



## Isotopic Characterization of the Major Water Source of Rm. Valcea Area, Romania

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(Received: 14 August 2010;

Accepted: 4 August 2011)

AJC-10253

Hydrology and climate studies are an important topic in the current research field due to increased human activity, translated in high demand of fresh water, pollution and global warming. The measurement of oxygen and hydrogen stable isotopes is an essential element in determining the origin, path and history of a water source. Differences between stable isotopes concentrations give an idea about certain hydrological processes that took place. The aim of the present study is to obtain an isotopic fingerprint of the major water source of Rm. Valcea area, the Bradisor reservoir and to present the isotopic variations for oxygen-18 and deuterium along one year. The isotopic composition of the water samples was determined by a continuous-flow isotopic ratio mass spectrometer (CF-IRMS Delta V Plus) coupled with an isotopic equilibration module (GasBench II). The results show a cyclic variation in time of the stable isotopes concentration for the water reservoir, in good correlation with the amount of precipitation and temperatures.

**Key Words:** Stable isotopes, Oxygen-18, Deuterium, Isotopic ratio mass spectrometer, Drinking water.

### INTRODUCTION

$^{18}\text{O}$  (oxygen-18) and  $^2\text{H}$  (deuterium) are the most common and abundant stable isotopes used in characterizing a water source and the physical processes affecting it. Their isotope ratios ( $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$ ) can be used to determine the origin, path and history of the water. Knowing the baseline isotopic composition of the waters from a region creates a starting point for isotope-based applications ranging from fingerprinting sources of water to groundwater resource and quality studies and ultimately as part of the global isotope map of climatic processes<sup>1</sup>.

The aim of this study is to obtain an isotopic fingerprint of the major water source of Rm. Valcea area, Bradisor reservoir of Romania; in particular to present the isotopic variations for oxygen-18 and deuterium. Bradisor reservoir (with a bulk volume of 39 million cubic meters and its own power plant) supplies with water an area with more than 150,000 people and is the last stage of the Lotru basin. The Lotru basin has an average height of 1374 m, 4 major effluents, 7 reservoirs and 3 power plants, being situated in a mountain valley<sup>2-4</sup>.

Surface waters may originate from rainfall, or *via* groundwater discharge or by some combination of both. The compositional range of surface waters is always liable to exceed that of ground waters in a particular area, partly because of the evaporative effects, but also because those surface waters resulting more or less directly from rainfall can reflect the extremes of individual rainfall events<sup>1</sup>.

Once these surface waters are exposed to the atmosphere in waterways or lakes, they are potentially subject to modification by evaporative fractionation. The kinetic processes involved tend to cause isotopic ratios to deviate in a correlated way from values approximately consistent with the world meteoric line (WML) of Craig (1961), which has a  $\delta^2\text{H}$  *versus*  $\delta^{18}\text{O}$  slope of 8, to values that define a lower slope. Slope values depend critically on atmospheric humidity, with the lowest slopes produced by lowest humidity. The amount of evaporation, on the other hand, is indicated by the displacement of the sample along the evaporative line, which in extreme cases can result in positive  $\delta$ -values. Clearly, lakes are more likely than rivers to suffer evaporative modification since residence times will normally be longer, thus allowing time for more contact and exchange with the atmosphere<sup>1</sup>.

### EXPERIMENTAL

The water samples were collected monthly, at depth, from the inlet of the Bradisor power plant, in the period November 2007 to October 2008. The concentration of deuterium was determined using isotopic equilibration followed by mass spectrometric analysis.

**General procedure:** To measure the hydrogen isotopic composition, water samples of 200  $\mu\text{L}$  were equilibrated with gaseous hydrogen  $-\text{H}_2$ . The resulting gas was analyzed *versus* standard mean ocean water (SMOW) standard to determine the isotopic ratio of hydrogen  $^2\text{H}/^1\text{H}$ . The isotopic composition is given as a  $\delta$  value:

$$\delta (\%)_{vs\ SMOW} = \left( \frac{R}{R_s} - 1 \right) \times 1000$$

where, R is the isotopic ratio of the sample and R<sub>s</sub> is the isotopic ratio of the SMOW standard (Standard Mean Ocean Water)<sup>5-7</sup>.

**Detection method:** The hydrogen isotopic composition of the water samples was determined with a Delta V Plus Thermo continuous-flow isotopic ratio mass spectrometer (CF-IRMS) coupled with an isotopic equilibration preparation module (GasBench II).

**RESULTS AND DISCUSSION**

The results for deuterium and oxygen-18 analysis in water samples from Bradisor reservoir are given in Table-1.

