correlated well with those of the chlorite-sericite sub-facies of the greenschist facies of the regional metamorphism and indicated a temperature range between 320 and 350 ºC. This is also suggested by the mineral assemblages of chlorite + K-feldspar and chlorite + quartz. The presence of phengite with an elevated content of Mg, Fe and Si (Table 1) together with K-feldspars in altered gneiss indicated according to a MASSONNE and SCHREYE barometer (1987) that the pressure of the regional metamorphism was about 5 kbar, while the depth was not greater than 18-19 km. It is interesting to note that minerals with an increased content of Mn were found in the metamorphosed sedimentary rocks, which indicated that these rocks most probably served as a source of manganese during the contact metasomatic ore-forming processes. The contact metasomatic processes related to the quartzlatite dyke intrusions were basically low temperature in character. This is indicated by the absence of any of the most typical scarn minerals.

Analyses of the samples from the contact zone between the quartzlatite dykes and gneisses and/or schists revealed the presence of epidote, chlorite, calcite, muscovite-phengite and quartz. The chemical composition of some of these minerals obtained using microprobe analyses is presented in Tables 1-3.

Typical mineral assemblages in metamorphosed rocks of the Toranica ore deposit are illustrated in ACF diagrams (Figure 3 – A,B,C,D). This mineral assemblage is of primary character and shows no replacement

Table 1. Microprobe analyses of Mn-bearing actinolite and phengite from the regional and contact metamorphic rocks of the Toranica ore deposit (in %)
Tabela 1. Sestava Mn-aktinolita in phengita v (%) določena z elektronskim mikroanalizatorjem

Mineral	**Actinolite**			**Phnengite**					
Sample	173/2			173/3		173/5	173/6		173/90
SiO_2	54.56	53.73	54.28	49.11	47.71	48.06	48.87	47.99	48.97
TiO_2	0.10	0.06	0.09	0.32	0.45	0.32	0.06	-	0.38
Al_2O_3	0.85	0.65	0.93	29.44	28.05	31.50	30.47	30.16	32.14
FeO	15.28	15.46	15.58	5.22	6.22	4.47	4.61	5.67	2.56
MnO	3.10	3.44	3.29	0.19	0.08	-	0.12	0.17	0.11
MgO	12.32	12.03	12.32	1.03	1.91	1.05	0.85	0.58	1.65
CaO	11.25	12.24	11.74	0.01	-	0.05	0.11	-	-
Na_2O	0.16	0.17	-	0.25	0.04	0.49	-	-	0.42
K_2O	0.06	0.05	-	10.01	10.64	9.78	10.57	10.65	9.75
Total	97.68	97.83	98.23	95.58	95.10	95.72	95.66	95.22	95.98
Si	8.00	7.93	7.95	3.30	3.26	3.22	3.28	3.27	3.23
Al_{IV}	-	0.07	0.05	0.70	0.74	0.78	0.72	0.73	0.76
Al_{VI}	0.14	0.04	0.11	1.64	1.52	1.70	1.69	1.68	1.73
Ti	0.01	0.01	0.01	0.16	0.02	0.02	-	-	0.01
Fe	1.87	1.91	1.91	0.29	0.36	0.25	0.26	0.32	0.14
Mn	0.39	0.43	0.41	0.01	-	-	0.01	0.01	-
Mg	2.69	2.65	2.69	0.10	0.19	0.10	0.08	0.06	0.16
Ca	1.77	1.94	1.84	-	-	-	0.01	-	-
Na	0.04	0.05	-	0.03	0.01	0.06	-	-	0.05
K	0.01	0.01	-	0.86	0.93	0.84	0.91	0.92	0.82
X_{Fe}	0.41	0.42	0.41	-	-	-	-	-	-
X_{Na}	-	-	-	0.03	0.01	0.07	-	-	0.06

Table 2. Microprobe analyses of Mn-bearing calcite, albite and K-feldspar from the regional and contact metamorphic rocks of the Toranica ore deposit (in %)
Tabela 2. Sestava Mn-kalcita albita in K glinenca (v %) iz regionalno in kontaktno metamorfnih kamnin iz rudišča Toranica določena z elektronskim mikroanalizatorjem

Mineral	**Calcite**						**Ab**	**Kfs**
Sample	173/1	173/2	173/3	173/4	173/6		173/3	173/3
SiO_2	-	-	-	-	-	-	69.05	63.81
TiO_2	-	-	-	-	-	-	-	-
Al_2O_3	-	-	-	-	-	-	19.29	18.85
FeO	0.47	0.96	0.33	0.62	0.57	0.25	0.09	-
MnO	3.32	6.02	1.93	2.04	3.48	3.39	-	-
MgO	0.16	0.21	0.01	0.28	-	0.09	0.03	-
CaO	53.38	49.00	54.98	53.80	52.98	52.85	0.13	-
Na_2O	-	-	-	-	-	-		
K_2O	-	-	-	-	-	-		
Total	57.33	56.19	57.25	56.74	57.03	56.58	99.97	99.97
X_{Na}	-	-	-	-	-	-	0.99	0.04

Table 3. Microprobe analyses of Mn-bearing chlorites and epidotes from the regional and contact metamorphic rocks of the Toranica ore deposit (in %)

Tabela 3. Sestava Mn-klorita in epidota (v %) iz regionalno in kontaktno metamorfnih kamnin iz rudišča Toranica določena z elektronskim mikroanalizatorjem

Mineral	**Chl**							**Ep**						
Sample	173/1	173/2	173/3	173/4	173/5	173/9C		173/1	173/3	173/4	173/6		173/9A	173/9C
SiO_2	28.36	31.39	27.02	29.48	24.28	25.67	26.52	38.33	38.02	38.52	38.69	38.51	38.24	38.49
TiO_2	-	0.02	-	0.16	0.03	0.16	-	-	0.01	0.03	-	0.06	-	0.02
Al_2O_3	16.88	14.12	20.03	20.87	21.75	21.32	22.01	24.22	24.47	24.78	25.66	24.99	23.56	26.41
Fe_2O_3	-	-	-	-	-	-	-	12.01	12.44	11.14	10.02	11.36	12.90	9.11
FeO	23.49	23.63	25.21	15.55	36.41	24.05	21.08	-	-	-	-	-	-	-
MnO	4.16	1.98	2.01	1.65	0.74	4.00	4.68	0.44	0.44	0.87	0.51	1.35	1.52	0.94
MgO	14.95	16.69	14.25	20.93	5.28	14.12	13.98	0.06	0.11	0.03	-	0.17	-	-
CaO	0.20	0.40	0.28	0.36	-	0.12	0.08	23.11	22.74	22.31	22.76	21.78	21.65	23.19
Na_2O	0.27	0.17	0.09	0.13	-	0.17	0.12	-	-	-	0.11	-	-	0.07
K_2O	0.03	0.09	0.02	0.02	0.09	0.04	-	0.01	-	0.03	0.10	0.24	-	0.03
Total	88.34	88.49	88.91	89.12	88.58	89.65	88.47	98.18	98.23	97.71	97.85	98.46	97.87	98.26
X_{Fe}	0.47	0.44	0.50	0.29	0.79	0.49	0.46	-	-	-	-	-	-	-

by a high-temperature mineral paragenesis. However, minerals typical for the high-temperature skarn facies, such as wolastonite, diopside-hedenbergite and hornblende, were not found during this study. Instead of the wolastonite, calcite and quartz were formed, while instead of the hornblende there was crystallized actinolite, which contains elevated concentrations of Mn with 3.10 to 3.44 % of MnO. Like the actinolite, the calcite also exhibited an increased amount of manganese with the concentration level of MnO in the range of 1.96 to 6.02 % (Table 1 and 2). The elevated content of Mn in these minerals could serve as a source of Mn during the contact-mineralizing processes. In addition, chlorite from the contact metamorphic zone is also a Mn-bearing mineral with MnO in the range 0.74 to 4.16 % (Table 3). The MgO content in the analyzed chlorites ranges from 5.28 to 20.93 %, while the concentration of CaO varies between 0.08 and 0.40 %. Once again, the presence of manganese in concentrations such these could act as a source for this element in the frame of the contact-mineralizing processes.

Ilvaite, a Mn-pyroxene (bustamite) and johansenite, which were also determined during this study of samples from the Toranica mine, are stable at lower temperatures, mostly between 350 and 400 °C, respectively. Based on this we supposed that in the Toranica ore deposit, these minerals most probably crystallized at a relatively low temperature, which did not exceed 400-420 °C. The mineral assemblages found in the samples from mineralized skarns and in the contact zone between the quartzlatite and schists are very similar to those found in regionally metamorphic rocks of greenschists facies. The only difference was that the chlorite of the greenschists facies contains a smaller amount of Fe, while calcite is enriched with Mn, and the only amphibole present is actinolite. These results suggested that the temperatures of formation of the mineral assemblages were not above those characteristic for the regional metamorphism of the greenschists facies.

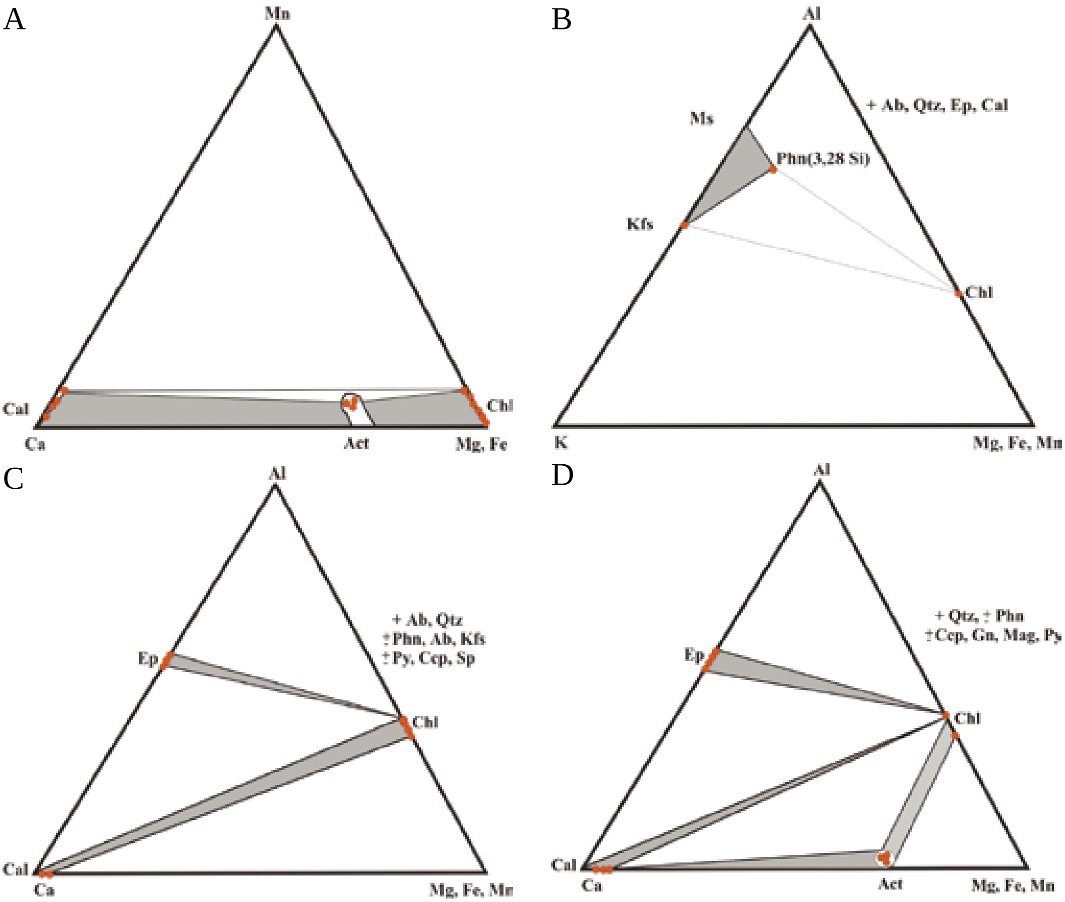

Figure 3. Typical mineral assemblages in contact metamorphic rocks from the Toranica Pb-Zn ore deposit: A cipolino, B metagranites C metamorphosed graphite schist, phylite and metagranite, D contact skarn. The mineral compositions were all measured by electron microprobe

Slika 3. Značilne mineralne parageneze v kontaktno metamorfnih kamninah iz Pb-Zn rudišča Toranica: A cipolino, B metamorfozirani graniti, C metamorfozirani grafitni skrilavci, filiti in metamorfozirani graniti, D kontaktni skarn. Sestava posameznih mineralov je določena z elektonskim mikroanalizatorjem

Conclusions

Mineral assemblages of actinolite-phengite and sericite-chlorite-epidote facies are a direct result of the contact metamorphic-metasomatic processes that took place in the Toranica ore deposit. They were related to the lithological complex of quartz-graphitic schists containing the Pb-Zn mineralization of economic importance. The mineral paragenesis determined during this study suggested that the temperature of their formation did not exceed the range 320 to 420 °C. The presence of phengite indicated that metamorphic-metasomatic processes originated under a pressure of about 5 kilobars and at a depth of 18-19 km.

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Topographic setting, proximity to the rivers and technical factor influence on the well yield of the dolomite aquifers in Slovenia

Vpliv topografske lokacije, bližine rek in tehničnih faktorjev na izdatnost vodnjakov v slovenskih dolomitnih vodonosnikih

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Abstract: Influences of topographical setting and technical factors which contribute to different hydraulic values of transmissivity, hydraulic conductivity, specific capacity and maximum yields in dolomite aquifers in Slovenia, are discussed. Topographical setting of wells and their proximity to rivers show great influence, while technical factors like well depth and penetration degree are of no importance. The presented factors should be considered in advance when planning new locations for water exploitation wells, to predict hydraulic parameters and locate well adequately.

Povzetek: V prispevku so predstavljeni vplivi lokacije in tehnične izvedbe vodnjakov na vrednosti transmisivnosti, koeficienta prepustnosti, specifične izdatnosti in maksimalnih pretokov v dolomitnih vodonosnikih v Sloveniji. Topografska lokacija in bližina vodnjakov do rek imata velik vpliv na vrednosti hidravličnih parametrov, medtem ko globina vodnjakov in stopnja popolnosti nimata opaznega vpliva.

Key words: topographical setting, well depth, dolomite aquifers, Slovenia
Ključne besede: topografska lokacija, globina vodnjakov, dolomitni vodonosniki, Slovenija

INTRODUCTION

Wells in Slovenia are drilled into various lithological units, mostly in alluvial sediments and sedimentary rocks. Among the latter, dolomites are preferable compared to the limestones or sandstones. Dolomite rocks cover about 8 % of Slovenia's surface and occur from Permian through most of the Triassic, and Jurassic, Cretaceous and up to Paleocene (VERBOVŠEK, 2003). As the water well supply is increasingly focused into groundwater exploitation, knowledge of several factors which influence the well yield, is essential. The purpose of this paper is to analyze the influence of several factors on four hydraulic parameters, namely hydraulic conductivity *K*, transmissivity *T*, specific capacity *q* (=Q/s), which represents well yield divided by belonging drawdown, and maximum yield Q_{max}, representing the highest value of well discharge obtained by pumping on the well.

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Several studies of influencing factors have been made to explain variations in well yields by examining factors in various locations and rock types (HENRIKSEN, 1995; SUN, 1995; MABEE, 1999; WLADIS AND GUSTAFSON, 1999; EFTIMI, 2003; HENRIKSEN, 2003). Slovenia has an intense topographical relief, ranging from sea surface up to 2864 m. The relief greatly influences the distribution of rainfall and along with the geological properties characterizes the runoff and aquifer recharge. Topographical setting should therefore be of greater importance to the aquifer yield. Also, proximity to rivers is studied in this paper, as aquifers near the rivers can be recharged directly from the surface water bodies. Greater well depth can contribute to higher yield, as the greater number of fractures can be captured and fully penetrating wells should similarly have higher yield due to the capturing of whole aquifer thickness. The influence of four factors (topographical location, proximity to rivers, well depth and degree of partial penetration) is presented and discussed in this paper and comparison of the results is given with the other studies.

MATERIALS AND METHODS

Hydraulic parameters have been obtained from hydrogeological reports of several geological and drilling companies in Slovenia. Aquifer tests described in the reports were performed by submersible pumps or by airlift tests. Even if the parameters obtained by the latter tests do not characterize the aquifer properties exactly, they can still be used for aquifer characterization, as errors usually do not exceed one order of magnitude (WLADIS AND GUSTAFSON, 1999). It should be noted that in all hydrogeological reports, the methods of Cooper-Jacob and Theis were used for determination of K and T, and these are not always applicable to fractured aquifers. The values of hydraulic conductivity, which is further recalculated from the transmissivity via the equation T=Kd, are additionally influenced by the estimated values of aquifer thickness d, and sometimes this parameters not well known. All these factors can cause the unreliability of calculated hydraulic parameters, especially K.

For the study of influence of different factors on well yield, a hydrogeological relational database was constructed. Database consists of several linked tables, describing *main data* (ID, location, name, depth ...), *lithology* (depth of different beds, their age ...), *hydrogeology* (discharge, transmissivity, hydraulic conductivity, specific capacity ...), *casing* and *other data*. The location of wells was obtained from a map of dolomite outcrops in Slovenia, developed in a GIS environment, and based on the Base Geological Map of Yugoslavia (OGK, covering whole Slovenia) in scale 1:100.000.

For investigation of topographic control the wells were separated into 6 topographic settings (Figure 1): V (valley bottoms), R (ridges), P (plateaus), S (slopes), F (flatlands in topographic lows) in H (foothills), and topography was defined from the topographical map in scale of 1:25.000 (national map TK25). For the study of proximity to rivers wells were divided into two classes, being closer (<200 m) or farther (>200 m) from the major watercourses, marked as rivers on the 1:25.000 topographic maps TK25 of Slovenia. The limit of 200 m was chosen for two reasons. The main one is that the value of 200 m is usually taken as a radius of influence of the well in short-term transient pumping conditions, so the wells within this distance from the rivers can be influenced by infiltration from the rivers. In addition, the 200 m was chosen as a upper limit of the classes of Mabee (1999) because even with this dataset, the number of data for wells near the rivers is small compared to those farther away. With further division into smaller classes, the number of data of nearer wells and the quality of analysis would decrease. Of course, this limit is purely artificial, so the results could differ for some other classification. Among the technical factors, well depth and degree of partial penetration were analyzed. For the former, data were classified into five classes according to well depth, each class occupying 50 m (0-50 m, 50-100 m, 100-150 m, 150-200 and > 200 m). In similar way, wells were divided into two categories – fully or partially penetrated wells.

Statistical methods were used for the analysis, as they are known to represent the best method for description and prediction of water well parameters (Eftimi, 2003). The distribution and the values of geometric mean and geometric standard deviation are given along with the other data. For all four influences, the differences among the classes were compared by two statistical tests (t and M-W), described later in the text.

