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THE ANALYSIS OF THE CHEMICAL COMPONENTS OF KARST SPRING KÁCS AND SÁLY WITH MULTIVARIANT STATISTICAL METHODS

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Summary: Karstic aquifers are very vulnerable sources of groundwater on the Earth. The karst springs of Kács and Sály are important reservoirs, as they provide drinking water for more than 10 settlements in the north-eastern part of Hungary. I monitored these and six other springs for two years. The aim was to know their function and conditions furthermore their relationships with other karst spring in their neighbourhood. In order to explore the relationship with the different karst springs I used cluster analysis.

Key words: statistical methodology, cluster, discriminant, karst water

1. INTRODUCTION

Drinking water is a treasure. Nowadays it is even more so, when the growing human population has a huge impact on its environment, especially on the water. On the Earth, 25% of the population get their drinking water from karstic aquifers (Ford and Williams 2007). This percentage is expected to rise substantially in the future. The karst is a 3-dimensional ecological system; the effects of both anthropogenic activity and natural phenomena appear very quickly, that's why it is so vulnerable. In addition to karst water quantity, quality is becoming increasingly important.

The karst springs of Kács and Sály are situated at the south-east piedmont of Bükk Mountains between Mezőkövesd and Miskolc. They supply drinking water for 12 settlements in the southern part of Borsod-Abaúj-Zemplén County. This group of springs is very interesting, as their temperature is higher than that of other, natural karst sources of the Bükk Mts. It means that they are not only fed by the infiltrating waters, but also have supply from rising groundwater. The presence of thermal karst at the foreground of Bükk Mts is proved (several thermal baths are well-known, Mezőkövesd-Zsóry, Bogács, Miskolctapolca).

To explore the function of these springs we monitored them and 8 other points for 2 years, with systematic, fortnightly sampling. The chemical composition of the samples was measured in the field and also in laboratory. Hydrochemical analysis not only provides information about water quality, but also insight into the functioning of the karstic aquifers.

I wanted to know if there was a relationship between the water of thermal wells, and sources in the neighbourhood and the water bodies of Kács and Sály. But unfortunately there's no long time series data available, only data measured 1 time. So I chose modern statistical tools to explore the relationships. In hydrology cluster analysis is a common method to analyse the groundwater's chemical properties.

Kács and Sály are situated in the foothills of Bükk Mountain, in the north-eastern part of Hungary. The springs stem in a valley head, in Eocene limestone, at 195-202 m asl. so they can be considered the lowest discharge level in these mountains. The catchment area is located in Southern Bükk, built up mostly of Triassic limestone, which has poor water conductivity ability. Near the Sály spring, there is also a dolomitic formation, that's why this spring has higher magnesium ion content than the others. The situation and the geology of the study area are shown on Fig.1.

