Installation of a laboratory for stable isotope analysis in Croatia

Roller-Lutz Z.[a], **Mandić M.**[a], **Bojić D.**[a], **Lutz H.O.**[a,b], **Kapelj S.**[c]

[a] Laboratory for Environmental Studies, Medical Faculty, University of Rijeka, Croatia
[b] Physics Faculty, Bielefeld University, Bielefeld, Germany
[c] Faculty of Geotechnical Engineering, Varaždin, University of Zagreb, Croatia

1. Background

Karst is characterized by high permeability, porosity and crevices in which water moves in complex subterranean networks. Thus, water resources in karst areas are very sensitive to pollution. This is of particular significance for Croatia since about 50% of the country is karst. Related studies are a national priority, therefore, a Laboratory for Environmental Studies at the University of Rijeka with a new IRMS system has now been installed.

2. The new laboratory

The heart of the new laboratory is a Thermo-Finnigan Delta^{plus}XP mass spectrometer (Fig.1), fitted with a gas bench, an autosampler (96 sample positions) and a dual inlet.

Fig.2. In-house water-standards storage

Fig.1. Mass spectrometer

In-house water-standards have been produced in fairly large quantities (approx. 35 litres each) by collecting various types of waters with different δ-values. After filtering and boiling for sterilization, they are stored in stainless-steel barrels under argon atmosphere (Fig. 2).

Their δ^{18}O values (VSMOW) have been determined in an inter-laboratory comparison of our measurements, those of the Max-Planck-Institute for Biogeochemistry in Jena (Germany), and of Joanneum Research Graz (Austria). The corresponding values and the resulting means are given in Table I.

	Origin of water	Rijeka	Jena	Graz	Mean
DZW	De-ionized water from Žut island (Adriatic)	- 1.62	- 1.58	- 1.66	- 1.62
RTW	Rijeka tap water	- 8.43	- 8.54	- 8.59	- 8.52
MGS	Snow from Moelltal Glacier (Austria)	-19.98	-19.93	-19.89	-19.93
AAS	Antarctic snow	-26.45	-26.24	-26.39	-26.37

Table I: In-house water standards and the corresponding δ^{18}O (‰ VSMOW) values.

Three of the internal standards (DZW, MGS, AAS) are used as references, one (RTW) serves as quality control. Assuming a linear relation between the "measured" (as given by the NT software) and the "expected" (VSMOW) δ-values of the DZW, MGS and AAS standards, the regression equation thus derived is used to normalize the δ-values of the unknown samples (cf.,e.g.,[1]). The RTW quality control sample is required to lie within 0.1 ‰ of its VSMOW value. Fig. 3. below shows a typical example of this procedure.

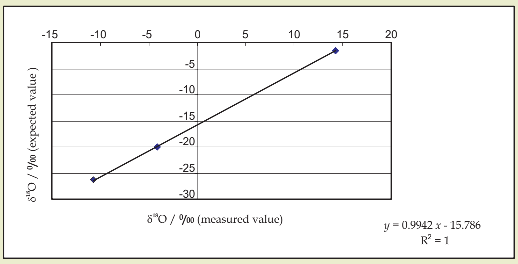

Fig. 3. Example of the DZW, MGS and AAS regression line for a particular run. In this run, the "measured" data for the RTW quality control, inserted into the regression equation, yield a δ-value of 8.43 ‰, which differs from the "expected" value (-8.52 ‰ VSMOW) by 0.09 ‰.

3. First results

We present examples for the three main Gacka river springs (Pećina, Tonković(a) vrelo, Majerovo vrelo). Gacka river is located within the zone of deep karst of the Dinarides at an altitude of about 400 m above sea level (Fig. 4). The climate of the region is continental, but it may occasionally be influenced by maritime air masses from the Mediterranean region.

Fig. 4. Position of Gacka river and spring area within Croatia.