Results and discussion

Distribution of data

Visual inspection of probability plots was checked for 8 different distributions. The results show that lognormal distribution fits best to all studied parameters. Verification of lognormal distribution for most parameters was further confirmed by statistical normality tests, namely Kolmogorov-Smirnov (K-S), its Lillliefors' modification (L) and Shapiro-Wilk's (W) test (Table 1). The latter is thought to be the most powerful among all, especially in case of small data samples and for the lognormal distribution (de Sá, 2003). According to K-S test, all parameters are distributed lognormally, and L and W tests shows some of the parameters distributed as non-lognormal on 95 % confidence level. As lognormal distribution was confirmed for almost all parameters by statistical tests, two different tests were used for analyzing the differences among the groups. The first, student's *t-test* assumes normal distribution of data, whereas for the nonparametric *Mann-*

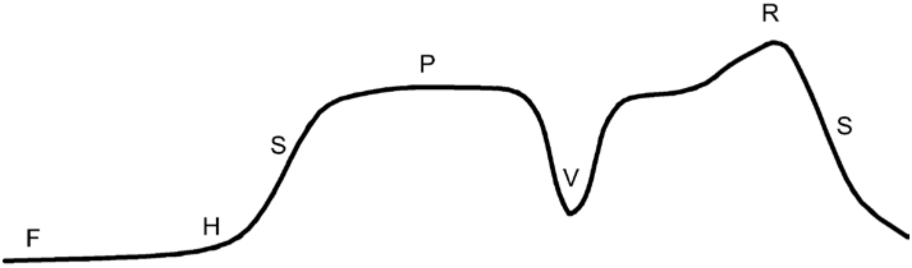

Figure 1. Topography classes. V: valley bottoms, R: ridges, P: plateaus, S: slopes, F: flatlands in topographic lows and H: foothills.

Slika 1. Topografski razredi. V: doline, R: grebeni, P: planote (višje ležeče izravnave), S: pobočja, F: ravnine (nižje ležeče), H: vznožja

Table 1. P-values of normality testing of log-transformed data (N: number of samples, K-S: Kolmogorov-Smirnov test, L: Lilliefors test, W: Shapiro-Wilks test). Asterisk * indicates significant results on 95 % level and therefore non-lognormal distribution of data. Lower values indicate higher deviations from normality.

Tabela 1. Rezultati testiranja normalne porazdelitve (N: število vzorcev, K-S: Kolmogorov-Smirnov test, L: Lilliefors test, W: Shapiro-Wilks test). Zvezdica * označuje signifikantne rezultate na 95 % stopnji zaupanja in torej porazdelitev, ki ni normalna. Manjše p-vrednosti kažejo na večja odstopanja od normalnosti.

Parameter	N	K-S	L	W
K	122	< 0.1	< 0.01 *	< 0.01 *
T	105	> 0.2	< 0.05	0.03 *
q	299	> 0.2	> 0.2	0.22
Q_{MAX}	286	< 0.1	< 0.01 *	0.01 *

Whitney test distribution is not important. As the data were found to be lognormal, the values are presented by geometric mean x* and geometric standard deviation s* (LIMPERT ET AL., 2001), as these should be used in case of this distribution and especially when describing the heterogeneous media (ABOUFIRASSI AND MARIÑO, 1984; DE MARSILY ET AL., 2005).

Topographical setting

Geometric means of parameters (Table 2) indicate that the values of most parameters can be found in flatlands (*F*), with this topographical setting being there times on first and once on second place. The values of parameters *K* and *T* are about one or more orders of magnitude greater in this class than in the others. Flatlands are followed by valleys (*V*) (once on first and three times on second place). The lowest values are observed in plateaus or high flats *(P)* (three times on last place), whereas the other three topographic settings (ridge *R*, foothill *H* and slope *S*) lie in between. Differences among the topographic groups were further tested by t-tests and M-W tests. Results (Table 2, Figure 2 for T and Q_{max}) show significant differences between classes V↔S, P↔F, S↔F, and also V↔R, V↔H, V↔P for practically all parameters, and non-significant differences between V↔F, R↔P, R↔S, R↔H, P↔H and S↔H. According to the values of hydraulic parameters, the topographic classes of valleys and also flatlands can be therefore generally distinguished from the ridges, slopes, foothills and plateaus. Less productive settings are indistinguishable among themselves, and the same conclusion can be made for the most productive groups (V and F) among themselves. Lower values of parameters on the slopes can be explained by greater runoff and lesser infiltration compared to flat areas. The water also tends to drain the higher topographic locations towards the lower locations, so the latter receive additional recharge this way, plus possible recharge from surface waters. Comparison to other studies (MABEE, 1999, LEGRAND, 1967) shows similar results, as the greatest values of well yield could be found in the topographic lows (valley/fjord bottoms and flats) and there existed no difference among the wells in valley bottoms and among the ones in flats (HENRIKSEN, 1995). Insignificant differences between some of the classes can be attributed to great variability, so the range of well yield values overlaps between topographic categories (YIN AND BROOK, 1992).

Table 2. Values and results of M-W and t-tests for influence of topography on hydraulic parameters (95 % confidence level). x*: geometric mean, s*: geometric standard deviation, N: both tests are non-significant, Y: both tests are significant. When these two tests differ, the first letter indicates results of M-W tests and second of t-tests. Some M-W-tests were not possible due to insufficient data and are indicated by -.

Tabela 2. Vrednosti in rezultati M-W in t-testov za vplive topografske lokacije na hidravlične parametre (95 % stopnja zaupanja). x*: geometrijska srednja vrednost, s*: geometrijski standardni odklon. N: oba testa nesignifikantna, Y: oba testa signifikantna, v ostalih primerih, kjer se rezultati testov razlikujejo, označuje prva črka rezultate M-W testa in druga t-testa. Ponekod M-W testi zaradi premajhnega št. podatkov niso bili možni in so označeni z -.

Hydraulic conductivity / Koeficient prepustnosti K (m/s)

N	**x***	**s***		**V**	**R**	**P**	**S**	**F**	**H**
69	-5.35	1.16	**V**alley	-	-	-	-	-	-
2	-5.94	0.37	**R**idge	N	-	-	-	-	-
24	-5.89	0.95	**P**lateau	Y	N	-	-	-	-
17	-6.14	1.09	**S**lope	Y	N	N	-	-	-
5	-4.63	0.12	**F**latland	N	NY	Y	Y	-	-
1	-6.30	-	Foot**H**ill	-N	-N	-N	-N	-Y	-

Transmissivity / Transmisivnost T (m^2/s)

N	**x***	**s***		**V**	**R**	**P**	**S**	**F**	**H**
66	-3.24	1.13	**V**alley	-	-	-	-	-	-
5	-3.88	1.51	**R**idge	N	-	-	-	-	-
20	-4.34	0.77	**P**lateau	Y	N	-	-	-	-
8	-4.33	0.59	**S**lope	Y	N	N	-	-	-
4	-2.72	0.11	**F**latland	N	N	Y	Y	-	-
1	-3.94	-	Foot**H**ill	-N	-N	-N	-N	-Y	-

Specific capacity / Specifična izdatnost q (l/s/m)

N	**x***	**s***		**V**	**R**	**P**	**S**	**F**	**H**
164	-0.21	0.80	**V**alley	-	-	-	-	-	-
9	-0.76	0.45	**R**idge	Y	-	-	-	-	-
36	-1.02	0.96	**P**lateau	Y	N	-	-	-	-
54	-0.61	0.90	**S**lope	Y	N	Y	-	-	-
14	-0.09	0.85	**F**latland	N	NY	Y	N	-	-
36	-0.69	1.16	Foot**H**ill	Y	N	N	N	N	-

Maximum discharges / Maksimalni pretoki Q_{max} (l/s)

N	**x***	**s***		**V**	**R**	**P**	**S**	**F**	**H**
117	0.78	0.56	**V**alley	-	-	-	-	-	-
9	0.21	0.32	**R**idge	Y	-	-	-	-	-
44	-0.06	0.66	**P**lateau	Y	N	-	-	-	-
46	0.31	0.60	**S**lope	Y	N	Y	-	-	-
16	0.50	0.58	**F**latland	N	N	Y	N	-	-
40	0.35	0.81	Foot**H**ill	Y	N	Y	N	N	-

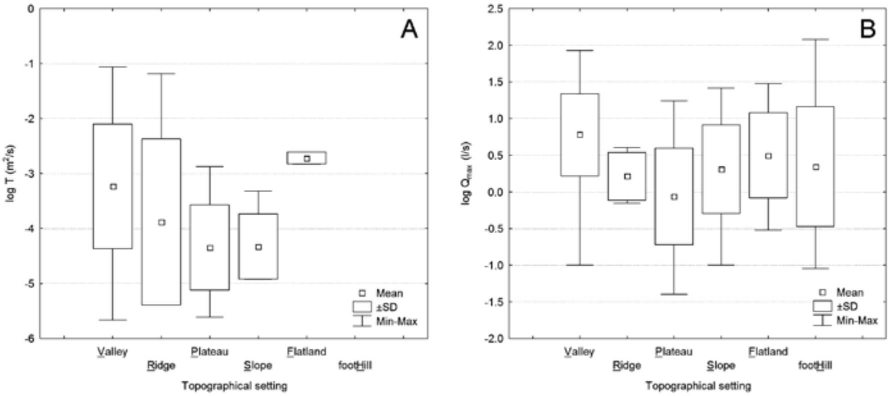

Figure 2. Box-plots of transmissivity (A) and maximum discharges (B) classified by topographical setting on Figure 1. Due to only one value in the Foothill class, this class is not shown in (A).

Slika 2. Škatlasti diagrami transmisivnosti (A) in maksimalnih pretokov (B), razdeljenih po topografski lokaciji (sl. 1). Podatki za razred Vznožje (H) niso prikazani za primer (A), ker je št. vzorcev premajhno (N=1).

Proximity to rivers

Results in Table 3 indicate that values are always higher in wells close to the rivers, being greatest (almost two orders of magnitude) for transmissivity. Differences are significant by both tests for all parameters except for hydraulic conductivity *K*. However due to very low number of data near the rivers (N=2), the results for *K* are to some extent unreliable. When compared to study of MABEE (1999), wells were in his case classified into 4 classes (<60, 60–100, 100–200 and>200 m) of proximity to surface water bodies, no significant differences were observed among the categories. Proximity to the rivers obviously has a major effect on hydraulic parameters, and this can be explained by recharge from the nearby rivers. In some of the wells the water level prior to and after the pumping was only a few meters below the surface, so the hydraulic connection between the well and the rivers could be established. However, this can not be checked for all wells, as the database was not complete and for many of the analyzed parameters the water table levels were not known. It is expected, nevertheless, that the proximity to the rivers should have an influence only on parameters Q_{max} and *q*, and not also on *K* and *T*, which are defined as aquifer properties. The results for *K* as discussed above, somewhat unreliable, and the explanation why the values of T are also significantly different, can be given in two ways. The rocks can be more intensively fractured in the vicinity of rivers as many valleys follow the tectonic lineaments. The influence of these lineaments can not be confirmed, as there is not enough data on tectonic properties of the rocks. Secondly, the *K* and *T* can be incorrectly calculated as the Cooper-Jacob and Theis equations do not always apply to fractured aquifers (VERBOVŠEK, 2005), so the values of these two parameters are somewhat unreliable.

Table 3. Influence of proximity to major rivers on hydraulic parameters. FAR indicates wells located more than 200 m from the rivers and NEAR those within this range

Tabela 3. Vplivi bližine rek na hidravlične parametre. FAR označuje vodnjake, oddaljene več kot 200 m od večjih rek, NEAR pa bližnje

	N	x*	s*	Min	Max	t &MW
Hydraulic conductivity / Koeficient prepustnosti K (m/s)						
Near	2	-4.55	0.66	-5.02	-4.09	N
Far	116	-5.58	1.13	-8.06	-3.41	
Transmissivity / Transmisivnost T (m^2/s)						
Near	7	-1.77	0.69	-3.11	-1.06	Y
Far	95	-3.68	1.06	-5.66	-1.19	
Specific capacity / Specifična izdatnost q (l/s/m)						
Near	45	0.30	0.76	-1.56	1.55	Y
Far	253	-0.55	0.89	-2.60	2.05	
Maximum discharges / Maksimalni pretoki Q_{max} (l/s)						
Near	34	1.11	0.47	-0.28	1.78	Y
Far	238	0.37	0.67	-1.40	2.08	

Well depth

Results (Table 4, Figure 3 for T and Q_{max}) show no systematic relation of decreasing hydraulic parameters with well depth. Significant differences though exist between some groups, but they are more or less random and have no logical explanation. This is in agreement with study of Loiselle and Evans (1995), where no change in fracture yield was observed with increasing depth. The explanation for non-significant differences could be that although there is a tendency to increase water supply by increasing the depth of a well, this chance also decreases because the interconnecting fractures and the ability of rocks to store and transmit water decrease with depth (LeGrand, 1967). However, this effect can be observed in deeper wells (more than few thousand meters), usually drilled for the oil exploitation. In this study, the majority of the analyzed wells are drilled to the depth of 300 m, and the fractures occur through the whole depth interval. The well depth should therefore not exhibit any influence of the well productivity, as observed. Other authors (Mabee, 1999) have nevertheless found that some of the shallower wells are more productive than the deeper ones, but the wells were located in metamorphic rocks, which are not directly comparable with the dolomites. To conclude, heterogeneity is most likely one of the major factors influencing well yield with depth, if this does not exceed some hundreds of meters.

Partial penetration

Values of geometric mean are higher for partially penetrating wells, except for *K*, where these two values are approximately the same. However, both t and M-W tests do not prove the differences, as seen from Table 5. This factor thus does not influence the parameters significantly. Similar results that transmissivity obtained by Cooper-Jacob method is affected only minimally by partial penetration, was observed in confined aqui-

Table 4. Influence of well depth. Classes are divided into five groups: 1: 0-50 m, 2: 50-100 m, 3: 100-150 m, 4: 150-200 m, 5: more than 200 m of well depth

Tabela 4. Vplivi globine vodnjakov. Vodnjaki so razdeljeni v pet razredov: 1: 0-50 m, 2: 50-100 m, 3: 100-150 m, 4: 150-200 m, 5: več kot 200 m globine

<table>
<tr><td colspan="9"><i>Hydraulic conductivity / Koeficient prepustnosti K (m/s)</i></td></tr>
<tr><td>N</td><td>x*</td><td>s*</td><td></td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td></tr>
<tr><td>1</td><td>-4,49</td><td>-</td><td>1</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>9</td><td>-5,44</td><td>1,26</td><td>2</td><td>N-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>17</td><td>-4,87</td><td>0,64</td><td>3</td><td>N-</td><td>N</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>15</td><td>-5,38</td><td>0,88</td><td>4</td><td>N-</td><td>N</td><td>NY</td><td>-</td><td>-</td></tr>
<tr><td>16</td><td>-6,04</td><td>1,09</td><td>5</td><td>N-</td><td>N</td><td>NY</td><td>N</td><td>-</td></tr>
<tr><td colspan="9"><i>Transmissivity / Transmisivnost T (m^2/s)</i></td></tr>
<tr><td>N</td><td>x*</td><td>s*</td><td></td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td></tr>
<tr><td>0</td><td>-</td><td>-</td><td>1</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>5</td><td>-3,81</td><td>0,69</td><td>2</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>16</td><td>-2,72</td><td>0,75</td><td>3</td><td>-</td><td>Y</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>12</td><td>-3,30</td><td>0,92</td><td>4</td><td>-</td><td>N</td><td>N</td><td>-</td><td>-</td></tr>
<tr><td>16</td><td>-3,93</td><td>1,06</td><td>5</td><td>-</td><td>N</td><td>Y</td><td>N</td><td>-</td></tr>
<tr><td colspan="9"><i>Specific capacity / Specifična izdatnost q (l/s/m)</i></td></tr>
<tr><td>N</td><td>x*</td><td>s*</td><td></td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td></tr>
<tr><td>17</td><td>-0,60</td><td>0,99</td><td>1</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>44</td><td>-0,64</td><td>0,99</td><td>2</td><td>N</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>57</td><td>-0,16</td><td>0,77</td><td>3</td><td>NY</td><td>Y</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>49</td><td>-0,55</td><td>0,81</td><td>4</td><td>N</td><td>N</td><td>Y</td><td>-</td><td>-</td></tr>
<tr><td>33</td><td>-0,86</td><td>1,02</td><td>5</td><td>N</td><td>N</td><td>Y</td><td>N</td><td>-</td></tr>
<tr><td colspan="9"><i>Maximum discharges / Maksimalni pretoki Q_{max} (l/s)</i></td></tr>
<tr><td>N</td><td>x*</td><td>s*</td><td></td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td></tr>
<tr><td>34</td><td>0,13</td><td>0,76</td><td>1</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>66</td><td>0,23</td><td>0,71</td><td>2</td><td>N</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>79</td><td>0,72</td><td>0,58</td><td>3</td><td>Y</td><td>Y</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>62</td><td>0,66</td><td>0,46</td><td>4</td><td>Y</td><td>Y</td><td>N</td><td>-</td><td>-</td></tr>
<tr><td>45</td><td>0,35</td><td>0,76</td><td>5</td><td>N</td><td>N</td><td>Y</td><td>Y</td><td>-</td></tr>
</table>

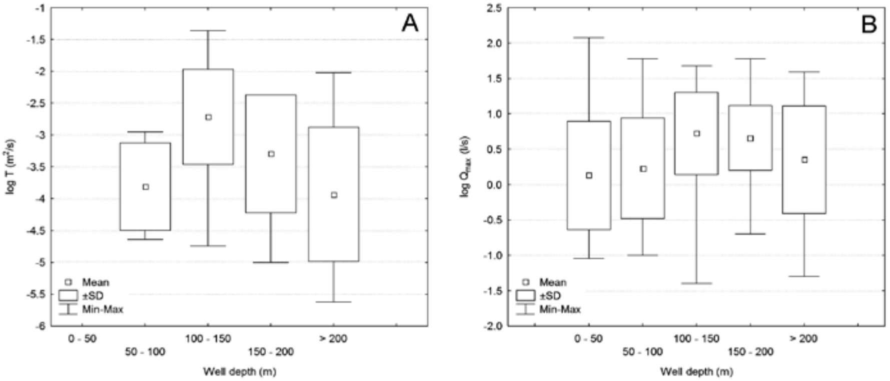

Figure 3. Box-plots of transmissivity (A) and maximum discharges (B), classified by well depth

Slika 3. Škatlasti diagrami transmisivnosti (A) in maksimalnih pretokov (B), razdeljenih po globini vodnjakov

Table 5. Influence of partial penetration of wells (fully or partially penetrating well)
Tabela 5. Vplivi popolnosti vodnjakov. *Fully*: popoln vodnjak, *Partially*: Nepopoln vodnjak.