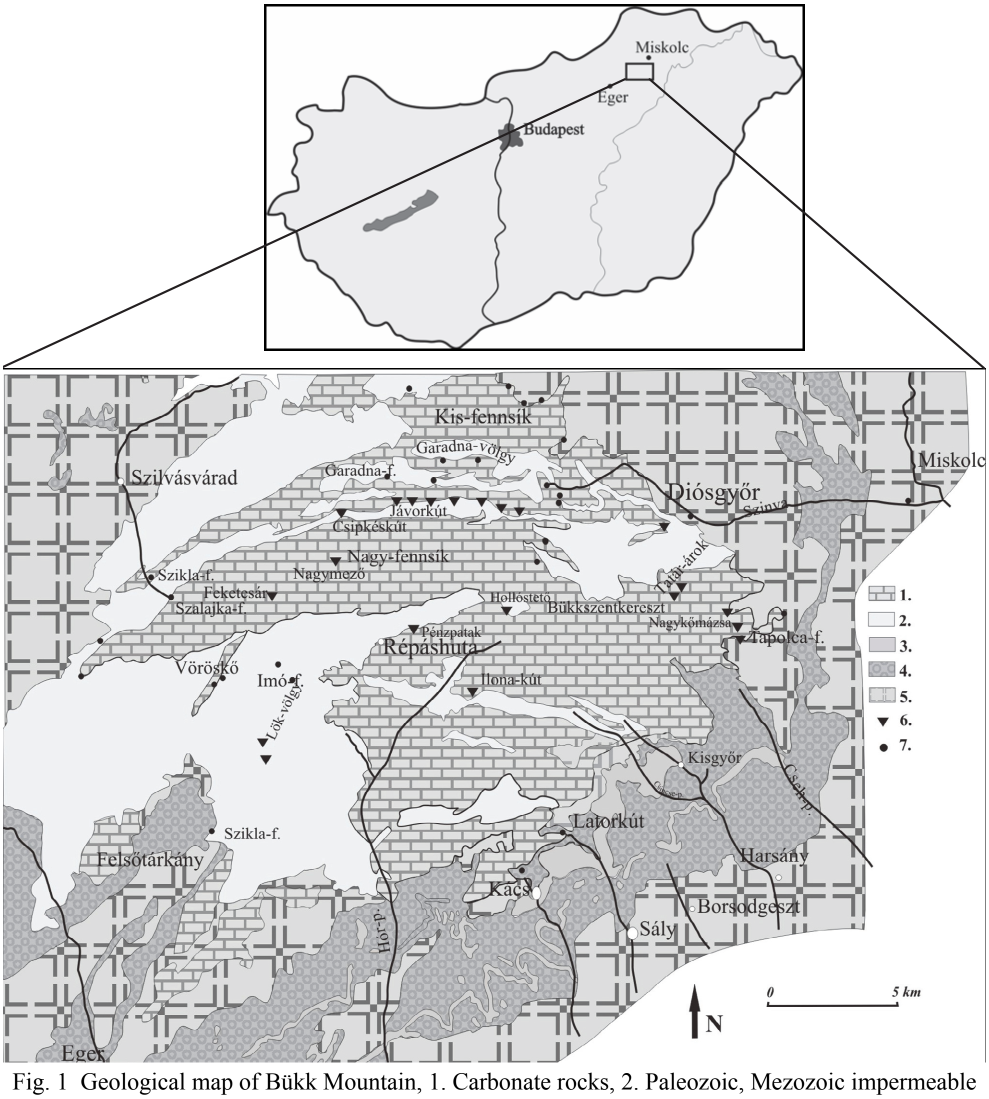

Fig. 1 Geological map of Bükk Mountain, 1. Carbonate rocks, 2. Paleozoic, Mezozoic impermeable rocks, 3 Eruptiv rocks, 4. Rhyolit tuffs, 5. Holocene sediments, 6, Swallow holes, 7. Sources (after Almássy and Scheuer (1967))

The sampling points are the following:

- Kács1: also called Máriás-spring, it is situated in the center of Kács village. The electrical conductivity is the highest in this spring.
- Kács5: The main karst spring of the system, and its water is lukewarm, with little variation of the temperature, which is 14,5°C. It is found above the Kács village.
- Kács6 and Kács7: springs with a temperature of 20-21°C, they are sitauted next to Kács5
- Kács8: also called Tükör-spring. Its water also has a temperature of 21°C, and it can be found beside Kács6 and Kács7.
- Sály1: it is the other main source of the system Kács and Sály. Its temperature is higher than Kács5, 15-16°C, and the magnesium ion content is also higher than the other springs. It is situated 5 km north of Sály.

Bársonyos: A really cold spring, with a temperature of 11°C, and not so high conductivity. It is situated in the Middle of the Bükk Mountains, in the vicinity of Lillafüred.

2. METHODOLOGY

2.1. The field and laboratory measurements, the analysed components

The sampling was carried out fortnightly. I measured the temperature, pH and electrical conductivity with a WTW Cond 40i device. I also measured the components of the carbonate system such as total hardness, calcium, magnesium and HCO_3^- ions. Then I analysed the samples in laboratory by spectrophotometer regarding the phosphate, sulphate, potassium, sodium and chloride content. I followed the methodology suggested by Krawczyk (1996) and Hoffmann and Pellegrin (1997).

2.2. Statistical methodology

The first step during the statistical analysis was to calculate the mean, the minimum and maximum, the standard deviation and the median of the different chemical components for each data series of each sampling points. Although the above statistics give us important information about the different springs, they do not give information about the relationship between the sampling points.

I also calculated the correlation coefficients, and the results are shown in Table 1. It can be seen that conductivity correlates strongly with the sodium, potassium and sulphate ions, and it has correlation with the HCO_3^-ion, but there is no significant correlation with the temperature. Although some ions are more soluble if the temperature is increasing, such as the magnesium ion (it is well known that its solubility is growing with the temperature). The sodium and potassium ions correlate with each other, with the electrical conductivity, but also with the bicarbonate ions.

The correlation coefficient gives us information about the relationships between the different chemical components in a sample, but does not inform us about the relationship between the different samples that are spatially separated. Modern geomathematics advise us to use cluster analysis for such cases.