The three springs have different δ-values (Fig. 5a) although they are located at approximately the same altitude. This indicates that they are fed from different altitudes, the water of Majerovo vrelo coming from the highest altitude, followed by Tonković vrelo and then Pećina. The corresponding differences are roughly 150 m each if a δ-value vs. mean altitude relation of -0.30 ‰ /100 m is assumed [2]. The nearby spring Živulja has a small and well defined catchment at about 1000 m asl. We have measured the spring's δ-value (-11.3 ‰, mean of three measurements), thus obtaining an absolute calibration. In Fig. 6. we plot the corresponding altitude vs δ-value relation, yielding the average catchment altitudes of the main three springs (or any other nearby springs, e.g. Klanac).

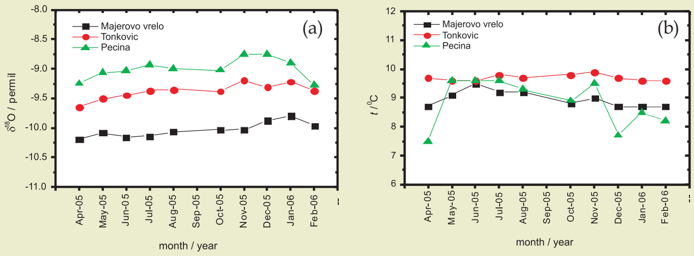

Fig. 5. δ^{18}O-values in ‰ VSMOW (a) and water temperatures (b) of three Gacka river springs. The lines connecting the data points are to guide the eye only.

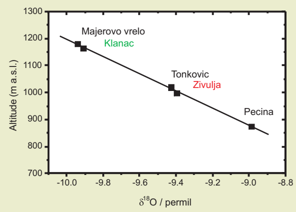

Fig. 6. The mean catchment altitudes of four Gacka springs, calibrated by means of the nearby spring Živulja. The straight line shows the relation (-0.3‰)/100 m.

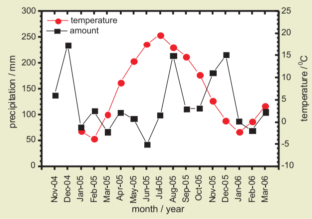

Fig. 7. Monthly precipitation amount and mean (ambient) temperature in the Gacka river area [3]. The lines connecting the data points are to guide the eye only.

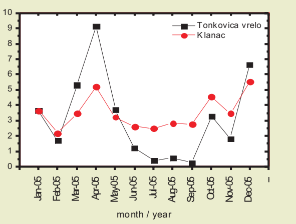

Fig. 8. Flow rates of Tonkovića and Klanac springs[3]. The lines connecting the data points are to guide the eye only.

4. Conclusions

The new IRMS system has been used for δ^{18}O stable isotope analysis of water, and presently we add δ^{13}C analysis of carbonates as another method. An equilibration device will soon allow for improved precision and high throughput for δ^{18}O as well as δ^{2}H measurements.

The system has been applied to the study of three springs of the Gacka river. One may conclude that their catchment areas (particularly Majerovo and Tonković) are connected to large and well mixed reservoirs, but of course more detailed studies are required, applying a wider variety of tracers as well as modelling.

The end users are the national institutions responsible for water management, foremost the Croatian Water Resources Management (Hrvatske Vode), the IAEA/WMO GNIP network and the local water supply organisations.

Acknowledgement

We gratefully acknowledge support by the Ministry for Science, Education and Sport (MZOS) of Croatia (projects 062-0982709-0510 and 160-0982709-1709), and the International Atomic Energy Agency (IAEA projects CRO/8/006 and /007). Water samples were collected by the group cooperating in the IAEA projects. We are indebted to Harm Moraal and his colleagues (Northwest University, South Africa) for providing us with the Antarctic snow, to Ines Krajcar Bronić (Institute Ruđer Bošković) for very stimulating discussions, and to Albrecht Leis (Joanneum Research Graz) for sharing his IRMS experience with us.

References

[1] S. T. Nelson, Rapid Commun. Mass Spectrom. 14, 1044 (2000)
[2] P. Vreča, I. Krajcar Bronić, N. Horvatinčić, J. Barešić, J. Hydrol. 330, 457 (2006)
[3] Data are from the Croatian Meteorological and Hydrological Service.

Vienna, 21-25 May 2007.