	N	x*	s*	Min	Max	t & M-W
Hydraulic conductivity / Koeficient prepustnosti K (m/s)						
Fully	8	-5,55	0,89	-6,66	-4,26	N
Partially	114	-5,57	1,13	-8,06	-3,41	
Transmissivity / Transmisivnost T (m^2/s)						
Fully	5	-4,09	0,66	-4,86	-3,28	N
Partially	101	-3,53	1,14	-5,66	-1,06	
Specific capacity / Specifična izdatnost q (l/s/m)						
Fully	39	-0,60	0,74	-2,60	1,55	N
Partially	259	-0,47	0,96	-2,60	2,05	
Maximum discharges / Maksimalni pretoki Q_{max} (l/s)						
Fully	32	0,29	0,65	1,48	1,48	N
Partially	243	0,46	0,68	2,08	2,08	

fers (Halford et al., 2006). Higher values of most parameters in partially penetrating wells are contradictory to expectations that well yields should be higher in fully penetrating wells, as longer well screens can be placed than in partially penetrating ones (Kruseman and de Ridder, 1994). The non-significant results can be interpreted by the fact that the wells, drilled in productive aquifer with high transmissivity are usually not drilled to capture the whole aquifer depth, if they encounter the productive fractures. The partially penetrating wells therefore mostly capture the aquifers with good yield. In addition, the wells which penetrate more than 70 % of the complete aquifer thickness, are regarded as fully-penetrating, as they activate the whole thickness. All of these factors generate the insignificant differences between the two classes.

CONCLUSIONS

The results can be concluded in following points:

All data is lognormally distributed by visual estimates of probability plots. Statistical testing by Kolmogorov-Smirnov, Lilliefors and Shapiro-Wilks' tests confirms lognormal distribution for most of data. The selection of non-parametric Mann-Whitney or parametric t-tests for distinguishing the classes does not greatly influence the results, as they give the same significant results in most cases (but not the same p-values).

Topographic setting has great effect on hydraulic parameters. The highest values of hydraulic parameters can be found in flatlands, followed by locations in valleys. The least productive settings are the plateaus or high flats, whereas the other three (ridges, foothills and slopes) lie in between. Significant differences are confirmed by t and M-W tests for those classes which have the greatest or the lowest values. Influence of *proximity to rivers* shows the wells closer to rivers to have higher hydraulic values than those farther away. This is confirmed by all tests except for K. All parameters are higher in the first groups, what can be explained by recharge of the wells from the rivers; however this conclusion can be made only for Q_{max} and q, and not also on K and T. The latter parameters can be incorrectly calculated, as discussed below, and the rocks can be also more intensely fractured in the vicinity of the rivers, as valleys frequently follow tectonic lineaments. *Well depth* does not influence the hydraulic parameters significantly. Although there are noticeable differences between the 50 m thick classes, they are more or less random. The degree of *partial penetration* does not influence any of the parameters.

To describe the data more accurately, hydraulic conductivity and transmissivity should be calculated by appropriate methods for fractured aquifers (VERBOVŠEK, 2005), as from reports used in this study it is not clear whether the values of K and T could stand for the values of the fractures or of the matrix. In all hydrogeological reports, the methods of Cooper-Jacob and Theis were used for determination of K and T, and these are not always applicable to fractured aquifers. Appropriate usage of these methods would eliminate these uncertainties and enable to compare the influences of matrix versus fractures. Some more factors, not available to this study, could be studied, such as detailed petrographic studies of dolomites or proximity to tectonic lineaments. When planning new locations for water exploitation wells, all the presented factors should be considered in advance, to predict hydraulic parameters and locate well adequately.

POVZETEK

Vpliv topografske lokacije, bližine rek in tehničnih faktorjev na izdatnost vodnjakov v slovenskih dolomitnih vodonosnikih

V prispevku so predstavljeni vplivi topografske lokacije, bližine rek, globine ter stopnje popolnosti vrtin in vodnjakov (v nadaljevanju "vodnjakov") na naslednje hidravlične parametre: transmisivnost T, koeficient prepustnosti K, maksimalne pretoke Q_{max} ter na specifično izdatnost q (=Q/s). Podatki so pridobljeni iz hidrogeoloških poročil o vrtinah in vodnjakih v dolomitnih vodonosnikih v Sloveniji, nekateri manjkajoči podatki pa so bili dobljeni s pomočjo karte dolomitnih plasti v GIS okolju, izdelane na osnovi OGK.

Pri določanju vpliva topografske lokacije so bili vodnjaki razdeljeni v 6 topografskih razredov (sl. 1) po karti v merilu 1:25.000: V (doline), R (grebeni), P (planote oz. višje ležeče izravnave), S (pobočja), F (nižje ležeče ravnine) in H (vznožja). Za analizo vplivov bližine rek so bili ločeni v dva razreda glede na oddaljenost (manj in več kot 200 m) do vodotokov, označenih kot reke na kartah 1:25.000. Globina vodnjakov je bila razdeljena v pet razredov po 50 m, stopnja popolnosti vodnjakov pa v dva razreda glede na to, ali je vodnjak izvrtan do neprepustne podlage ali ne. Rezultati so predstavljeni s statističnimi vrednostmi (EFTIMI, 2003; DE SÁ, 2003), razlike med razredi pa so določene z neparametričnimi Mann-Whitney (M-W) in parametričnimi t-testi.

Rezultati v nadaljevanju so podani ločeno za vsak parameter. *Porazdelitve.* Vsi para-

metri so porazdeljeni logaritemsko normalno (tabela 1), kar dokazujejo vizualne ocene porazdelitev ter večina od treh testov normalnosti (Kolmogorov-Smirnov, Lilliefors ter Shapiro-Wilks). *Vpliv topografije*. Geometrične srednje vrednosti večine hidravličnih parametrov so najvišje v nižje ležečih ravninah (F), saj so vrednosti *T* in *K* tudi do dveh redov velikosti višje kot pri ostalih razredih (tabela 2, slika 2). Ravninam sledi razred dolin (V), najnižje vrednosti pa se nahajajo v planotah (P). Vrednosti v ostalih razredih (grebeni R, vznožja H in pobočja S) ležijo med omenjenimi. Medsebojna testiranja med razredi kažejo signifikantne razlike med razredi V↔R, V↔S, V↔H, P↔F, S↔F in V↔P za skoraj vse parametre ter nesignifikantne med razredi V↔F, R↔P, R↔S, R↔H, P↔H in S↔H. Vrednosti parametrov visoko izdatnih razredov se torej dokazljivo ločijo od nizko izdatnih, nasprotno pa se visoko izdatni (npr. doline in ravnine) ne ločijo med seboj. Rezultati so v skladu z opazovanji številnih avtorjev (LeGrand, 1967; Henriksen, 1995; Mabee, 1999), kjer so, podobno, najbolj izdatni vodnjaki locirani v topografsko nižje ležečih predelih. *Bližina rek* ima precejšen vpliv, saj so vrednosti vseh parametrov višje v razredu oddaljenosti manj od 200 m. Razlike povsod, razen pri koeficientu prepustnosti *K*, potrjujejo tudi M-W in t-testi (tabela 3). Vendar so tudi rezultati testov za *K* vprašljivi, saj je število podatkov za en razred izredno majhno (N=2). Rezultati se sicer ne skladajo s analizo Mabee-ja (1999), verjetno zato ker je bila v slednjem primeru uporabljena drugačna klasifikacija v štiri razrede (<60, 60–100, 100–200 ter >200 m) z manjšo oddaljenostjo od rek. Večjo izdatnost vodnjakov lahko razložimo z napajanjem iz bližnjih rek, obenem pa je lahko tudi razpokanost kamnin v teh območjih višja, saj doline dostikrat sledijo tektonskim conam. *Globina vodnjakov* nima večjega vpliva. Čeprav so razlike med nekaterimi razredi signifikantne (tabela 4, slika 3), so bolj ali manj naključne. Rezultati se skladajo z opazovanji ostalih avtorjev (LeGrand, 1967; Loiselle and Evans, 1995). Čeprav se naj bi z globino vodnjakov njihova izdatnost povečevala, obstaja tudi efekt, ki izdatnost zmanjšuje, saj se število povezanih vodonosnih razpok z globino manjša, toda ta efekt je opazen šele pri vodnjakih, globokih več tisoč metrov. Večina vodnjakov, vključenih v to študijo, je plitvejša od 300 m in v teh globinah so razpoke porazdeljene približno enakomerno po celotni globini, kar najverjetneje povzroča nesignifikantne razlike med razredi. Ali je *vodnjak popoln ali nepopoln*, prav tako ne vpliva bistveno na analizirane parametre, saj so vsi M-W in t-testi nesignifikantni (tabela 5). Vrednosti so za transmisivnost, specifično izdatnost in maksimalne pretoke višje pri nepopolnih vodnjakih, kar je v nasprotju z oceno, da so popolni vodnjaki izdatnejši, ker je z njimi možno zajeti več vodonosnega sloja (Kruseman and de Ridder, 1994). Neznačilne razlike med razredoma nastanejo skoraj zagotovo zaradi dejstva, da nepopolni vodnjaki niso izvrtani do podlage prav zato, ker že prej zajamejo zadosten del izdatnega vodonosnika in se vrtanje takrat ustavi. Zato so taki nepopolni vodnjaki po izdatnosti primerljivi s popolnimi in razlik med razredi ni.

Transmisivnost in koeficient prepustnosti sta pridobljena iz hidrogeoloških poročil, kjer sta izračunana preko Cooper-Jacobove ter Theisove metode, ki pa nista vedno primerni za karakterizacijo kraško-razpoklinskih vodonosnikov (Verbovšek, 2005). Uporaba ustreznih metod bi zato omogočila bolj poglobljeno analizo rezultatov, obenem pa bi bilo v nadaljnje primerno analizirati tudi vplive dodatnih faktorjev, npr. bližino tektonskih elementov, petroloških lastnosti kamnin ter ostalih tehničnih lastnosti vodnjakov. V članku so namreč zajeti le nekateri faktorji, ki pomembno vplivajo na hidravlične parametre, pri načrtovanju in izgradnji vodnjakov pa bi bilo potrebno upoštevati čim več tako geoloških vplivov, pa tudi značilnosti lokacije in način izvedbe.

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Meteorological Climate Change effect of the Ataturk Dam in Turkey at Eastern Anatolia

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Abstract: In Turkey, the significant amount of energy produced obtained of hydroelectrical power stations. Water constructions such as dam's reservoir in arid and semi-arid regions effects each other with climate and hydrology of environment. Therefore meteorological conditions have to be established and monitored at the hydroelectrical power stations. Droughts are among the most significant natural hazards that might damage human life and property under different meteorological and environmental conditions. The simplest methodology of temporal climate change assessment is the standardized precipitation index (SPI) which is used to quantify the precipitation deficit for several time scales, for example time averaging periods. The SPI is commonly used for the identification of various climate change characteristics such as the rain duration change, magnitude change, and intensity change at different standard truncation levels. The relationships between the drought duration and magnitude are provided in the form of scatter diagrams with the best straight-line fits. These are obtained for different truncation levels. Precipitation based drought description has been extended to triple-variable additionally including temperature and humidity time series. Such contours can be prepared for any base precipitation value but in this study average precipitation value is adopted as the truncation level. In this study is related to construction of the most important main project in the Southeastern Anatolia Project (GAP) area, the Ataturk Dam.

Keywords: Standardized precipitation index, climate change, drought, dam basin

INTRODUCTION

The Standardized Precipitation Index (SPI) is a way of measuring drought that is different from the Palmer drought index (PDI). Like the PDI, this index is negative for drought, and positive for wet conditions. But the SPI is a probability index that considers only precipitation, while Palmer's indices are water balance indices that consider water supply (precipitation), demand (evapotranspiration) and loss (runoff).

Weather is the state of the atmosphere at a specific place and time. Climate is a long-term average of weather in an area. Both are influenced by the amount of solar radiation the area receives, by local terrain and nearby large bodies of water, by changing geological and biological conditions and by other factors. Forecasters can often predict weather because of its local and generally sequential nature, but it is difficult to predict the longer-range of atmospheric chaotic motion. Climate predictions can be even harder to make because these factors operate over larger areas and longer periods of time.

Scientific paper

We know that climate has changed in the relatively recent past, but we are unsure about the causes of the change. We cannot yet predict climate change; data and models on which to base these predictions are still incomplete. Accurate climate predictions will soon be as critical as accurate weather predictions, however. Human-induced changes in the quantities of atmospheric carbon dioxide and ozone will lead to climate changes, but we're not sure what these changes will be.

The water resources and the atmosphere are extensions of each other, and human activity has changed the atmosphere as it changed the water resources. By establishing of the Ataturk Dam as important main project in the Southeastern Anatolia Project (GAP) area, pollutants injected into the air by construction phase can have regional consequence for the water resources and for all inhabitants.

Potentially the most destructive atmospheric problems are depletion of the ozone layer, global warming, and acid rain.

Ozone Layer Depletion

Table 1. Average ozone change, 1969-1986 (Smith, R.C., et al., 1992)

Latitude	Summer	Winter	Annual
1. 53° – 64°N	+ 0.4 %	– 6.2 %	– 2.3 %
2. 40° – 52°N	– 2.1 %	– 4.7 %	– 3.0 %
3. 30° - 39°N	– 1.9 %	– 2.3 %	– 1.7 %

Ozon depletion in the stratosphere above various latitudes of the Northern Hemisphere between 1969 and 1986. A 1991 NASA study showed that between 1978 and mid – 1990 the decreases in ozone were about twice the percentages shown here. Ozone is a molecule formed of three atoms of oxygen. Ozone forms naturally when lightning strikes through air; larger quantities are generated spontaneously in the stratosphere. A diffuse layer of ozone mixed with other gases-the ozone layer-surrounds the world at a height of about 20-40 kilometers. Seemingly harmless synthetic chemicals released into the atmosphere – primarily chlorofluorocarbons (CFC s) used as cleaning agents, refrigerants, fire-extinguishing fluids, spray-can, propellants, and insulating foams- are converted by the energy of sunlight into compounds that attack and partially deplete the region's atmospheric ozone. Ozone levels in the stratosphere have decreased by about 3 % over some countries like Turkey since 1969 (Table.1). The amount of depletion varies with latitude and with the seasons because of variations in the intensity of sunlight. This decline in ozone alarms scientists because stratospheric ozone intercepts some of the high-energy ultraviolet radiation coming from the sun. Ultraviolet radiation injures living things by breaking strands of DNA and unfolding average amounts of ultraviolet radiation, but increased amounts could overwhelm those protein molecules. Species normally exposed to sunlight have evolved defenses against defenses. Land plants such as soybeans and rice would be subjected to sunburn that decreases their yields. Even plankton in the uppermost 2 meters of water resources would be affected; recent research in fact indicates an alarming decrease in phytoplankton primary productivity of between 6 % and 12 % in dam lake waters. A 1 % decrease in atmospheric ozone would probably be accompanied by a 5 % to 7 % increase in human skin cancer. Strong ultraviolet light can also suppress the immune system and cause eye cataracts. The quantity of photochemical smog shrouding the urban areas will also increase as ozone levels fall.

Since the building of the Ataturk Dam, the industry at the Southern Anatolia at some cities like Gaziantep, Harran have increased, which results by increasing of emissions of CO_2, methane, and other greenhouse gases. These gases have contributed to a general warming of the district. The surface temperature of the region fluctuates slowly over time. The regional temperature trend has been generally upward in the 18 000 years since the last ice age, but the rate of increase has recently accelerated. This rapid warming may be the result of an enhanced greenhouse effect, the trapping of heat by the atmosphere. Glass in a greenhouse is transparent to light but not to heat. The light is absorbed by objects inside the greenhouse , and its energy is converted into heat. The temperature inside a greenhouse rises because the heat is unable to escape. On earth greenhouse gases-carbon dioxide, water vapor, methane, CFCs, and others-take the place of glass. Heat that would otherwise radiate away from the planet is absorbed and trapped by these gases, causing a rise in surface temperature. Greenhouse mechanism on the water resources:

1. Sunlight penetrating the atmosphere warms the Earth's surface,
2. The earth's surface radiates heat to the atmosphere, and some escapes into space,
3. Greenhouse gases in the atmosphere absorb some of the heat and trap it near the earth's surface,
4. When greenhouse gases-and heat-build up, dam lake water surface temperatures rise and the temperature of the atmosphere increases (Figure.1) (WATSON ET AL.,1990),

Standardized precipitation index (SPI)

The wide variety of disciplines affected by drought, its diverse geographical and temporal distribution, and the many scales drought operates on make it difficult to develop both a definition to describe drought and an index to measure it. Many quantitative measures of drought have been developed in the United States, depending on the discipline affected, the region being considered, and the particu-

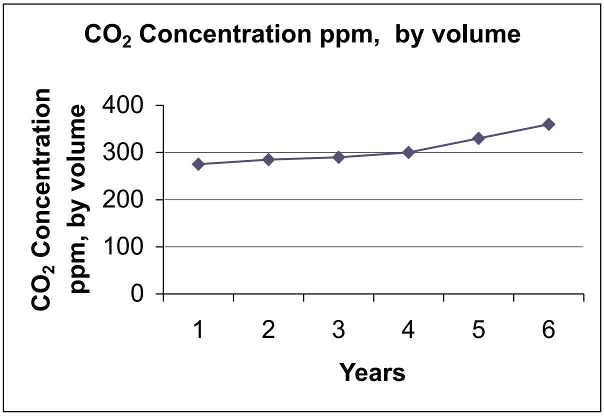

Figure 1. CO_2 concentration increase ppm, by volume (WATSON ET AL., 1990)

lar application. Several indices developed by Wayne Palmer, as well as the Standardized Precipitation Index, are useful for describing the many scales of drought.

Common to all types of drought is the fact that they originate from a deficiency of precipitation resulting from an unusual weather pattern. If the weather pattern lasts a short time (say, a few weeks or a couple months), the drought is considered *short-term*. But if the weather or atmospheric circulation pattern becomes entrenched and the precipitation deficits last for several months to several years, the drought is considered to be a *long-term* drought. It is possible for a region to experience a long-term circulation pattern that produces drought, and to have short-term changes in this long-term pattern that result in short-term wet spells. Likewise, it is possible for a long-term wet circulation pattern to be interrupted by short-term weather spells that result in short-term drought.

The simplest methodology of temporal drought assessment is the standardized precipitation index (SPI) and run analysis which are used to quantify the precipitation deficit for several time scales. In drought analysis, the given time series are estimated as X_1, X_2, ….., X_n , then the standardized precipitation series is given as

$$x_i = \frac{X_i - \overline{X}}{S_x} \qquad (1)$$

where $\overline{X}$, is the arithmetical mean of the given series, S_x is the standardized variation. As given in the below Figure (2) the obtained drought periods L_1, L_2, ……, L_m are taken by using the run analysis which are used to quantify the precipitation deficit for time averaging periods.