The aim of the analysis was to find out if the thermal karst wells have some influence on the system of Kács and Sály. I took into account every chemical component with the same weighting factor. The result of the analysis can be plotted in a dendrogram, where we can see the relationships clearly.

Table 1 Correlation matrix for each chemical components

Correlations	T°C	pH	CμScm^{-1}	Total Hardness	Mg	HCO_3	Na	K	SO_4
T°C	1.000	-0.140	-0.372	-0.426	0.110**	-0.231	-0.268	-0.219	-0.302
pH	-0.140	1.000	0.240**	-0.024	-0.022	0.002	0.099**	0.279**	0.084*
CμScm-1	-0.372	0.240**	1.000**	0.277**	0.002**	0.098**	0.415**	0.517**	0.511**
Total Hardness	-0.426	-0.024	0.277**	1.000	0.098**	0.678**	0.225**	0.190**	0.211**
Mg	0.110**	-0.022	0.002**	0.098**	1.000	0.184**	0.165**	0.161**	-0.033
HCO3	-0.231	0.002	0.098**	0.678**	0.184**	1.000	0.192**	0.177**	-0.007
Na	-0.268	0.099**	0.415**	0.225**	0.165**	0.192**	1.000	0.308**	0.371**
K	-0.219	0.279**	0.517**	0.190**	0.161**	0.177**	0.308**	1.000	0.298**
SO4	-0.302	0.084*	0.511**	0.211**	-0.033	-0.007	0.371**	0.298**	1.000

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed).

Clustering can be interpreted as a coding process, which features a lot of complex objects described by a number, and the number of its group (cluster number). This code reflects the general and common features of the objects related to one group, so this means the objects in the same group are similar. Of the available methods I applied hierarchical classification. Initially this method considers every element as being in a different group, then merges the classes step by step until every element is in a single class. I chose the Ward clustering methodology for the hierarchical classification. It is based on the information loss resulting of merging the observations in groups. This information loss is the sum of the squared deviation from the group average.

The monitoring of the results was carried out using discriminant analysis. I had to validate the existence of the groups defined by the cluster analysis. The discriminant analysis shows for which variables are the groups created different, namely if class membership can be predicted or not with a selected group of independent variables (Kovács 2010). I used the Wilks' λ statistic for the discriminant analysis. The phenomena in the groundwater is influenced by some parameters more, others less. Wilks' λ gives us the measure of this influence. Its value is between 0 and 1, if it is 1, this means that the examined parameter does not influence the process, but if it is 0, or approximates 0, it has great influence on the groundwater's processes.

2.3. Results

The water of all analysed springs is of a calcium-bicarbonate nature chemically. I found relevant differences in one spring, named Kács1 during the analysis. I measured higher electrical conductivity during the test period, and also higher values of sulphate and phosphate concentrations. The average chemical composition of the analysed sources is shown on the Fig. 2. The dissolved mineral content of the Kács1 sample is higher than the other springs. But its temperature is lower than the other spring's temperature. This discrepancy is partly due to the location of the spring. Kács1 is found in the middle of the settlement, where there is no sewage system at all. The effect of this load was seen almost in each sample, because the phosphate and nitrate contents were always higher than the threshold limit. The other reason is its catchment area. It is built not only of limestone, but a great part of it is rhyolite tuff, which enriches the water with many soluble ions.

