Installation of a laboratory for stable isotope analysis in Croatia

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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 XP mass spectrometer (Fig.1), fitted with a gas bench, an autosampler (96 sample positions) and a dual inlet.

Fig. 1. Mass spectrometer

In-house water-standards and the corresponding δ¹⁸O (‰ VSMOW) values.

Table 1: In-house water standards and the corresponding δ¹⁸O (‰ VSMOW) values.

<table>
<thead>
<tr>
<th>Origin of water</th>
<th>Rijeka</th>
<th>Jena</th>
<th>Graz</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>DZW De-ionized water from Zut island (Adriatic)</td>
<td>-1.62</td>
<td>-1.58</td>
<td>-1.66</td>
<td>-1.62</td>
</tr>
<tr>
<td>RTW Rijeka tap water</td>
<td>-8.43</td>
<td>-8.54</td>
<td>-8.59</td>
<td>-8.52</td>
</tr>
<tr>
<td>MCS Snow from Moelltal Glacier (Austria)</td>
<td>-19.98</td>
<td>-19.93</td>
<td>-19.89</td>
<td>-19.93</td>
</tr>
</tbody>
</table>

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Three of the internal standards (DZW, MCS, 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, MCS and AAS standards, the regression equation thus derived is used to normalize the δ-values of the unknown samples (cf., e.g.,[2]). 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.

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.

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 -0.3‰ /100 m is assumed[2]. The nearby spring Zivulja 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. Klanač).

Fig. 5. δ¹⁸O-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.

4. Conclusions

The new IRMS system has been used for δ¹⁸O stable isotope analysis of water, and presently we will also add δ¹⁰C. Analysis of carbonates as another method. An equilibration device will soon allow for improved precision and high throughput for δ¹³C as well as δ¹⁸O 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 by 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.

References

[3] Data are from the Croatian Meteorological and Hydrological Service.

Acknowledgment

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Fig. 3. Example of the DZW, MCS 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‰.

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

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