The drought amplitude is given as the deficit summation under each drought period as M_1, M_2,……., M_m. The cumulative deficit is given as

$$M_j = \sum_{i=1}^{m} \left| X_o - x_i \right| \qquad (2)$$

where m is the drought number during the drought period and X_o is the standardized mean level for every drought label. Also the drought intensity can be given as the ratio of drought amplitude to drought period.

$$I_J = \frac{M_j}{L_j} \qquad (3)$$

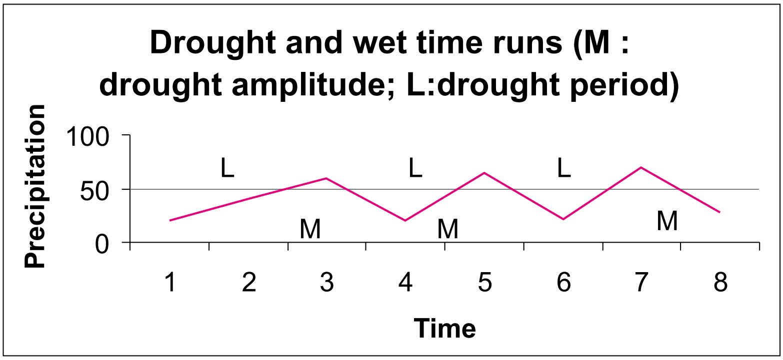

Figure 2. Drought and wet time runs (M_j: drought amplitude; L_j: drought period)

In every cutting point L_{max}, $L_{min,}$ M_{max}, M_{min} and I_{max}, I_{min} can be found as the drought property values. In addition, for understanding of every drought property the statistical parameters (mean, standardized deviation,…. and the others) can be found. The real amplitude, M_r (mm) can be found by opposite of the standardized method as

$$M_r = MS_M + \overline{X}_M \qquad (4)$$

where $\overline{X}_M$ and S_M are the mean of the amplitudes and the standardized deviation, respectively. Taking 9 rain measurement stations to give the drought periods as in Figure 3 and in Figure 4.

Considering the precipitation amounts at Figure 4 the amounts of the 2.value and 3. value lies below the diagram which shows the critical values for the drought periods (Table 2.).

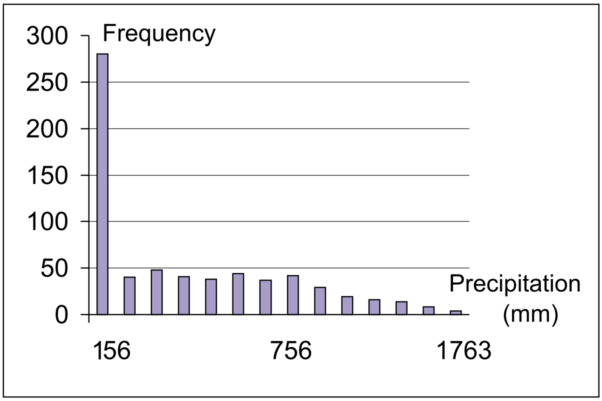

Figure 3. Histogram of Precipitation at Ataturk Dam District before the Dam Building

Table 2. The drought duration, amplitude, intensity, humidity and temperature in the maximum drought period before the Dam Building (Anonymous, 1989)

Cities	attitude	latitude	Month	Ampl.	I=[M/L]	Humidity(%)	(^{0}C)
Adiyaman	38.28	37.75	7	4.06	0.65	81.7	32.31
Diyarbakir	40.12	37.92	13	3.83	0.7	86.0	32.00
Gaziantep	37.37	37.08	7	3.97	0.76	88.4	29.50
Malatya	38.32	38.35	12	6.28	0.7	87.0	29.30
Elazığ	39.22	38.67	15	5.28	0.7	89.0	29.35
Batman	41.17	37.87	5	2.40	0.64	89.0	30.60
Siirt	41.93	37.93	9	3.72	0.62	86.2	30.95
Mardin	40.73	37.3	12	3.05	0.76	86.1	30.57
Urfa	38.77	37.13	16	4.24	0.74	81.0	32.70
		TOTAL:	**96**	**36.83**	**6.27**		

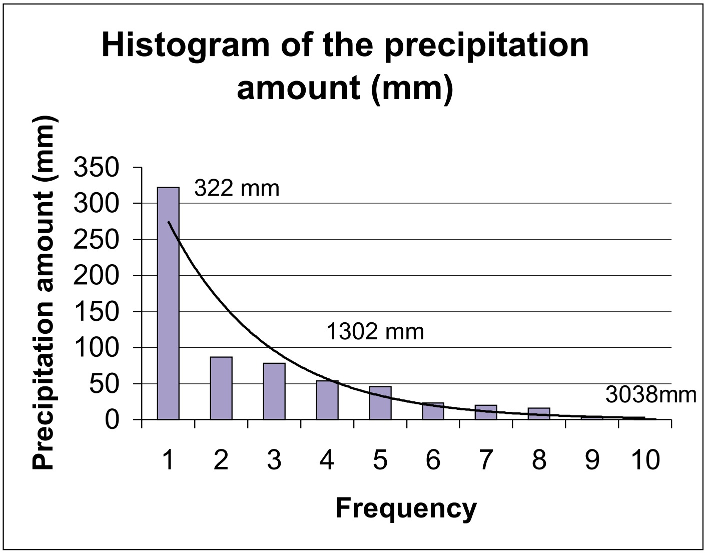

Figure 4. Histogram of Precipitation at Ataturk Dam District after the Dam Building

Standardized Precipitation Index (from National Climatic Data Center, NOAA):

1) exceptionally dry : –2.00 and below
2) extremely dry : –1.99 to –1.60
3) severely dry : –1.59 to –1.30
4) moderately dry : –1.29 to –0.80
5) abnormally dry : –0.79 to –0.51
6) near normal: –0.50 to +0.50
7) abnormally moist : +0.51 to 0.79
8) moderately moist : +0.80 to +1.29
9) very moist : +1.30 to +1.59
10) extremely moist : +1.60 to +1.99
11) exceptionally moist : +2.00 and above

The ***Palmer Z Index*** measures short-term drought on a monthly scale. The Palmer ***Crop Moisture Index (CMI)*** measures short-term drought on a weekly scale and is used to quantify drought's impacts on agriculture during the growing season.

The ***Palmer Drought Severity Index (PDSI)*** (known operationally as the *Palmer Drought Index (PDI)*) attempts to measure the duration and intensity of the long-term drought-inducing circulation patterns. Long-term drought is cumulative, so the intensity of drought during the current month is dependent on the current weather patterns plus the cumulative patterns of previous months. Since weather patterns can change almost literally overnight from a long-term drought pattern to a long-term wet pattern, the PDSI (PDI) can respond fairly rapidly.

The hydrological impacts of drought (e.g., reservoir levels, groundwater levels, etc.) take longer to develop and it takes longer to recover from them. The ***Palmer Hydrological Drought Index (PHDI)***, another long-term drought index, was developed to quantify these hydrological effects. The PHDI responds more slowly to changing conditions than the PDSI (PDI).

While Palmer's indices are water balance indices that consider water supply (precipitation), demand (evapotranspiration) and loss (runoff), the ***Standardized Precipitation Index (SPI)*** is a probability index that considers only precipitation. The SPI is an index based on the probability of recording a given amount of precipitation, and the probabilities are standardized so that an index of zero indicates the median precipitation amount (half of the historical precipitation amounts are below the median, and half are above the median). The index is negative for drought, and positive for wet conditions. As the dry or wet conditions become more severe, the index becomes more negative or positive. The SPI is computed by NCDC for several time scales, ranging from one month to 24 months, to capture the various scales of both short-term and long-term drought.

Time scale

The number of months extending through the end of the current month. Some processes are rapidly affected by atmospheric behavior, such as dryland agriculture, and the rate at which grasses and brush dry out, and the relevant time scale is a month or two. Other processes have longer time scales, typically several months, such as the rate at which shallow wells, small ponds, and smaller rivers become drier or wetter. Some processes have much longer time scales, such as the rate at which major reservoirs, or aquifers, or large natural bodies of water rise and fall, and the time scale of these variations is on the order of several years.

Five quantities are computed as part of the Standardized Precipitation Index procedure. They follow as a consequence of an observation made by Dr. Tom McKee (1993, 1995), State Climatologist for Colorado, that users are interested in one or several among the following types of information:
What is the absolute amount of precipitation?
What is the absolute departure from limatology?
What is the relative departure from climatology?
How frequent are such departures from climatology?
How can this be expressed as a single number comparable across climates?

1. **Accumulated Precipitation -** The total precipitation that has fallen during the indicated number of months, through the end of the month displayed.
2. **Accumulated Precipitation Departure -** The amount by which the indicated accumulated precipitation is above or below the long term average for exactly the same set of months. The local seasonal cycle of long-term average precipitation is automatically accounted for. A departure of 0 indicates totals are exactly equal to climatological values.
3. **Accumulated Precipitation Percent of Average -** The observed accumulated precipitation, over the time scale of interest and extending through the end of the last month indicated, divided by the long-term average precipitation which would be expected to accumulate over the same set of months, and then multiplied by 100. A value of 0 indicates no precipitation at all, and a value of 100 percent indicates that the amount is equal to the climatological average.

4. **Percentile, or “Probability of Non-Exceedance” -** This quantity indicates how often a value of the magnitude observed is seen, its degree of “unusualness”. A value of 0 means that zero percent of the other values in the record do not exceed that value, or in other words, that all other values exceed that value, so that the value in question is so low that it seldom if ever occurs. A value of 50 indicates that half of the historical values are higher and 50 percent are lower. A value of 75 indicates that 75 percent of the values are as low as this value, or conversely, that only 25 percent of the values are higher than the given value. A value of 99 means that 99 percent of the observed values are lower, and that this value is in the top 1 percent of all values. Values near 50 are not unusual; values near 0 or 100 are very unusual.
5. **Standardized Precipitation Index** - The SPI was formulated by Tom Mckee, Nolan Doesken and John Kleist of the Colorado Climate Center in 1993. The purpose is to assign a single numeric value to the precipitation which can be compared across regions with markedly different climates. Technically, the SPI is the number of standard deviations that the observed value would deviate from the long-term mean, for a normally distributed random variable. Since precipitation is not normally distributed, a transformation is first applied so that the transformed precipitation values follow a normal distribution.

   The Standardized Precipitation Index was designed to explicitly express the fact that it is possible to simultaneously experience wet conditions on one or more time scales, and dry conditions at other time scales, often a difficult concept to convey in simple terms to decision-makers. Consequently, a separate SPI value is calculated for a selection of time scales, covering the last 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 15, 18, 24, 30, 36, 48, 60, and 72 months, and ending on the last day of the latest month.

Methodology - First, a time series of the precipitation value of interest is generated. Then, a frequency distribution is selected and a statistical fit to the data is determined. The cumulative distribution is formed from the fitted frequency distribution. The percentile for the particular time series element of interest, usually the latest one, is selected from the cumulative distribution. For “ties” (multiple instances of the same value), the upper value is used (probability of non-exceedance). For any other theoretical probability distribution, the analogous point on its associated cumulative frequency distribution can be determined. Here, the normal distribution is used, with mean zero and standard deviation of one, and value in standardized units of a given percentile is found can be readily determined. For the normal distribution, these are exactly the same as units of standard deviations. The Standardized Precipitation Index can be thought of as the number of standard deviations that the precipitation value of interest would be away from the mean, for an equivalent normal distribution and adequate choice of fitted theoretical distribution for the actual data. In effect, the method consists of a transformation of one frequency distribution to another frequency distribution, in this case the widely used normal, or Gaussian, distribution.

In this case, following McKee et al. (1993, 1995), we have chosen to use the incomplete beta distribution (see, for example, Wilks, 1995, p 95-97). This distribution is very robust and can deal with the wide range of extreme climates found in the western United States, especially those where monthly and seasonal precipitation of zero is common and expected. Guttman (1998, 1999) has examined the properties of the SPI in great detail, and has determined that the Pearson III distribution is likely to give essentially equivalent results, and in some instances slightly better. We have not yet modified the code (as of May, 2001) to use the Pearson III, but the incomplete beta distribution in use is quite close.

Precipitation Analysis in Time

The analysis of precipitation variation through time and over space will frequently yield relationships between short-term precipitation intensities and longer-term totals, between intensity and duration, and between intensity, duration and area. Thus, the analysis of the character and organization of precipitation in time and space frequently yields results which span both the temporal and spatial dimensions. Such relationships will commonly exhibit a site or area-dependency, so that temporal and spatial relationships may provide a convenient means of studying the character and organization of precipitation at the ground surface. In turn of course, the character and organization, both in time and in space, are determined by the nature and magnitude of the meteorological processes producing the precipitation, thus providing the all-important link between the two major parts. In practice, of course, no two rainstorms nor any two climates are identical, even over the long term. Many of the techniques involved in the analysis of precipitation character and organization, therefore, are aimed at distilling the considerable variation in precipitation amount over all time and space scales to produce a generalized result which may be used, either for modelling or forecasting, in a particular area or for a specific location. A key feature of the analysis of precipitation in both time and space therefore involves the use of probability theory, and elements of mathematics and statistics.

The study of the character and organization of precipitation in and through time may take a variety of forms. Precipitation is highly variable over a variety of time scales, so that it is first important to identify what may be called the ‘ precipitation climatology ’of a location when precipitation occurs seasonally and within the day, and why such variations are present. The precipitation climatology will be determined primarily by the nature of the prevailing precipitation-producing processes. There is of course considerable global geographical variation in such processes, and also often a marked seasonal and monthly variation in either their nature or magnitude, or both. The influences of process may also extend to daily variation in precipitation and to the diurnal variation in precipitation amount. It is important to ascertain the general nature of precipitation in an area: The normal expectations in amount, intensity and distribution through the year or day, and in particular, to isolate any longer-term trends or oscillations through time. Secondly, the character of precipitation amount (intensity) through time within a typical, or even a particular, precipitation event, be it a temperature frontal depression or a small rain shower over the tropical district. There are some characteristics, which may be used to distinguish a conventional storm from a synoptic disturbance. Commonly for all types of precipitation event it is also possible to characterize them in terms of mathematical relationship between intensity and duration, and in particular to derive a relationship between intensity maximum over a range of durations. Much of the analysis of precipitation data, in common with many hydrological analyses, is concerned with attempting to predict the magnitude or the frequency of events. This may adopt a stochastic approach, where it can be attempt to derive probabilities for events of given magnitude, or a physical approach, through the estimation of probable maximum precipitation (PMP), where a knowledge of precipitation processes is used.

The study of precipitation extremes is afforded by the estimation of the probable maximum precipitation (PMP). It is in fact largely a physical estimate of what might be the greatest possible precipitation given a certain set of extreme atmospheric conditions, notably the moisture content of the atmosphere. It is usually applied with respect to a given area, generally a drainage basin, and includes also estimates for the rate of inflow of moisture over the basin, and the maximum likely amount of that moisture which can be precipitated. The PMP is ‘the theoretical greatest depth of precipitation for a given duration that is physically possible over a particular drainage area at a certain time of year.

Properties of Ataturk Dam and Hydro-Elektrical Power Plant (IRCOLD, 1999)

Location: SanliUrfa
Purpose: Irrigation and Energy
Construction (starting and completion) year: 1983 - 1992
Embankment type: Rockfill
Dam Volume: 84 500 000 m^3
Height (from river bed): 166.00 m.
Reservoir volume at normal water level: 48 700 00 hm^3
Reservoir area at normal water level: 817.00 km^2
Irrigation area: 872 385 ha
Installed capacity: 2400 MW
Annual energy generation: 8900 GWh

Ref: IRCOLD, 1999: Turkish National Committee on Large Dams, “Dam Engineering in Turkey”, Ankara, Turkey.

Drought Management in Turkey

In Turkey at the Southeastern Anatolian Region the water potential like the other natural resources remains constant, despite the fact that the population increased continuously. The natural water supply falls to minimum levels in summer time when the demands are maximum. The periodic droughts in the country causes important problems and necessitates the development of the projects for water storage, to meet the demands in the drought periods. For drought management the state of ground water reserves, surface and ground water relations, water quality, preservation of wetlands and the sustainability of the natural life must be developed. To estimate the magnitude and duration of the droughts beforehand for the operation of the reservoirs, the policies for the drought management must be planned. To meet the valuable results, meteorological, hydrological and ecological investigations, measurements and their analysis must be done precisely. Irrigation plans based on the river basin have been made in order to minimize the effect of drought. To reduce the impact of drought on yield, studies on preventing the planting of crops which consume most water, determining the time that crops requires most water and giving the water to that crops at that certain time, and giving the priority to the crops that requires water most were carried on annually during the drought period.In that drought period some measures such as giving the water to fig will decrease the effect of the drought in the Southeastern Region of Turkey. On the other hand, instead of small basins large river and regional basins must be chosen, also long term precipitation and flow series must be produced, correct runoff coefficients must be determined by investigating the land use, soil quality, soil texture, soil classes, geologic formation and vegetation in the basins by using geographic information systems and minimum, maximum and average flows in the rivers must also be determined. By using the mathematical models the “ basin water yields” for the wet, normal and drought periods must be determined for the projects providing technical and economical optimum solutions.

In Turkey the droughts are caused by the absence of precipitation; the severe deficiency in the hydrologic system or in the agricultural and domestic demand areas does not completely match the deficiency caused by precipitation. River flows, snow melt, reservoir levels and changes in ground water levels are the most important parameters for drought processes. A definition can not be found up to now and methods defining coefficients related to drought can not be developed. The risk decreases storage capacity increase and very large and uneconomical structures are needed. For this reason suitable solutions must be developed. In Southeastern Anatolia 75 % of the water resources is being used in irrigation sector. Therefore, the demands in the drought periods can be fully solved by constructing storage reservoirs. This solution is not accepted as a rational solution economically and evaluated as waste of resources. In these periods the demands must be met by making shortages in water supply. But the shortage of irrigation water can cause a decrease in the benefits. In the drought year periods, the magnitude of drought can be estimated with a probability beforehand, so that some proportions of water shortages can be made and as a solution the water required for the minimum production, which will not endanger the plants life, can be given to the plant. During the drought period, the operations which will provide the necessary withdrawal from the ground water requirements must be encouraged. The cost of the storage structures constitutes the most important component of the drought management project. Therefore storage structures become dominant factor in the determination of the project economy. The project design must be determined according to the different conditions of the regions and the principles of the operation studies must be made by the simulations. Also these principles must satisfy the economic criteria as well. In the reservoir operation studies, the average flow of the river on which the dam is built and the variations in this flow must be evaluated as a function of the water withdrawal pattern from the reservoir. The design of the dams and its appurtenant structures must be done according to this criteria.

The measurement of the river flow precisely for long periods is important to obtain reliable results which are the main input for the reservoir operation studies.

For five year drought period the application of the following criteria for the design of the storage reservoirs is evaluated as a rational method:

1. It must meet the 65 % of the annual demands in the most drought year.
2. It must meet the 95 % of the water requirements in the operation period.
3. It must make shortages in the consecutive five years.
4. It must meet the 75 % of the irrigation water requirements in the most critical consecutive five year period.
5. It must provide irrigation water at least during the half of the irrigation period.

Water Resource Development In South-Eastern Anatolia Region (GAP)

The southeastern Anatolia Project is the most comprehensive project ever implemented in Turkey. Beyond the dams, hydroelectric power plants and irrigation schemes on the Euphrates and the Tigris Rivers, Southeastern Anatolia Project, as an integrated project envisages the development of communication, housing, industry, education, health and other services. The objectives for the development of the Southeastern Anatolia region are set as follows:

1. To develop all the land and water resources in the Region, in order to achieve accelerated economic and social development,
2. To alleviate disparity between the Region and other regions by increasing production and welfare levels in the region,
3. To increase the productivity and employment capacity in the region,
4. To meet increased need for infrastructure resulting from population explosion and urbanization,
5. To organize economic and physical infrastructure in rural areas, in such a way as to utilise the resources, in the most useful ways and to direct urban growth in desired directions,
6. To contribute to the national objectives of sustained economic growth and export promotion by efficient utilisation of the region's resources.