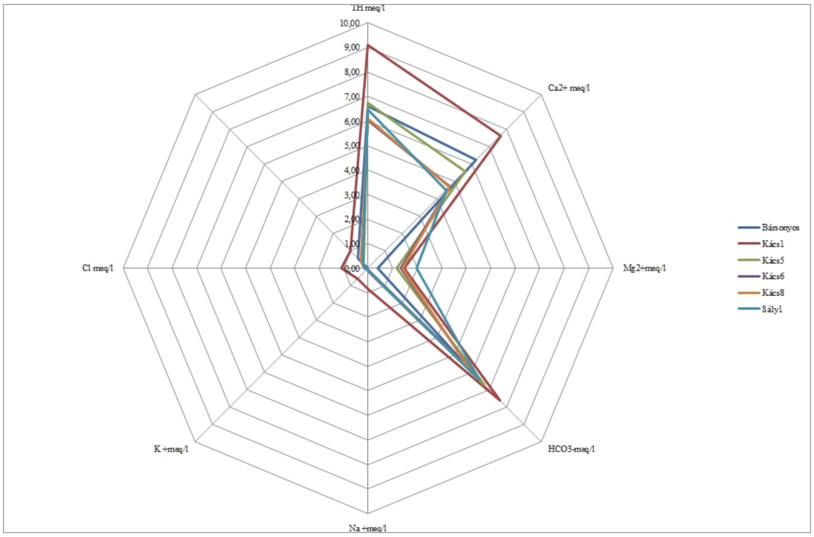

Fig. 2 The chemical composition of the different springs

The above figure shows very well that the chemical parameters of the different springs are similar. The difference is mostly in the quantity of the ion content and not in the quality. According to this fact I thought that after the clustering there would be 3 groups of the different springs. My hypothesis was that the lukewarm springs (Kács5 and Sály) would be in one group, then the warmer springs in another group (such Tükör-forrás, Kács6 and Kács 7), while the third would be formed by the cold water springs (Kács1 and Bársonyos).

However the cluster analysis gave a different result. The finally received cluster centres are shown in the Table 2. As it can be seen, only two groups were formed. The cluster centres show a cold water group and a lukewarm group. In the first group all the tested chemical components have lower value than in the other group. The difference is well marked regarding the potassium, sodium and bicarbonate ions.

Table 2 Final cluster centers

Final Cluster Centers		
	Cluster	
	1	2
T°C	15.31	11.84
C μScm^{-1}	101.32	153.19
pH	7.32	7.27
SO_4^{2-}mg/l	21.98	48.41
PO_4^{2-}mg/l	0.42	1.22
HCO_3^- mg/l	373.13	463.84
Na^+ mg/l	3.90	19.97
K^+mg/l	3.23	23.24
TH mg/l	318.33	455.10
Mg^{2+} mg/l	15.99	17.78

The dendrogram shows (Fig. 3) that the sampled springs can be classified in 2 groups. The sample Kács1 is one group and the other samples are all in the other group, the Bársonyos spring with cold water, the lukewarm water Kács5, Sály1 and the warm Tükör spring (Kács8). The discriminant analysis showed the same result, so the classification was correct. So in the first group we find the real karst waters, till in the second group the other one.

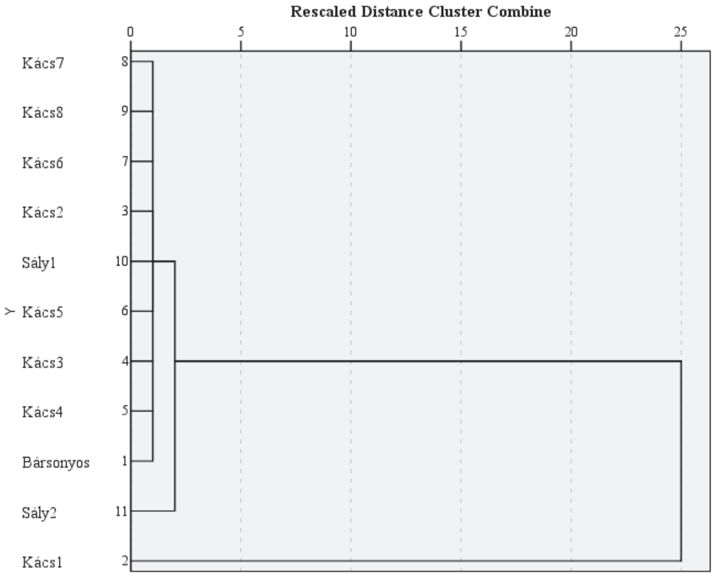

Fig. 3 Dendogram using Ward linkage

The chemical components and variables that the classification was based on are all inorganic ions. Since the correlation coefficient shows the pH has no strong relationship with the other components, that's why I left it out as a classification variable. It seems that the most important classification variables are as follows: the electrical conductivity, the temperature, and the sulphate and phosphate-ion contents. Based on this fact the chemical composition of sample Kács1 is significantly different from the sources and sample points. Therefore in order to ascertain whether there is a real similarity between warm, cold, and lukewarm karst water sources, a study was performed where the data of the spring Kács1 was not taken account. The result is shown on the Fig. 4.

The picture has become more refined and formed the three groups I originally anticipated. So the springs Kács5 and Sály1 really belong together, but they are far from the warm sources as Kács6, Kács7 and Kács8 is, although the sample points are only about some 10 m far away from each other.

Then I wondered if the data of only one sample from the sources and thermal wells from neighbouring catchment area can be placed among the classes, and whether there is any connection with the sources. I carried out the cluster analyses for two time series. If the data of the Kács1 samples were included, I received the same two groups; Miskolctapolca was similar, and could be included in the group with Kács5, Sály1 and Bársonyos springs. But when I tested only the so-called "real" karst springs in themselves, Bársonyos spring and Miskolctapolca are in separate groups (Fig. 5). So it seems that in the period 2004-2006 there was no detectable relationship between the karst springs Kács and Sály and

Miskolctapolca. However the summer of 2006 was not a typical year. There was a heavy rainfall period in the Bükk Mountain, and due to an inundation some karst wells ceased their functioning. It was observed that in this period the discharge of Kács spring increased.

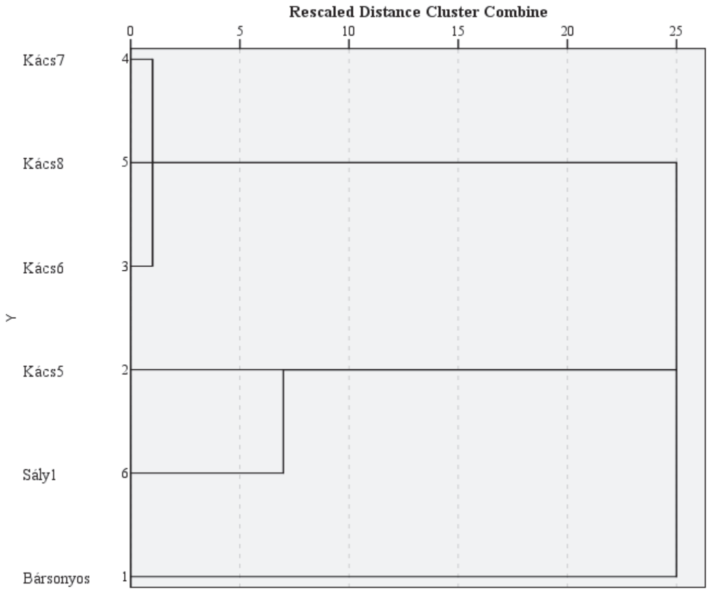

Fig. 4 Result of cluster analysis without sample Kács1

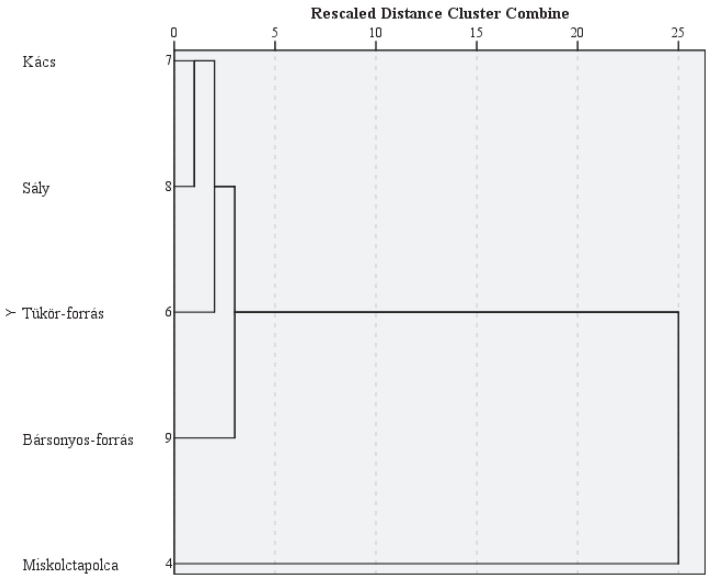

Fig. 5 Result of cluster analysis regarding the sample Miskolctapolca

3. CONCLUSIONS

The field sampling and the laboratory analysis results produced that we could classify the parameters important from the hydrological point of view. Hydrochemical techniques provide significant information about the functioning of karstic aquifer systems and they complement hydrodynamical methods. Chemical compounds can be considered natural tracers that provide information about the structure and dynamics of karst aquifers.

The aim of this study was to detect the possible relationships between the springs using statistical methods. Although regarding the basic chemical composition the sources are close to each other, they form distinct groups. On the whole it can be said that the cluster analysis is an appropriate method to classify karst springs with short or long term data series. Especially if besides the discharge or water level data, time series of chemical components are available.

Since the karst sources of Mountain Bükk are very important drinking water reservoirs for the part of Northern-Hungary, it is important to clarify the possible relationships. The aquifers located in Bükk Mts. have very uncertain borders.

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