Southeastern Anatolia Project is the biggest development project ever undertaken by Turkey, and one of the biggest of its kind in the world. The integrated, multi-sectoral project includes 13 major projects which are primarily for irrigation and hydropower generation, planned by the State Hydraulic Works (DSI). A a large scale and multi-sectoral regional development project, this project comprises the lower reaches of the Euphrates and Tigris rivers within the boundaries of Turkey. The region covers an area of 75 358 km^2 in the upper Mesopotamia. This project aims to develop the water resources of these rivers, which are the two main branches of the Tigris-Euphrates basin (The Shatt-Al- Arab), together with the available groundwater resources in the region. At the border where the branches of the Euphrates and Tigris rivers leave Turkey, the annual average run-offs are 30 billion m^3 and 16 billion m^3, respectively, the total of which corresponds to 25% of the country's average run-off. The project envisages the construction of 22 dams, in which one is the Ataturk Dam, and 19 hydroelectric power plants on the Euphrates and Tigris rivers and their tributaries. It is planned that at full development over 1.7 million ha of land will be irrigated and 27 billion kWh of electricity will be generated annually with an installed capacity over 7500 MW. The area to be irrigated accounts for 19 % of the economically irrigable area in Turkey (8.5 million ha), and the annual electricity generation accounts for 22 % of the country's economically viable hydro-power potential (125 billion kWh). Southeastern Anatolia Project is now one of the most ambitious regional development projects ever attempted in the world. It covers, in addition to the irrigation and hydropower schemes, all the related social and economic sectors including industry, transportation, mining, telecommunications, health, education, tourism and infrastructure. The fundamental development strategy are given as four components:

1. Develop and manage the region's soil and water resources for irrigation, domestic and industrial purposes in an efficient manner;
2. improve land use by encouraging optimal cropping patterns and better agricultural practices;
3. promote private entrepreneurship with emphasis on the agro-industries;
4. improve social services, educational facilities and employment opportunities with a view to keep local population away from migrating to big cities as well as attracting qualified workforce to the region.

Southeastern Anatolia Project Regional Development Administration was established in 1989 to carry on the major function of multi-sectoral planning within a regional perspective. Sustainability goals were determined for strengthening the integrated development process and for the mitigation of the socio-economic disparities in the Southeastern Anatolia region.

DISCUSSION

Over the past decades, increasing climate variability and extreme weather have affected millions of people and disrupted regional economies. Climate change is inevitable and through water it has serious consequences for many sectors, including health and sanitation, food security, energy and nature. Everyone is affected, but the poor and remote are hit first and hardest. It is imperative to increase our efforts towards abatement of greenhouse gases emissions and to initiate actions to better cope with today's climate variability, which is a first step towards coping with climate change. A greater appreciation of climate issues amongst water policy makers and planners, water managers and society is the basis for effective actions in a sector that is essential to all facets of sustainable development. Even though climate is driven by global processes, most adaptation actions will need to be taken at the community, basin, national and regional level. Climate variability and weather extremes will derail achieving the development goals in the next 15 years. Development activities without considering climate change will further increase vulnerability.

Categories of action include infrastructure development, timely warning and forecasting systems, risk reduction, risk sharing and data management, spatial planning and institutional capacity development and reform, based upon community level decision making. To support these actions data are needed from extended observational systems and networks. The Dialogue on Water and Climate (DWC) was launched in 2001 to develop and promote adaptation strategies that help reduce the vulnerability of the poor against the detrimental effects of climate variability and climate change. In many countries and regions the multistakeholder dialogue process has been put in place at the regional, national and basin levels. Through these dialogues a wide range of stakeholders can examine which information is required for awareness raising, what measures can be taken to cope with the effects of climate change, and how climate can best be factored into water resources management policies.

Recommendations

- Enhance policies and measures towards adaptation to the impacts of climate variability and change, along with continuing efforts on further reduction of greenhouse gas emissions.
- Continue the informed multi-stakeholder approach at national, basin and regional level to prepare action plans for adaptation.
- Integrated Water Resources Management should become the inter-sectoral framework under which the water and climate agenda needs to be implemented.
- Develop national, basin and regional capacities (policies, strategies, research and implementation) and secure financial support for preparation and implementation of national water sector adaptation plans.
- Create a “ Water and Climate Alliance” as an international umbrella to continue building bridges between the climate and water sector, encourage capacity development to better cope with climate impacts, and facilitate obtaining financial support for national, basin and regional level adaptation plans.
- Enhance efforts to integrate and mainstream the initiatives developed under the Water and Climate Associated Program with related processes like disaster preparedness and management strategies.
- Mainstream the climate variability and change into nartional water and land management policies and management practices.
- Reverse the trend of further deteriorating insitu data collecting and observational networks.

RESULTS

The main objective of the research is to demonstrate the application of modern water resource systems planning techniques that have been well developed in theory to a real water resources planning study in scope of climatic change in Turkey in such a way that the decision-makers are assisted in choosing among alternative development plans for the basin. The ultimate expectation is that the research will help to develop a better understanding of the water resources management in scope of climatic change and to explore the possibilities of integrated river basin management.

The storms themselves are usually considered to be independent of urbanization. That is, the storms are not thought to be greatly affected or changed by the gradual evolution of an urban area.

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Hydrogeological characteristics of the „Olympija“ source, Sarajevo

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Abstract: "Olympia" Source (519 asl) is situated in foothill of the olympic mount-aines Igman and Bjelašnica, 15 km westhern from Sarajevo town. Karst aquifer of the joint-cavernous porosity egsist into Middle Triassic limenstones and dolomites. In substratum lies impermeable Lower Triassic layes and in overlayer are impermeable Upper Cretaceous layers, also. By flowing production "Coca-Cola" well at first time in this area, on 171m depth underground potable water is reached under Upper Cretaceous flish.

Key words: Triassic, Upper Cretaceous flish, karst aquifer, groundwater

INTRODUCTION

Hydrogeological research works for requirements of company Coca Cola HBC Sarajevo, for the first time in the area of Sarajevo, with well CC Well, researched was underground water of arthesian aquifer in the flysch of the upper Cretaceous. Performed research works have scientific and practical significance and they are resulted in establishment of potable water source "Olimpija" that is bottled in the plant of Coca Cola. In the papers, basic hydrogeological characteristics of this water source are represented.

Location of the Water Source

Water source "Olimpija" is located in Bosnia and Herzegovina, 15 km to the west of Sarajevo, at the locality Mostarsko raskršće,

Geographic location and communication conditions of the water source are favorable. Alongside the water source is a motorway Sarajevo-Mostar, regional road Sarajevo - Kiseljak and railway road Sarajevo - Mostar.

Water source is situated in the valley of the river Zujevina at the altitude of 519 m. a.s.l. River Zujevina, in this part of its watercourse, cuts the watertight rocks of the lower Triassic (T_1) and Upper Cretaceous (K_2). The so-called "Olympic Mountains" Igman and Bjelašnica which peaks are between 1,500 till above 2,000 m a.s.l. are situated on the south side of the source.

Geological characteristics

Geological composition of the wider area is represented by sediments of the Triassic, Upper Cretaceous, Miocene and Quaternary (Figure 2).

Triassic sediments are widely distributed in those terrains. All stages of the Triassic are distinguished in the typical south alpine genesis.

Scientific paper

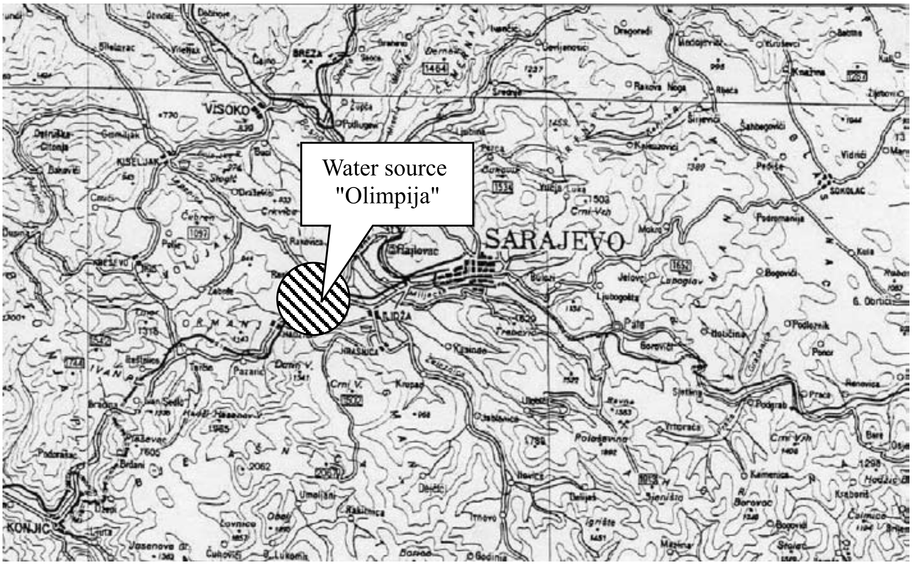

Figure 1. Geographical Location of Water Source “Olimpija”, S 1: 500.000

Sediments of the Lower Triassic (T_1) are confirmed in southwest part of the source. They are composed of sandstone, argillites, clayey marls and sandy limestone. They lay over the Permian-Triassic (P, T) marly limestone with lenses of gypsum and anhydrite. Total thickness of the clastite of the Lower Triassic is about 500 m.

The Middle Triassic – Anisian (T_2^1) is developed in the facie of dolomite, dolomitic limestone and limestone. Carbonates of the Anisian outcropping in the southwest of Mostarsko raskršće and they are confirmed by the drilling of “CC Well” in the water source “Olimpija”. Those sediments are very cracked and karstificated and lay over the clastite of the Lower Triassic. Their thickness is 200-400 m.

Sediments of the Ladinian (T_2^2) are situated in the smaller areas, in the western part of Mostarsko raskršće. They are represented by volcanic-sedimentary formation, i.e. by sandstone, chert, tuffa, schist, spilite and diabase in the lower and laminar limestone with the nodules of chert at the higher levels. Thickness of the Ladinian deposit is 100-300 m.

The Middle and the Upper Triassic ($T_{2,3}$) are represented with limestone and dolomite. The mountain Igman is, mainly, composed of these sediments. They are intensively tectonised and karstificated. They lay concordantly over the older Ladinian formations and in the higher level they gradually changing in megalodon limestone of the upper Triassic. Thickness of the carbonates of the Middle and Upper Triassic is 300 - 500 m.

The Upper Triassic (T_3) is represented by megalodon limestone, which is discovered at Igman and Bjelašnica mountains, and the thickness is about 700 m.

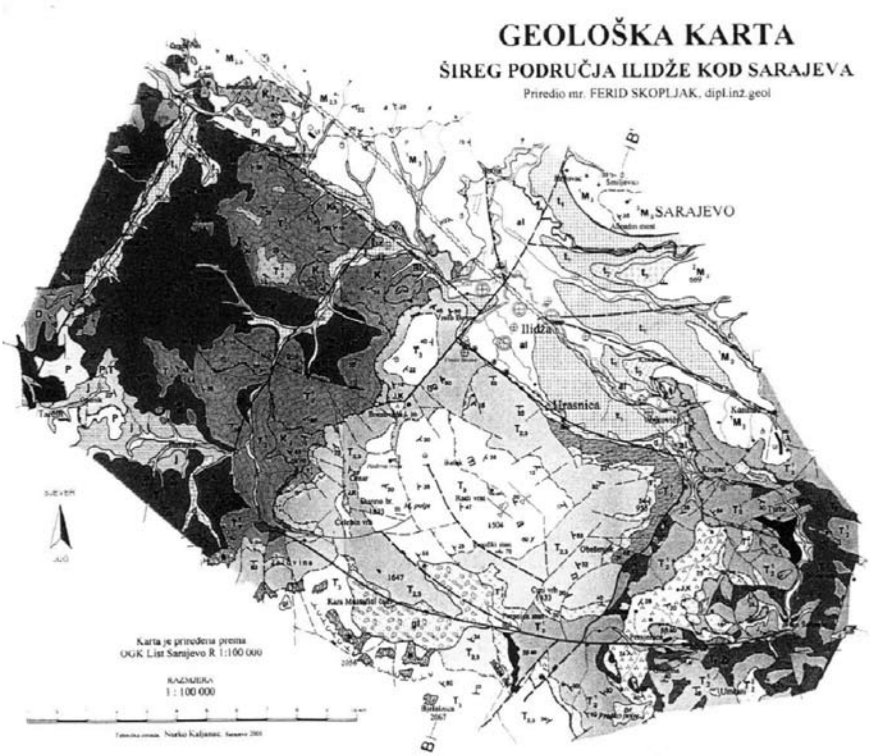

Figure 2. Geological map of Ilidža near Sarajevo area

Sediments of the flysch of the Upper Cretaceous (K_2) has significant distribution in the region of Mostarsko raskršće, Blažuj, Rakovica and Hadžići. They are composed of marl, argillite, calcarenite, marly limestone and breccia limestone. Those sediments are discordant to the Triassic carbonates. The thickness is 140 - 400 m.

Sediments of the Upper Miocene (M_3^1) are situated in the northern part of Mostarsko raskršće. They are represented by marl, argillite, claystone and incoherent sandstones. Total thickness of this series is about 500 m.

Quaternary sediments (Q) are confirmed in the valley of Zujevina river. They are represented by the sediments, such as: debris, gravel and sand. The thickness is 7 - 16 m.

Hydrogeological Characteristics

On the basis of the porosity structure and permeability of the rocks that participate in the composition of the terrain of the wider area of water source "Olimpija", the following rocks arte selected:

- Practically watertight rocks,
- Mostly watertight complexes,
- Poorly permeable rocks of the fractured porosity,
- Well permeable rock masses of intergranular porosity, and
- Well permeable rocks of cavernous-fractured porosity.

Practically watertight rocks are sediments of the Upper Miocene (M_3^1). Since they are characterized by insignificant and isolated porosity, they are expressively watertight rocks. They have a function of the complete hydrogeological barrier.

Mostly watertight complexes are sediments of the Upper Cretaceous (K_2). Those flysch rocks are mostly watertight and have function of the hydrogeological barrier. At some places, inside of the watertight complex, in the facie of sandstone and breccia limestone, they could accumulate smaller quantity of underground water. In the region of the water source "Olimpija", the sediments of the Upper Cretaceous represent watertight roof of the limestone aquifer.

Poorly permeable rocks of the fractured porosity are the sediments of the Lower Triassic (T_1). Those sediments, together with the sediments of Permian-Triassic (P,T) from the floor, have poor permeability and they mainly represent watertight complex of rocks. However, in the zone of the fault of Zujevina river, they could be more permeable, if they are in the facie of the sandstone and limestone.

Well permeable rock masses of intergranular porosity are subsurface, alluvial sediments. The coefficients of permeability and transmissivity are $k = 4.6–7.4 \times 10^{-3}$ m/s and $T = 7.3–11.8 \times 10^{-2}$ m²/s, respectively. In these formations, the deposit of underground water is formed as unconfined aquifer, which is exploited by shallow drilled wells.

Well permeable rocks of cavernous-fractured porosity are carbonate deposits of Anisian (T_2^1), Middle and Upper Triassic ($T_{2,3}$) and Upper Triassic (T_3). There are characterized with expressive fractured – cavernous porosity and good permeability. The transmissivity coefficient of these formations is $T = 2.05 \times 10^{-3} – 1.52 \times 10^{-1}$ m²/s. These rocks are the main, deep karst aquifer of this area.

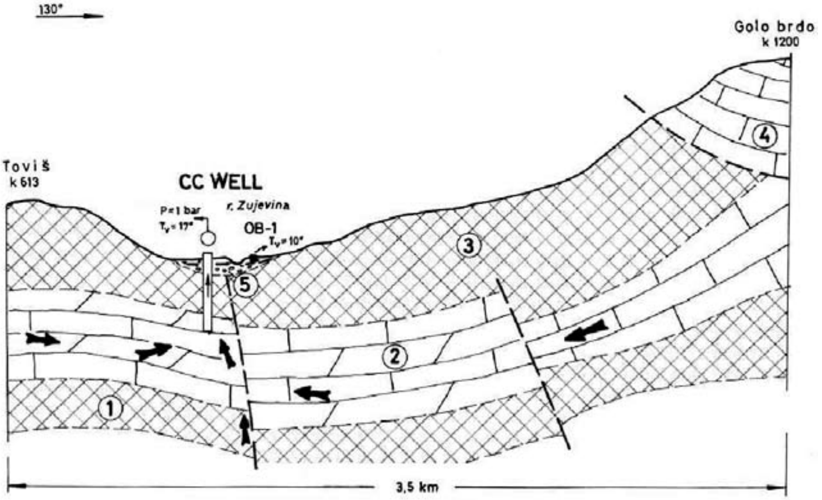

Figure 3. Hydrogeological cross-section of investigation area (Poorly permeable rocks of the fractured porosity – 1; Well permeable rocks of cavernous- fractured porosity – 2 and 4; Mostly watertight complexes – 3; Well permeable rock masses of intergranular porosity – 5)

Type and Site of Source Exploitation

The water exploitation structure is vertically drilled well - 198 m deep. The well is located in the Company Plant, between the building of “souvenir shop” and parking area (Figure 4), and the well is protected with safety fence from trespassing. The water from the well is transported with pipeline to the Plant facilities.

The following hydrogeological profile is determined along the well:

0.00 – 15.00 m
debris, gravel, sand (Q) - subsurface
aquifer

15.00 – 171.00 m
argillite, marls, marly limestone
and sandstones (K_2) - roof barrier

171.00 – 198.00 m
limestone (T_2^1) - karst aquifer

Well Construction:

- 0.00 – 48.0 m
  pipes ∅ 219.1 / 5 mm with thread
  - INOX AISI 316 L
- 48.0 – 51.16 m
  reduction ∅ 219.1 / 127 mm - INOX AISI 316 L
- 51.5 – 188.8 m
  pipes ∅ 127 / 5 mm with thread - INOX AISI 316 L
- 188.8 – 190.45 m
  packer INOX AISI 316 L with rubber gaskets
- 190.45 – 198 m
  open hole

Capacity, long term capacity, static and dynamic levels are determined through the test pumping. Pumping test was performed with the submerged pump with three capacities, i.e. three drawdowns, till the quasi-stationary conditions have been reached. The test lasted 168 hours, and the achieved results are given in the Table 1.

Figure 4. The Coca Cola Well (“CC Well”)

Table 1. The test lasted 168 hours, and the achieved results

Pumped quantity (l/s)	Static level (1 bar) (m)	Depression level (m)	Drawdown (m)	Specific Capacity (l/s/m)
$Q_1 = 24$	+10	8.47	$S_1 = 18.47$	$q_1 = 1.29$
$Q_2 = 33.1$	+10	15.50	$S_2 = 25.50$	$q_2 = 1.29$
$Q_3 = 41.3$	+10	22.58	$S_3 = 32.58$	$q_3 = 1.27$

Long-Term capacity of the well is determined on the bases of the calculation and results of the test pumping and it is: $Q_{ex.} = 32$ l/s, with drawdown S = 25.0 m.

Water Quality Characteristics

The water quality analyses are conducted in verified laboratories, and indicate that water is completely in accordance with the regulation of the World Health Organization, European Union and Bosnia and Herzegovina legislation and that the quality of water reflects stability during the hydrological cycle.The physico-chemical analyses indicate that the water from the source "Olimpia" is hydro carbonate-calcium-magnesia type, with mineralization of about 420 mg/l and temperature 16.5 °C. Water does not contain ammonia, nitrate, nitrite, heavy metals, dangerous gases and other inappropriate chemical elements.Microbiological analyses indicate complete absence of bacteria in water.Radiology analyses confirm that the water is useable as potable water. The content of tritium (3H) have the value of 1.2 TU what indicates that underground water did not have any connection with surface or atmosphere water in the last 50 years. Quality of underground water is confirmed by the decision of the authorized Ministry in Bosnia and Herzegovina, according which the underground water can be used for production:

- Bottled potable carbonated and non carbonated water,
- Nonalcoholic and beverage drinks,
- Drinking water enriched with minerals - mineral water,
- In food processing industry, and
- Other industrial requirements.

The Regime of Underground Water

Regime and quality of water of the source "Olimpija" is stabile during the whole hydrological cycle. Those positive characteristics are the result of the geological composition, structural placement and hydrogeological

Table 2. Data of the measured pressure at the top and self-discharge of the well during in the years 2002 and 2003

	2002 - 2003											
	XII	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
PRESSURE (bar)	0.85	0.95	0.85	0.80	1.0	0.9	0.95	0.85	0.80	0.85	1.0	1.0
CAPACITY (l/s) ***(P=0,7 bar)***	-	5.35	5.30	5.25	5.50	5.40	5.50	5.30	5.35	5.40	5.70	5.5

Table 3. Basic parameters of water quality of the well, determined by analyses in different hydrological periods

Hydr. period	pH	Temper	Mineralization	$KMnO_4$	NH_4	NO_2	NO_2	Cl	SO_4	Mn	Fe
		°C	mg/l								
24-12-02	7.3	16.3	430	2.1	0.00	0.70	0.00	5.0	5.8	0.001	0.018
27-03-03	7.4	16.5	420	2.0	0.02	3.7	<0.02	1.3	4.8	<0.002	0.005
02-04-03	7.2	16.3	397	2.4	0.00	0.80	0.00	0.7	1.0	0.00	0.02
08-07-03	7.2	16.5	399	3.12	0.00	3.54	0.00	1.4	1.0	0.00	0.01
03-11-03	7.0	16.5	420	3.55	0.00	0.88	0.00	1.0	1.0	0.00	0.02

characteristics of the source and its wider surrounding area.

Data of the measured pressure at the top and self-discharge of the well during in the years 2002 and 2003 are as follows in Table 2.

Measuring of water temperature along the whole profile of the well during "flow-metering" and video recording of the well, has confirm that the water temperature is constant (T = 16.5 °C).

Chemical composition of the water expresses stability in the different hydrological conditions during one-year period of observation. Mineralization of water is 400 to 430 mg/l. During the period of observation, the water keeps its hydro-carbonate – calcium – magnesia type with insignificant changes of the concentration of certain elements in the chemical composition.

Basic parameters of water quality of the well, determined by analyses in different hydrological periods are as follows in Table 3.

The Reserves of Underground Water

Reserves of the underground water in the source are calculated and verified by the authorized Ministry of Bosnia and Herzegovina (Decision N° 07-18-37/04 dated April 16, 2004).

Confirmed reserves of potable underground water of the source "Olipija" are as follows (according to Bosnia and Herzegovina legislation and classification):

Balanced (P*roved*) Reserves:

- Reserves of Category A
  Q = 5.25 l/s (165,564 m^3/god)
- Reserves of Category B
  Q = 18.75 l/s (591,300 m^3/god)
- Reserves of Category C_1
  Q = 8.00 l/s (252,288 m^3/god)

Potential and Evaluated (P*robable and Possible*) Reserves:

- Reserves of Category C_2
  Q = 9.20 l/s (293,284 m^3/god)
- Reserves of Category D_1
  Q = 15.00 l/s (437,040 m^3/god)
- Reserves of Category D_2
  Q = 12.00 l/s (378,432 m^3/god)

Protection of Aquifer

Limestone aquifer, which scopes underground water "Olimpija", has very favorable, natural protection aspects. Wider source area, (over 4 km^2), is composed of watertight rocks of Upper Cretaceous flysch. In the floor of those sediments, at the depth of 168 m is the aquifer of underground water, developed in the Middle Triassic carbonates. Since the limestone aquifer is a confined aquifer, the drilled well has self-discharge of 5.25 l/s and pressure at the top of the well is 0.8-1.0 bars.

Vertical range of rocks, where, in the wider area, there are thick watertight rocks above the aquifer, is extremely favorable from the aspect of the sanitary protection of the water "Olimpija".

Technical characteristics of the well, in which the full steel pipes and INOX casing are installed up to the depth of 168 m and cemented up to the surface of the terrain, prevent any influence of surface water or pollution. Besides to that, the underground water in limestone aquifer is under considerably high pressure, meaning, the possibility of mixing the underground and surface water, objectively does not exist.

Those hydro geological and hydraulic characteristics of the aquifer are ideal conditions for the abstraction and exploitation of underground water because the natural protection conditions are provided.

In the close vicinity of water source "Olimpija" pollution of underground water from the housing, industrial or infrastructure facilities does not exist. All surface and wastewater from this area are taken away and drained by river Zujevina, stream Rakovica and sewage collector Hadžići-Blažuj. As it wass mentioned, the watertight rocks of the Upper Cretaceous, over 150 m thick, developed in the area of approx. 4 km^2, in the way of sanitary protection of the water source, have the first class importance and practically, they designate disposition of the drainage of the surface and waste water.

Zone of the aquifer feeding, is in the mountain area of Igman and Bjelašnica with preserved biodiversity that should be, according to the development projects of Sarajevo Canton, developed into "Geo-park". Besides to that, wider area of Igman is already included into protected zone of the water source Vrelo Bosne what is of the great importance for protection of the water source "Olimpija" at the same time. Mountain terrains in the southwest of the water source are also not inhabited and they are not burdened with urbanization or any other industrial activities. In some places, the weekend houses with periodical way of use are built. Favorable circumstance is constructed sewerage collector Hadžići-Blažuj that takes wastewater and surface influents from the region Binježevo, and the possibility of pollution of underground water even in the case of incident situation do not exist.

Another contribution to the favorable conditions of protection of the water source is the fact that water from the limestone aquifer is microbiologically sterile, without presence of coliform, live and other bacteria, sewage or organic origin. Also, chemical composition of the underground water is completely in accordance with the "Regulation for Potable water", without presence of heavy metal cyanide, greases and oils or other loads that are made by natural or anthropogenic influence. Low level of *tritium* indicates that underground water did not have any contact with surface water or precipitation in the last 50 years.

CONCLUSION

The aquifer is composed of middle triassic limestone formations, developed at the base of impermeable Upper Cretaceous Flysch deposit substratum 170 meters deep.

The well (CC Well)) was drilled to a depth of 198 m, where a confined aquifer under artesian pressure (0,8 bar) and a flow of 5.25 L was encontered.

Long-Term capacity of the well is determined on the bases of the calculation and results of the test pumping and it is$Q_{ex.}$ = 32 l/s, with drawdown S = 25.0 m.

Groundwater is of excellent quality, as deduced on the basis of physical, chemical and microbiological determinations.

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Graph topology and Types of residual equations for geometric leveling

Teorija grafov in tipi enačb popravkov v geometričnem nivelmanu

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Abstract: In the article graph topology and types of residual equation for geometric leveling are shown. Graph topology tells what is graph and how is formed. The edges in the graph tell us how bench marks are connected between each other and how many edges there is. In third chapter formulas for adjustment by parameter variation for geometric leveling are shown. It is shown, how directly from graphof leveling network incidence matrix **A** can be formed and what it represents. Like for the matrix **A** it is presented how to form matrix of normal equation **N** directly from the graph too. By the condition, that for all measures the mean error is equal to $m_1 = m_2 = \quad = m_l$.

Izvleček: V članku je na kratko opisana topologija grafa in tipi enačb popravkov za geometrični nivelman. Topologija grafa nam govori o tem, kaj je graf in kako je sestavljen. Povezave v grafu nam povedo, kako so reperji med seboj povezani in koliko je teh povezav. V tretjem poglavju so prikazane enačbe za posredno izravnavo geometričnega nivelmana. Prikazano je kako se direktno iz grafa nivelmanske mreže zapiše incidenčna matrika **A** in kaj nam ta matrika predstavlja. Prav tako je prikazan tudi postopek direktnega zapisa matrike normalnih enačb **N** direktno iz grafa pod pogojem, da so vsi pogreški meritev enaki $m_1 = m_2 = \quad = m_l$.

Key words: topology, adjustment, leveling, observation equation, incidence matrix ,loop, bench mark (point)

Ključne besede: topologija, izravnava, nivelman, enačbe popravkov, incidenčna matrika, zanka, reper

GRAPH TOPOLOGY

Figure 1. shows the marked points A, B, C and D. In our case all four points are connected by edges (edge is oriented link). We will use the expression edge for these connections, to simplify our communications. At the same time we would like to stress that we are not interested in the form of edges (straight or curved). For us it is important only whether the two given bench marks are connected or not. When they are connected more than ones we speak about multiple connections. Some of the connections on the Figure 1. are marked with an arrow. We speak about oriented edges.

Scientific paper

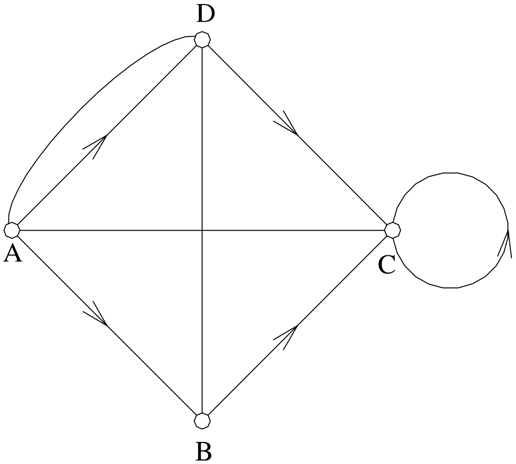

Figure 1. Marked points A, B, C and D
Slika 1. Označene točke A, B, C in D

Others are the so called un oriented edges. At the leveling network we will deal only with oriented edges. The bench mark can be connected by a close line (loop), as shown on the figure. It is the so called loop. Such loop in leveling network has no influence on adjustment, even when the loop consists of more bench marks. All the edges between two nodes, which they connect, can be presented by only one edge or loop.

Now we search only for the name of the whole picture. We will call it graph. We have to point out that edges AC and BC intersects each other. The intersect point is the fictive point, which in fact is not a point of the graph, but appears only because of drawing the graph (as a graph – drawing effect).

Connections in graph

Let u be number of points in the graph and n number of edges. We will try to find out their relation. Let us mention that these two numbers are independent. If we know u it does not mean that n is known too. Two cases are imposed to us by themselves. First graph without edge $n=0$ (called nullgraph). The second one represents so called ”full graph” in which each bench mark is linked to each other. In that case we are interested in number of edges of the fullgraph. Each of the u bench marks can be connected to $(u-1)$ number of bench marks. Together it represents u $(u-1)$ edges. At the same time we counted

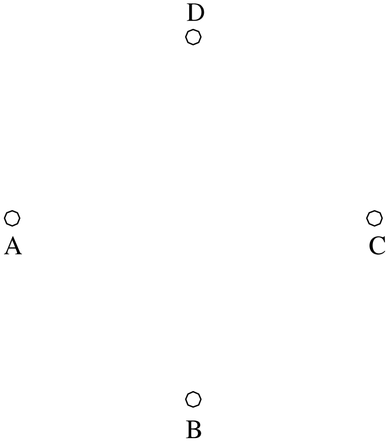

Figure 2. Nullgraph
Slika 2. Nični graf

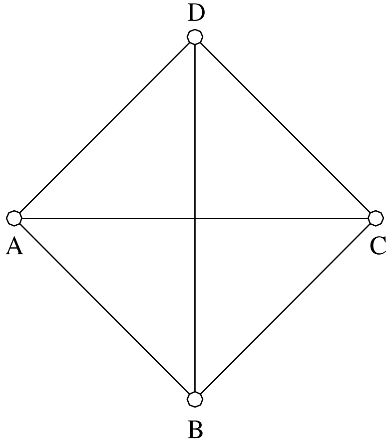

Figure 3. Fullgraph
Slika 3. Polni graf

each edge twice (forward and backward). That´s why the number must be devided by two.

At the end the maximal number of edges in a fullgraph is $n = \frac{1}{2} \cdot u(u-1)$

The nullgraph, where the number of edges is n=0 and a fullgraph, wherethe number of edges is $n = \frac{1}{2} \cdot 4(4-1) = 6$ are shown in Figure 2 and 3.

Formulas for adjustment by parameter variation

The best results adjustment by parameter variation are given by the method of least squares (MLS), based on equation (1). This method gives most probable values of unknowns, close to real values. The sum of all residuals, multiplied with correspondent weight, are minimised as shown in equation(1):

$$\Phi = v^T P v = \min \qquad (1)$$

$$\phi = \begin{bmatrix} v_1 & v_2 & \cdots & v_n \end{bmatrix} \begin{bmatrix} 1/m_1^2 & 0 & \cdots & 0 \\ 0 & 1/m_2^2 & \cdots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & \cdots & 1/m_n^2 \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \\ \vdots \\ v_n \end{bmatrix} = \min \qquad (2)$$

The residuals are:

$$\underset{n;1}{v} = \underset{n;u}{A} \cdot \underset{u;1}{x} + \underset{n;1}{1} \qquad (3)$$

and

$$v^T = (x^T A^T + I^T) \qquad (4)$$

Where values present:

v vector of residuals,
A incidence matrix,
x vector of unknown parameters,
l vector of absolutes terms.

Matrix **A** is an incidence matrix for the graph, which is in leveling equal to design matrix, showing geometry of leveling network, with elements (-1, +1 in 0).

Where:
—1 means, that the edge leaves the node (beginning of the edge),
1 means, that edge enters the node (end of the edge),
0 means, that node does not take part in the edge.

Graph consists of nodes and edges. There is u nodes - unknowns (points for which we would like to find the heigh X_i). The edge between nodes I and J, when we measure the heigh diferences is $X_i—X_j$. In the network

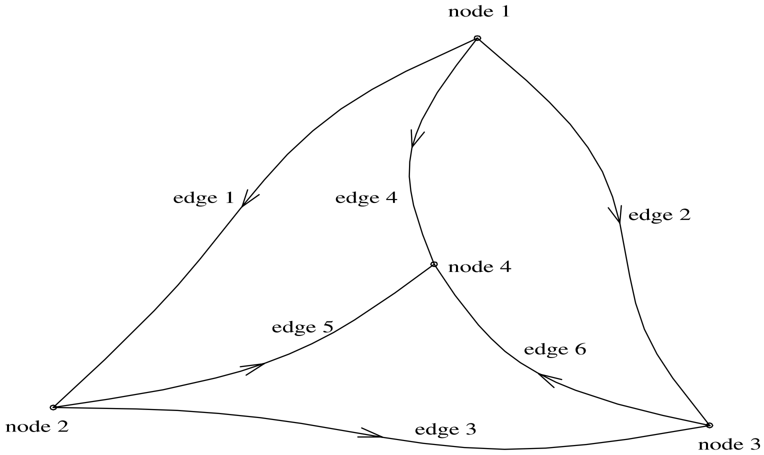

Figure 4. Graph with $n=6$ edges and $u=4$ nodes
Slika 4. Graf z $n=6$ povezav in $u=4$ vozlišči

graph all the measured edges betwen nodes I and J are substituted by a single equivalent edge IJ. Figure 3 shows the graph with $n=6$ edges and $u=4$ nodes.

FORMING A FROM THE LEVELING NETWORK GRAPH

From the Figure 3 could be written the incidence matrix **A** for the graph. It has the row for each edge and coulmn for each node. In our case the matrix is of the dimension 6x4, what means, that it has 6 rows and 4 columns. That matrix shows which nodes are connected to which edges. Input values -1 and +1 in the first row of the matrix show the data of the first edge. Row values are values of the edges while column values present values for nodes. Each row has two elements, which are equal to +1 and -1 all the other are equal to 0. For example, the edge 1 goes from the node 1 to the node 2, therefore $a_{11}=-1$ and $a_{12}=1$. On that basis we can write down incidence matrix **A** directly from the graph. Figure 4 shows incidence matrix **A** of the network graph on Figure 3.

$$A=\begin{bmatrix} -1 & 1 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ 0 & -1 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & 0 & 1 \\ 0 & 0 & -1 & 1 \end{bmatrix}$$

Figure 4: Incidence matrix **A**
Slika 4: Incidenčna matrika **A**

This occurs as incidence matrix in case when all points (bench marks) are free, what means that no haigh is known. When the height of any point is known, then we have to cancel a coulmn from the matrix. The matrix includes all information of the graph and is therefore called "fullgraph", in which no edge is missing (the fullgraph consists of $n=\frac{1}{2}\cdot u(u-1)$ edges). If we delete an edge from the graph we have to delete a row from the matrix at the same time.

Adjustment depend on the sort and form of the geodetic network, they may difere when already are in the linear format shape size or not. When functions are not linear we have to linearise them by Taylor´s series. In geometric leveling is these functions are linear:

The observation equation are:

$$\hat{L}_i = L_i + v_i = X_S - X_Z \qquad (5)$$

Where values present:

$\hat{L}_i$	adjusted measure size,
X_S	denoting end point of adjusted height of the measurement line L_i,
X_Z	denoting starting point of adjusted height,
v_I	- residual of L_i.

Equations, correspondent to the graph on Figure 3:

$$v_1 + L_1 = X_2 - X_1 = -X_1 + X_2 \qquad (6)$$

$$v_2 + L_2 = X_3 - X_1 = -X_1 \ldots\ldots\ldots + X_3$$

$$v_3 + L_3 = X_3 - X_2 = \ldots\ldots\ldots - X_2 + X_3$$

$$v_4 + L_4 = X_4 - X_1 = -X_1 \ldots\ldots\ldots\ldots\ldots\ldots + X_4$$

$$v_5 + L_5 = X_4 - X_2 = \ldots\ldots\ldots - X_2 \ldots\ldots\ldots + X_4$$

$$v_6 + L_6 = X_4 - X_3 = \ldots\ldots\ldots\ldots\ldots\ldots - X_3 + X_4$$

We have to introduce approximate height values:

$$X_S = X_S^0 + x_S \qquad (7)$$

$$X_Z = X_Z^0 + x_Z \qquad (8)$$

The equation (5) reads:

$$v_i + L_i = X_S^0 - X_Z^0 + (x_S - x_Z) \qquad (9)$$

and the residuals are:

$$v_i = x_S - x_Z - L_i + X_S^0 - X_Z^0 \qquad (10)$$

$$v_i = x_S - x_Z - l_i \qquad (11)$$

$$v_i = 1 \cdot x_S - 1 \cdot x_Z + \underbrace{(X_S^0 - X_Z^0 - L_i)}_{l_i} \qquad (12)$$

It causes, that the vector of free article is equal to:

$$l_i = X_{Si}^0 + X_{Zi}^0 - L_i \qquad (13)$$

respectively:

$$l_i = AX^0 - L_i \qquad (14)$$

Observation equations, which correspond to the graph on Figure 3 are:

$$v_1 = 1 \cdot x_2 - 1 \cdot x_1 + \underbrace{(X_2^0 - X_1^0 - L_1)}_{l_1}$$

$$v_2 = 1 \cdot x_3 - 1 \cdot x_1 + \underbrace{(X_3^0 - X_1^0 - L_2)}_{l_2}$$

$$v_3 = 1 \cdot x_3 - 1 \cdot x_2 + \underbrace{(X_3^0 - X_2^0 - L_3)}_{l_3}$$

$$v_4 = 1 \cdot x_4 - 1 \cdot x_1 + \underbrace{(X_4^0 - X_1^0 - L_4)}_{l_4}$$

$$v_5 = 1 \cdot x_4 - 1 \cdot x_2 + \underbrace{(X_4^0 - X_2^0 - L_5)}_{l_5}$$

$$v_6 = 1 \cdot x_4 - 1 \cdot x_3 + \underbrace{(X_4^0 - X_3^0 - L_6)}_{l_6} \qquad 15)$$

We can present the equation (16) in two different ways:
Dimension of the matrix $\underset{n;u}{matrix} = \underset{rows\times columns}{matrix}$.

$$\underset{n;1}{v} = \underset{n;u}{A}\cdot \underset{u;1}{x} + \underset{n;1}{l} \qquad (16)$$

$$\begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \\ v_6 \end{bmatrix} = \begin{bmatrix} -1 & 1 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ 0 & -1 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & 0 & 1 \\ 0 & 0 & -1 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} + \begin{bmatrix} l_1 \\ l_2 \\ l_3 \\ l_4 \\ l_5 \\ l_6 \end{bmatrix} \qquad (17)$$

and

$$\underset{n;1}{v} = \underset{n;u}{A}\cdot \underset{u;1}{x} + \underset{n;u}{A}\cdot \underset{u;1}{X^0} - \underset{n;1}{L} \qquad (18)$$

$$\begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \\ v_6 \end{bmatrix} = \begin{bmatrix} -1 & 1 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ 0 & -1 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & 0 & 1 \\ 0 & 0 & -1 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} + \begin{bmatrix} -1 & 1 & 0 & 0 \\ -1 & 0 & 1 & 0 \\ 0 & -1 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & 0 & 1 \\ 0 & 0 & -1 & 1 \end{bmatrix} \begin{bmatrix} X_1^0 \\ X_2^0 \\ X_3^0 \\ X_4^0 \end{bmatrix} - \begin{bmatrix} L_1 \\ L_2 \\ L_3 \\ L_4 \\ L_5 \\ L_6 \end{bmatrix} \qquad (19)$$

As known height can not be determined only from height differences. One or more of the heights X_i must be known. (Then the corresponding known X_i should be deleted from **A** it´s colum i).

Therefore we have to exclude each known height from the list of unknown heights. What means, that in incidential matrix **A** have to exclude each known height. As already mentioned the column in matrix represents a point (bench mark). Let`s presume that in the previous graph the first point is known. It means that it`s height is determined. Therefore we have to delete the first column from the matrix **A** at gives us a new shape.

$$A = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 1 \\ 0 & -1 & 1 \end{bmatrix} \qquad (20)$$

Since matrix **A** is changed, the whole observation equation in matrix – matric form changes into following form:

$$\begin{bmatrix} v_1 \\ v_2 \\ v_3 \\ v_4 \\ v_5 \\ v_6 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 1 \\ 0 & -1 & 1 \end{bmatrix} \begin{bmatrix} x_2 \\ x_3 \\ x_4 \end{bmatrix} + \begin{bmatrix} l_1 \\ l_2 \\ l_3 \\ l_4 \\ l_5 \\ l_6 \end{bmatrix} \tag{21}$$

As matrix **A** is alreday fixed we have to form a weighting matrix $\underset{n;n}{P}$. Elements for that matrix are given with following equations. This matrix is diagonal and includes the following articles.

$\underset{n;n}{Q_{ll}}$ cofactor matrix of measured values, which in our case are $\underset{n;n}{P} = \underset{n;n}{Q_l^{-1}}$ (22)

$p_i = \dfrac{1}{m_l^2}$ when mean square errors are given, (23)

$p_i = \dfrac{1}{d_i}$ at equable ground (differences between separate standing rooms are constant),respectively: (24)

$p_i = \dfrac{1}{n_i}$ at no equable ground (differences between separate standing rooms are not constant). (25)

Where:

p_i	measure weight,
m_l	mean square error,
d_i	difference between two measured points (bench marks),
n_i	number of standing rooms between two measured points (bench marks).

$$P = \begin{bmatrix} 1/m_l^2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/m_l^2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/m_l^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/m_l^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/m_l^2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/m_l^2 \end{bmatrix} \tag{26}$$

When all elements, that correspond to (MLS) are available, we can transfer normal equation from the
equation (1) ($\Phi = v^T Pv = \min$).

We insert equations (3), (17), and (22) into equation (1) and get the following expression.

$$\Phi = (x^T A^T + I^T)P(Ax + I) = x^T A^T PAx + I^T PAx + x^T A^T PI + I^T PI \tag{27}$$

We differentiate that expression and make it null. We get extreme point for the function. In our case we need the minimum point.

$$0 = d\Phi) = dx^T A^T PAx + x^T A^T PAdx + dx^T A^T PI + I^T PAdx \tag{28}$$

$$0 = d\Phi) = 2dx^T A^T PAx + 2dx^T A^T PI \tag{29}$$

$$0 = dx^T \underbrace{(A^T PAx + A^T PI)}_{A^T PAx + A^T PI = 0} \tag{30}$$

Settling the previous expression we get normal equations.

$$A^T PAx + A^T P \quad = 0 \tag{31}$$

$$\underset{u;u}{N} = \underset{u;n}{A^T} \; \underset{n;n}{P} \; \underset{n;u}{A} = \underset{u;n}{A^T} \; \underset{n;n}{Q_l^{-1}} \; \underset{n;u}{A} \tag{32}$$

$$\underset{u;1}{n} = \underset{u;n}{A^T} \; \underset{n;n}{P} \; \underset{n;1}{I} = \underset{u;n}{A^T} \; \underset{n;n}{Q_l^{-1}} \; \underset{n;1}{I} \tag{33}$$

Where:

N matrix of normal equations
n vector of free elements for normal equations

Record $N = A^T PA = A^T Q_{ll}^{-1} A$ in matrix form:

$$N = \begin{bmatrix} 1 & 0 & -1 & 0 & -1 & 0 \\ 0 & 1 & 1 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} 1/m_l^2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/m_l^2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/m_l^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/m_l^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/m_l^2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/m_l^2 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 1 \\ 0 & -1 & 1 \end{bmatrix} \tag{34}$$

FORMING **N** FROM THE LEVELLING NETWORK GRAPH

Matrix for normal equation **N** we can also put down directly from the graph, under the condition, that for all measures the mean error is equal to $m_1 = m_2 = \quad = m_l$! Along the diagonal of the matrix we put down how many edgess has each node (in our case the node 1 has three edges, that`s why we will put number 3 as the first element of the diagonal). Since we know **N** is a simetric matrix, we will put it`s elements (articles) above the diagonal. With element (article) -1 we describe, that two separate bench marks are connected between (direction of the arrows is not important), with 0 we point out that there is no edge between them.

Further is presented the matrix **N** , put down directly from the graph on the Figure 5. In our case the height of the first node is a priori defined, therefore for the further calculation we have to eliminate shaded part, representing that node. Number from 1 to 4 (in the row and column) represent names of nodes in graph.

Matrix $\underset{n;n}{N}$ is positively defined $\det(N) > 0$.

Matrix N is simetrical:

$N =$

	1	2	3	4
1	3	-1	-1	-1
2		3	-1	-1
3			3	-1
4				3

Direct record of the simetric matrix N for the graph on the Figure 5.

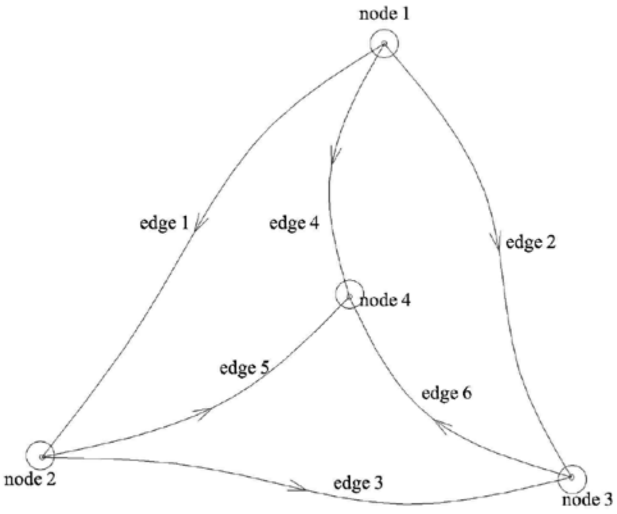

Figure 5. Direct record of the simetric matrix N

Slika 5. Direktni zapis simetrične matrike N

Record $n = A^T PI_{ll} = A^T Q_{ll}^{-1} I$ in matrix form:

$$n = \begin{bmatrix} 1 & 0 & -1 & 0 & -1 & 0 \\ 0 & 1 & 1 & 0 & 0 & -1 \\ 0 & 0 & 01 & 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} 1/m_l^2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/m_l^2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/m_l^2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/m_l^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/m_l^2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/m_l^2 \end{bmatrix} \begin{bmatrix} f_1 \\ f_2 \\ f_3 \\ f_4 \\ f_5 \\ f_6 \end{bmatrix} \tag{35}$$

in shortened form:

$$Nx + n = 0 \tag{36}$$

$$Nx = -n \tag{37}$$

$$N^{-1}Nx = -N^{-1}n \tag{38}$$

$$x = -N^{-1}n \tag{39}$$

$$O_{xx} = N^{-1} \tag{40}$$

Respectively:

$$x = -Q_{xx}n \tag{41}$$

Equations for calculating estimated accuracy a posteriori:

$$m_0 = \sqrt{\frac{v^T Pv}{n-u}} \tag{42}$$

m_0 mediate error of weight unit

$n-u$ number of supernumerary measurement (43)

$$m_{\dot{x}} = m_0 \sqrt{q_{xxu}} \tag{44}$$

m_{xi} mean error of unknown sizes

$$m_{l'i} = m_0 \sqrt{q_{l'l'i}} \tag{45}$$

$m_{l'i}$ mean error of adjusted sizes

$$m_{vi} = m_0 \sqrt{q_{vvi}} = m_0 \sqrt{q_{lli} - q_{l'l'i}} \tag{46}$$

m_{vi} mean error of residuals.

CONCLUSION

In the article graph topology and types of residual equation for geometric leveling are shown. Graph topology tells what is graph and how is formed. The edges in the graph tell us how bench marks are connected beetwen each other and how many edges there is. It is also shown that we can reduce the leveling network only to the nodes, because » so called » loops (links that start and finish at the same point) dont have any influence to the adjustment.

In third chapter formulas for adjustment by parameter variation for geometric leveling are shown. It is shown, how directly from graph of leveling network incidence matrix A can be formed and what is represents. Matrix A is the incidence matrix for the graph and represent the same as design matrix in leveling. Design matrix represents geometry of the leveling network. Despite that we can estimate the design of the network also with the number of the edges that are realised between nodes from the full graph. Like for the matrix A it is represented how to form matrix of normal equation N directly from the graph. By the condition, that for all measures the mean error is equal to $m_1=m_2=\ldots=m_l$.

Zaključek

Teorija grafov in tipi enačb popravkov v geometričnem nivelmanu

V članku je na kratko opisana topologija grafa in tipi enačb popravkov za geometrični nivelman. Topologija grafa nam govori o tem, kaj je graf in kako je sestavljen. Povezave v grafu nam povedo, kako so reperji med seboj povezani in koliko jih je. Razvidno je tudi, da lahko nivelmanske mreže zreduciramo samo na vozlišča, saj tako imenovane zanke (povezave ki se začnejo in končajo v isti točki) na izravnavo nimajo vpliva.

V tretjem poglavju so prikazane enačbe za posredno izravnavo geometričnega nivelmana. Prikazano je kako se direktno iz grafa nivelmanske mreže zapiše incidenčna matrika **A** in kaj nam ta matrika predstavlja. Matrika **A** je incidenčna matrika za graf, ki je v nivelmanu isto kot design matrika. Design matrika nam podaja geometrijo nivelmanske mreže. Design mreže lahko ocenjujemo tudi s tem, koliko povezav je realiziranih med vozlišči od polnega grafa. Prav tako je prikazan tudi postopek direktnega zapisa matrike normalnih enačb **N** direktno iz grafa pod pogojem, da so vsi pogreški meritev enaki $m_1=m_2=\ldots=m_l$.

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Uvod

Najpomembnejša bosenska srednjeveška prestolnica Bobovac[1] se nahaja v bližini bosenskega mesta Vareš. Čeprav je bila obravnavana v številnih znanstvenih delih jo še vedno premalo poznamo. Odgovori na nekatera (doslej sicer sploh nezastavljena) vprašanja bi nam lahko razkrili številne skrivnosti Bobovca in njegove širše okolice. Med pomembnejše sodi tudi vprašanje o poreklu imena Bobovac. Del odgovora nanj vsekakor predstavlja dejstvo, da je ime Bobovac prisotno v deželah v katerih živijo Slovani. To je vedel tudi hrvaški filolog Petar Skok (1881 -1956). Toponim Bobovac je namreč označil, kot izpeljanko od baltoslovanskega imena kulturne rastline iz družine metuljnic, bőb (lat. *Vicia faba*): toponim Bobovište pa je razlagal kot: *»mjesto bobom zasađeno«.*[2] Čeprav se zdijo zelo prepričljive, s tukaj predstavljenimi Skokovimi trditvami se ne morem povsem strinjati. Menim namreč, da je za nastanek imena Bobovac od bőbovih zrn veliko pomembnejša vrsta kamna iz katere je človek dobil kovino železo, limonit. Ta vrsta kamna, katere odkritje je pomenilo velik korak na poti v tako imenovano »železno dobo«, se že nekaj stoletij zaradi zrn podobnih bobovim na slovenskem jeziku označuje tudi kot *bôbovec* (nem. das Bohnenerz).[3]

Bobovec – rjavi železovec

V slovarju slovenskega knjižnega jezika je *bôbovec* predstavljen kot: *»rjavi železovec, ki nastaja v obliki oblih zrn v glini«.*[4] Označba *bôbovec* seveda ni povsem slučajno povezana z železom (dragoceno kovino, ki jo je že antični grški pesnik Homer primerjal z zlatom).[5] Da bi lahko bila prav ta označba povezana z imenom najpomembnejše bosenske srednjeveške prestolnice, je omenil tudi hrvaški arheolog Ivo Bojanovski (1915 - 1993).[6] Ali bi z njo lahko povezali tudi nekatere na današnjem slovenskem ozemlju obstoječe toponime, denimo, naselje Bobovk oziroma Bobovek, ki se nahaja v neposredni bližini mesta Kranj? V 50. letih 20. stoletja so namreč raziskovalci v omenjenem naselju odkrili poznoantične (rimske) grobove z bogatimi prilogami železnega orodja in orožja.

Toponimi z imenom Bobovec se nahajajo tudi na današnjem češkem in slovaškem ozemlju: v bližini češkega mesta Jindřichův Hradec in pomembnih rudnikov železa se nahaja starodavna vas Bobovec[8], v bližini slovaškega mesta Stará Bystrica pa se nahaja vrh Bobovec[9] ispod katerega se že nekaj stoletij pridobiva ruda železo.

Scientific paper

Omenjenim toponimom identični oziroma sorodni in (kar je najpomembneje) z železovo rudo nedvomno tesno povezani toponimi (Bobovac, Bobovec, Bobovište, Bobovišta in Bobovišća) se nahajajo tudi na današnjem hrvaškem ozemlju.[10]

SKLEP

Menim, da je tudi bosenska srednjeveška prestolnica Bobovac svoje ime (lahko) dobila po železovi rudi, oziroma po zrnih bôbovca: menim, da bi o tem lahko pričal tudi toponim Bobovišća[11], ki se nahaja v njeni neposredni bližini. Koliko je prestolnica Bobovac dejansko povezana z železovo rudo se zelo lepo vidi tudi v stavkih, ki jih je zapisal bosenski arheolog Pavao Anđelić[12] ter v dejstvu, da je bila v 20. stoletju okolica Bobovca med največjimi rudniki limonita v Titovi Jugoslaviji.[13]

Na tem mestu ne želim razpravljati o vprašanjih kdaj je bilo in zakaj je bilo v Bosni pozabljeno (slovansko oziroma slovensko) ime pomembne železove rude, ki se »skriva« tudi v prestolnici Bobovac: omenil bom samo (številne) raziskovalce, ki brez kakršnihkoli dokazov razvoj rudarstva v bosenski srednjeveški državi povezujejo s 14. i 15. stoletjem.[14] Bobovac ter imena bosenskih mest (Kupres, Olovo, Srebrenica) in vasi bi morali začeti uporabljati tudi kot prepričljive dokaze, da je od začetka tako imenovane »železne dobe« do danes, rudarstvo na današnjem bosenskohercegovskem ozemlju imelo neprekinjeno tradicijo.

REFERENCE, VIRI IN POJASNILA

[1] ANĐELIĆ, P., (1973): cit. n. 1, pp. 46,102 -105; Leta 1356 je v listini bosenskega bana in kralja Tvrtka I. (1353 - 1391) zapisano najstarejše doslej znano ime prestolnice: *Boboch.* V poznejših pisnih virih je (še preden je bila v drugi polovici 15. in v 16. stoletju povsem porušena in spremenjena v ruševine) označena tudi kot: *Baboch, Babouch, Babowch, Babunz, Bobofci, Bobouac, Bobouaz, Bobovac, Bobovaz, Bobovci, Bohovic in Dobobiku.* Od konca 19. stoletja do leta 1973 so ji bili posvečeni prvi znanstveni teksti. O tem glej: G. Stratimirović, Burg Bobovac Wissenschaftliche Mittheilungen aus Bosnien und der Hercegovina Dunaj 1894 pp. 323 - 327 (članek je bil objavljen že leta 1891 v sarajevskem Glasniku zemaljskog muzeja); Ć. Truhelka, Naši gradovi Sarajevo 1904 pp. 90 - 92; I. Bojanovski, Stari grad Bobovac i njegova konzervacija Naše starine 8. Sarajevo 1962 pp. 71 - 96; I. Bojanovski, Nastavak konzervatorskih radova na gradu Bobovcu Naše starine 9. Sarajevo 1964 pp. 167 - 174; A. Ninković, Konzervatorski radovi na Bobovcu Naše starine 12. Sarajevo 1969 pp. 55 - 60. Od leta 1959 do leta 1967 je bila sistematično raziskana: plod teh raziskav je bila monografska študija, ki jo je leta 1973 v Sarajevu objavil bosenski arheolog Pavao Anđelić (1920 - 1985). O tem glej: P. Anđelić, Bobovac i Kraljeva Sutjeska. Stolna mjesta bosanskih vladara u 14. i 15. stoljeću Sarajevo 1973. Kontinuiteto naseljenosti od antike do srednjeg veka ni omenil, čeprav je v študiji zelo lepo predstavil antične in srednjeveške temelje na katerih stoji prestolnica: o tem med drugim priča tudi njegova kronologija gradnje oziroma vloga, ki jo je pri gradnji imel bosenski ban Stipan II. Kotromanić (1300? - 1353).

[2] SKOK, P., (1971): Etimologijski riječnik hrvatskoga ili srpskoga jezika Zagreb 1971 pp. 176, 177 *»baltoslav. naziv za kulturnu biljku koja od drugih ie. jezika dolazi samo u lat. faba i u romanskim refleksima odatle (tal. fava, fr. feve).*

*U baltičkoj grupi potvrđena je samo u stprus. babo u femininumu kao i u latinskom. Prema tome je slavenska inovacija promjena roda od feminina u maskulimum. Ta promjena mogla je nastati zbog toga što se *boba osjećalo kao hipokoristik...Bóba f (Vuk) sa hipokorističkim akcentom upotrebljava se u metaforičkom značenju »malo što okruglo«...Imenica boba ima brojnu leksikološku familiju...Izvedenice od bob upotrebljavaju se više u pravorn nego u prenesenom značenju«.*

[3] Strmole D., (1987): Bobovec, Enciklopedija Slovenije 1. Ljubljana, pp. 293; http://www2.pms-lj.si/oddelki/mineralogija/bobovec.html. *»Bobovec je popularna oznaka za poseben tip limonitne železove Rude, ki so jo v preteklosti pridobivali na različnih mestih v Sloveniji. Posebno znana najdišča so v predgorju Julijskih Alp, znano fužinarsko mesto, kjer so talili železovo rudo, pa so na primer Železniki. Pogosto so bobovci bolj ali manj zaobljeni. Lahko so zelo majhni in imajo v premeru le nekaj milimetrov ali pa dosežejo decimetrske dimenzije in imajo maso kilogram in več. Običajno so temno rjavi, povsem neprozorni in so brez izrazite razkolnosti. V vrtačah in breznih se bobovci nakopičijo kot netopen preostanek zakrasevanja. Največkrat gre za preostanek Pirita* FeS_2 *in redkeje markazita* FeS_2*, ki se pojavljata kot akcesorna minerala v številnih karbonentnih kamninah v Sloveniji. Pri procesih oksidacije na površini kamnine sulfid preide v lahko topen sulfat, ki ga voda zlahka odnaša. Pri tem pirit in markazit prehajata v sekundarne železove minerale, kot sta goethit in lepidokrokit. Kristali pirita ali markazita z značilnim kovinskim sijajem ter kovinsko rumeno barvo spremenijo v večinoma rjavkasto maso različnih sekundarnih železovih mineralov, ki jo imenujemo limonit. Na prvotne kristale pirita lahko spominjajo le še posamezne kristalne ploskve kocke ali pentagonskega dodekaedra. Zelo redko se ohranijo popolni priimerki limonitiziranih kopuč kristalov pirita. To so psevdomorfoze limonita po piritu. Še pred dvesto leti je bilo pridobivanje železa iz bobovca zelo pomembna dejavnost. Z njo se je ukvarjal tudi baron Žiga Zois, ki je bil fužinar, naravoslovec, mineralog in zbiratelj. Med drugimi je zbral tudi nekaj izjemnih primerkov bobovcev in jih uvrstil v svojo zbirko mineralov, kamnin in rud«.....*

[4] Klopčič, M., Tomšič, F., Veselko, M., (1970): Slovar slovenskega knjižnega jezika I. Ljubljana pp. 157

[5] Razinger, B., (1995:) Tri rude z Gorenjskega Jeseniški zbornik 7. Jesenice, pp. 255 - 271

[6] Bojanovski, I., (1984): Razdoblje rimske uprave (Zbornik: »Visoko i okolina kroz historiju prethistorija, antika i srednji vijek 1.«) Visoko p. 67 *»Čini se da je i samo ime Bobovac vezano za rudarstvo (rudu), jer se bobovcem u slovenskom jeziku naziva jedna vrsta željezne rude«.*

[7] Valič, A., (1956/1958): Nove najdbe iz rimske dobe v okolici Kranja Arheološki vestnik 7/4 Ljubljana, pp. 444 - 458; P. Petru, Okvirna, časovna in tipološka klasifikacija gradiva iz južne nekropole v Bobovku pri Kranju Arheološki vestnik 9 - 10/1 Ljubljana 1957/ 1958 pp. 13 - 26; P. Petru - A. Valič, Drugo začasno poročilo o izkopavanjih v Bobovku pri Kranju Arheološki vestnik 9 - 10/2 Ljubljana 1957/1958 pp. 133 - 172

[8] Nekuda, V., (1975): Pfaffenschlag: zanikla středověka ves u Slavonic Brno; Vas Bobovec je omenjena že v enajstem stoletju: v petnajstem stoletju (v »husitskih« vojnah) je bila skorajda popolnoma uničena. O tern glej tudi: http://www.rudolec.cz/kanad-cz.html#hist

[9] htpp://www.starabystrica.sk/modules.php?name=News&file=article&sid=21038 *»Stará Bystrica sa čoraz väčšmi dostavala do pozornosti feudálov v osemnástom storočí. V roku 1767 bola v Starej Bystrici doložená jediná železiareň v Trenčianskej župe. Železná ruda sa t'ažila pod vrchom Bobovec«.*

[10] Skok, P., (1971): cit. n. 2, pp. 176, 177; G. Novak, Bobovišća (Bobovišće) Enciklopedija Jugoslavije 1 Zagreb 1955 p. 628 *»selo na zapadt2om dijelu otoka Brača. U okolici Bobovišča otkriveno je (1899) na lokalitetima Krug i Rat prethistorijsko naselje ranoga željeznog doba. U Vičjoj Luei postojalo je drugo naselje, iz kojega potječtc metalni nalazi (koljenice, šljemovi) grčke prove nijencije. U Luci Bobovišća otkriveni su (1850) ostaci rimskog groblja«.*

[11] Bojanovski, I., (1962): cit. n. 1, pp. 84, 85 *»Kalić je Desnik smjestio »blizu današnjeg sela Teševo« iznad Kr. Sutjeske. Šišić je mislio da Desnik treba tražiti »na desnoj obali gornje*

Bosne...naime oko gradova Bobovca, Sutiske i Trstionice...«. Čini nam se da je Šišićevo mišljenje najbliže istini, samo bismo ga modificirali utoliko što bi Desnik...identifieirali baš sa naširn Bobovcem... U blizini grada u Mijakovićima, u zaseoku Kolakovići, postoji i njiva Bobovišća.-Toponomastička izvedenica Bobovac, sa složenim sufiksom -ov-ac, vjerojatno je metaforički naziv, izveden od apelativa bob (Vicia faba maior). Ali bi se ovaj toponim mogao dovesti u vezu i sa muškim apelativom bòbân, bobana, u značenju kamen, saxum (vidi Akad. rječnik s.v.) što bi sa stvarnog stajališta odgovaralo, jer grad leži na visokoj stijeni! Moguće je da je naziv stijene (oronim) kasnije prešao i na sam grad! U tom bi se slučaju formant -an pred vrlo proširenim sufiksom -ovac izgubio, a do tog je moglo doči ili zbog kračeg izgovora ili, što je vjerojatnije, jer se zaboravilo na primitivno značenje riječi boban koja se u jezičnoj svijesti izjednačila sa apel. bob«. Citat je med drugim tudi dokaz, da v šestdesetih letih 20. stoletja I. Bojanovski ni povezoval popularno slovensko označbo bôbovec z imenom bosenske srednjeveške prestolnice.

[12] Anđelić, P., (1973): cit. n. 1, str. 12, 32; P. Anđelić, Doba bosanske srednjovjekovne države (Zbornik: »Kulturna istorija Bosne i Hercegovine«) Sarajevo 1984 str. 460, 461 *»Jedna primitivna radionica za preradu željezne rudače zajedno sa kovačnieom bila je smještena na povišenoj platformi predvorja; tu je nađeno kovačko ognjište, komadi djelomično rastaljene željezne rudače, manje količine kreča te nekoliko nedovršenih kovačkih proizvoda«.*

[13] Bojanovski, I., (1984): cit. n. 6, p. 67 *»Teže je odrediti motiv koji je potakao Rimljane da izgrade utvrđenje u ovom gorovitom i slabije naseljenom dijelu desitijatske zemlje, s rijetkim naseljima (gradinama), a teško je i zamisliti da je kroz ovaj duboko ispresijecani kraj vodila neka iole značajnija rimska komunikacija. Stoga bismo izgradnju utvrde na Bobovcu najradije povezali za rudarsku politiku careva u unutrašnjosti Dalmacije. Područje oko Bobovca je po rudnom bogatstvu bilo poznato i u srednjem vijeku, a i u naše vrijeme se iskorištavaju rudišta Borovice i Vareša«.*

[14] Dinić, M., (1955): Za istoriju rudarstva u srednjevekovnoj Bosni i Srbiji SANU Beograd i Ćirković, S., Kovačević D. Ćuk, R., (2002): Staro srpsko rudarstvo Beograd - Novi Sad

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(NEW) INSTRUCTIONS TO AUTHORS (from Sep. 2003)

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English version with extended "Povzetek", and additional roles (in Template for Slovenian authors) ***can*** *be written. Only exceptionally the articles in the Slovenian language with summary in English will be published. The contributions in English will be considered with priority over those in the Slovenian language in the review process.*

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Technical and Expert papers are the result of technological research achievements, application research results and information about achievements in practice and industry.
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Evaluations or critics contain author's opinion on new published books, monographs, textbooks, exhibitions …(up to 2 pages, figure of cover page is expected).
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barbara.bohar@ntf.uni-lj.si

References – can be arranged in two ways:
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or
- second possibility: [1] numerated in the same order as cited in the text: example[1]

Format of papers in journals:

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TEMPLATE

The title of the manuscript should be written in bold letters (Times New Roman, 14, Center)

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Abstract(Times New Roman, Bold/Normal, 11): The text of the abstract is placed here. The abstract should be concise and should present the aim of the work, essential results and conclusion. It should be typed in font size 11, single-spaced. Except for the first line, the text should be indented from the left margin by 10 mm. The length should not exceed fifteen (15) lines (10 are recommended).

Key words: a list of up to 5 key words (3 to 5) that will be useful for indexing or searching. Use the same styling as for abstract.

INTRODUCTION (TIMES NEW ROMAN, BOLD, 12)

Two lines below the keywords begin the introduction. Use Times New Roman, font size 12, Justify alignment.

There are two (2) admissible methods of citing references:

1. by stating the first author and the year of publication of the reference in the parenthesis at the appropriate place in the text and arranging the reference list in the alphabetic order of first authors; e.g.:
   “Detailed information about geohistorical development of this zone can be found in: Antonijević (1957), Grubić (1962), ...”
   “… the method was described previously (Hoefs, 1996)”
2. by consecutive Arabic numerals in square brackets, superscripted at the appropriate place in the text and arranging the reference list at the end of the text in the like manner; e.g.:
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CONCLUSIONS (TIMES NEW ROMAN, BOLD, 12)

This paragraph summarizes the results and draws conclusions.

Acknowledgements (Times New Roman, Bold, 12, Center - optional)

This work was supported by the ****.

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FIRST OPTION – in alphabetical order

Casati, P., Jadoul, F., Nicora, A., Marinelli, M., Fantini-Sestini, N. & Fois, E. (1981): Geologia della Valle del'Anisici e dei gruppi M. Popera – Tre Cime di Lavaredo (Dolomiti Orientali). *Riv. Ital. Paleont.*; Vol. 87, No. 3, pp. 391-400, Milano.

Folk, R. L. (1959): Practical petrographic classification of limestones. *Amer. Ass. Petrol. Geol. Bull.;* Vol. 43, No. 1, pp. 1-38, Tulsa.

SECOND OPTION – in numerical order

[1] Trček, B. (2001): *Solute transport monitoring in the unsaturated zone of the karst aquifer by natural tracers.* Ph.D. Thesis. Ljubljana: University of Ljubljana 2001; 125 p.

[2] Higashitani, K., Iseri, H., Okuhara, K., Hatade, S. (1995): Magnetic Effects on Zeta Potential and Diffusivity of Nonmagnetic Particles. *Journal of Colloid and Interface Science 172*, pp. 383-388.

Citing the Internet site:

CASREACT-Chemical reactions database [online]. Chemical Abstracts Service, 2000, updated 2.2.2000 [cited 3.2.2000]. Accessible on Internet:<http://www.cas.org/CASFILES/casreact.html>.

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IME PRIIMEK[1], …, IME PRIIMEK[X] (TIMES NEW ROMAN, 12, CENTER)

[x]Faculty of ... , University of ... , Address…, Country; e-mail: ... (Times New Roman, 12, Center)
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DOLŽINA IZVIRNEGA ZNANSTVENEGA ČLANKA NE SME PRESEGATI DVAJSET (20, VKLJUČNO S SLIKAMI IN TABELAMI), STROKOVNEGA ČLANKA ŠTIRI (4) IN OSTALIH PRISPEVKOV DVE (2) STRANI.

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Key words: a list of up to 5 key words (3 to 5) that will be useful for indexing or searching. Use the same styling as for abstract.

Ključne besede: seznam največ 5 ključnih besed (3-5) za pomoč pri indeksiranju ali iskanju. Uporabite enako obliko kot za izvleček.

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Dve vrstici pod ključnimi besedami se začne Uvod. Uporabite pisavo Times New Roman, velikost črk 12, z obojestransko poravnavo. Naslovi slik in tabel (vključno z besedilom v slikah) morajo biti pripravljeni v slovenskem in angleškem jeziku.

There are two (2) admissible methods of citing references – obstajata dve sprejemljivi metodi navajanja referenc:

1. by stating the first author and the year of publication of the reference in the parenthesis at the appropriate place in the text and arranging the reference list in the alphabetic order of first authors; e.g.:
1. z navedbo prvega avtorja in letnice objave reference v oklepaju na ustreznem mestu v tekstu in z ureditvijo seznama referenc po abecednem zaporedju prvih avtorjev; npr.:
   “Detailed information about geohistorical development of this zone can be found in: Antonijević (1957), Grubić (1962), ...”
   “… the method was described previously (Hoefs, 1996)”
2. by consecutive Arabic numerals in square brackets, superscripted at the appropriate place in the text and arranging the reference list at the end of the text in the like manner; e.g.:
2. z zaporednimi arabskimi številkami v oglatih oklepajih na ustreznem mestu v tekstu in z ureditvijo seznama referenc v številčnem zaporedju navajanja; npr.;
   “... while the portal was made in Zope[3] environment.”

RESULTS AND DISCUSSION – REZULTATI IN RAZPRAVA (TIMES NEW ROMAN, BOLD, 12)

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Tabele, sheme in slike je potrebno vnesti (z ukazom Insert, ne Paste) v tekst na ustreznem mestu. Večje sheme in tabele je potrebno ločiti na manjše dele, da ne presegajo ene strani.

CONCLUSIONS – SKLEPI (TIMES NEW ROMAN, BOLD, 12)

This paragraph summarizes the results and draws conclusions.
Povzetek rezultatov in zaključki.

Acknowledgements – Zahvale (Times New Roman, Bold, 12, Center - optional)

This work was supported by the ****.

REFERENCES - VIRI (TIMES NEW ROMAN, BOLD, 12)

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Ne glede na uporabljeno metodo pri seznamu citiranih referenc upoštevajte naslednjo obliko:

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Folk, R. L. (1959): Practical petrographic classification of limestones. *Amer. Ass. Petrol. Geol. Bull.;* Vol. 43, No. 1, pp. 1-38, Tulsa.

SECOND OPTION – in numerical order (v numeričnem zaporedju)

[1] Trček, B. (2001): *Solute transport monitoring in the unsaturated zone of the karst aquifer by natural tracers.* Ph.D. Thesis. Ljubljana: University of Ljubljana 2001; 125 p.

[2] Higashitani, K., Iseri, H., Okuhara, K., Hatade, S. (1995): Magnetic Effects on Zeta Potential and Diffusivity of Nonmagnetic Particles. *Journal of Colloid and Interface Science 172*, pp. 383-388.

Citing the Internet site:

CASREACT-Chemical reactions database [online]. Chemical Abstracts Service, 2000, updated 2.2.2000 [cited 3.2.2000]. Accessible on Internet:<http://www.cas.org/CASFILES/casreact.html>.

Citiranje internetne strani:

CASREACT-Chemical reactions database [online]. Chemical Abstracts Service, 2000, obnovljeno 2.2.2000 [citirano 3.2.2000]. Dostopno na svetovnem spletu: <http://www.cas.org/CASFILES/casreact.html>.

POVZETEK – SUMMARY (TIMES NEW ROMAN, 12)

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Razširjeni povzetek vsebine prispevka v Angleščini (od ene strani do približno 1/3 dolžine izvirnega članka).

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(Število citatov in indeksiranja člankov RMZ-M&G)

(prepared by Pezdič, J. - from search done by Šercelj, M., CTK Ljubljana

Citation index according to Web of Science 1970 –2006:

110 papers have 165 citations (4x before 1998, max. 49x in 2004)
(110 člankov je bilo citirano 165 krat – 4x pred 1998; največ 49x v letu 2004))

No. of indexing of RMZ- M&G in singular Databases
(Število indeksiranih člankov iz RMZ- M&G v posameznih bazah)

	Database Name	Total		before 1998
1:	Civil Engineering Abstracts	773	770	3
2:	CA SEARCH® - Chemical Abstracts® (1967- present)	760	475	285
3:	Inside Conferences	313	237	76
4:	Materials Business File	253	253	
5:	METADEX®	164	38	126
6:	ANTE: Abstracts in New Technologies and Engineering	158	158	
7:	GeoRef	154	30	124
8:	Aluminium Industry Abstracts	36	9	27
9:	PASCAL	30		30
10:	Energy Science and Technology	27		27
11:	TEME - Technology and Management	27		27
12:	Ei Compendex®	13		13
13:	CSA Aerospace & High Technology Database	12	12	
14:	Computer and Information Systems	10	10	
15:	Mechanical & Transportation Engineering Abstracts	8	7	
16:	Engineered Materials Abstracts®	3		3
17:	Corrosion Abstracts	3	3	
18:	Analytical Abstracts	1		1
19:	FLUIDEX	1		1
20:	Solid State and Superconductivity Abstracts	1	1	
21:	Electronics and Communications Abstracts	1	1	
		2748	**2004**	**744**

- Total No. of Databases (število vseh baz): 21
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- Total No. of indexing (število indeksov skupaj): 2748
- No. of indexing after 1998 (število indeksov po 1998): 2004
- No. of indexing between 1970-1998 (število indeksov med 1970-1998): 744

RMZ - Materials and Geoenvironment

RMZ-M&G, Vol. 53, No. 4 pp. 419-519 (2006)

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