Month	δ <sup>2</sup> H/ <sup>1</sup> H <sub>vsSMOW</sub> (%) <sup>a</sup>	δ <sup>18</sup> O/ <sup>16</sup> O <sub>vsSMOW</sub> (%) <sup>b</sup>	d-Excess (%)
November 2007	-72.11	-10.27	-34.52
December 2007	-71.87	-10.54	-33.29
January 2008	-71.45	-10.89	-31.59
February 2008	-67.96	-10.88	-28.13
March 2008	-57.33	-9.92	-21.02
April 2008	-56.32	-9.97	-19.82
May 2008	-54.57	-9.93	-18.22
June 2008	-82.88	-10.07	-46.02
July 2008	-89.49	-10.20	-52.15
August 2008	-89.09	-10.05	-52.30
September 2008	-72.71	-10.02	-36.03
October 2008	-76.49	-10.12	-39.45

a. Measurement uncertainty (k = 1) for δ<sup>2</sup>H/<sup>1</sup>H is 0.33 %.  
b. Measurement uncertainty (k = 1) for δ<sup>18</sup>O/<sup>16</sup>O is 3.5 %.

According to the values for δ<sup>2</sup>H/<sup>1</sup>H<sub>vsSMOW</sub>, showed in Fig. 1, it is observed and presumed the following: a) Nov 2007 - May 2008: The water is enriched in deuterium due to surface evaporation; b) May 2008 - Aug 2008: The water is depleted in deuterium, as precipitations are added; c) Aug 2008 - Oct 2008: The water is enriched in deuterium to the initial value of Nov 2007.

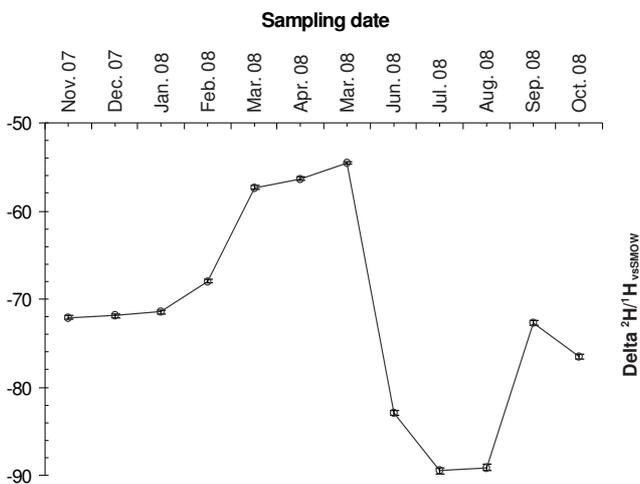


Fig. 1. δ<sup>2</sup>H/<sup>1</sup>H<sub>vsSMOW</sub> (%) variations for Nov. 2007 - Oct. 2008

According to the values for δ<sup>18</sup>O/<sup>16</sup>O<sub>vsSMOW</sub>, presented in Fig. 2, it is observed and presumed the following: a) Nov 2007 - Feb 2008: The water is depleted in oxygen-18, that can be explained by isotopic exchange with salts from the lake (carbonates, hydrocarbonates, etc.) that are more concentrated due to surface evaporation and lack of precipitation; b) March 2008 - May 2008: The water is enriched in oxygen-18; c) June 2008 - Oct 2008: The water maintains at the value of Nov 2007. Nevertheless, because the oxygen-18 content varies with only 1 %, the variations along one year can't be considered general rules.

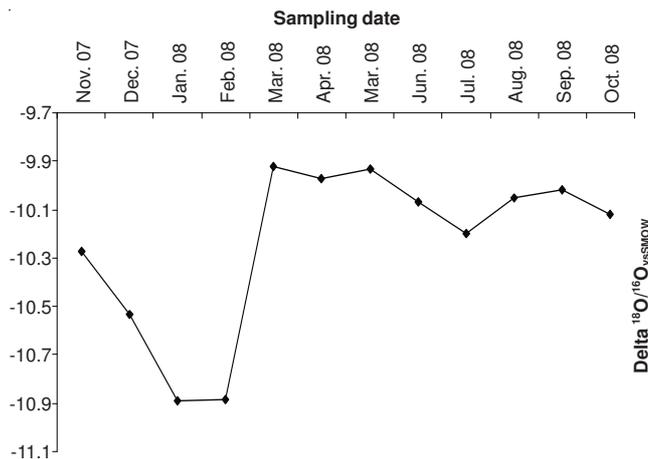


Fig. 2. δ<sup>18</sup>O/<sup>16</sup>O<sub>vsSMOW</sub> (%) variations for Nov. 2007 - Oct. 2008

After analyzing the two sets of isotopic values, we obtain (Fig. 3) the equation:

$$\delta D = 3.66 \delta^{18}O - 34 \% \text{ SMOW (standard mean ocean water)}$$

It is apparent that the water source lies along a lower slope than the MWL (δD = 8 δ<sup>18</sup>O + 10 % SMOW), exhibiting signs of evaporative enrichment in heavy isotopes. This slope value corresponds, according to literature, to a temperate region at medium altitude (Fig. 4). The correlation is not particularly good, but the samples came at different dates and are likely to have had local variations<sup>1,5,6,8-10</sup>.

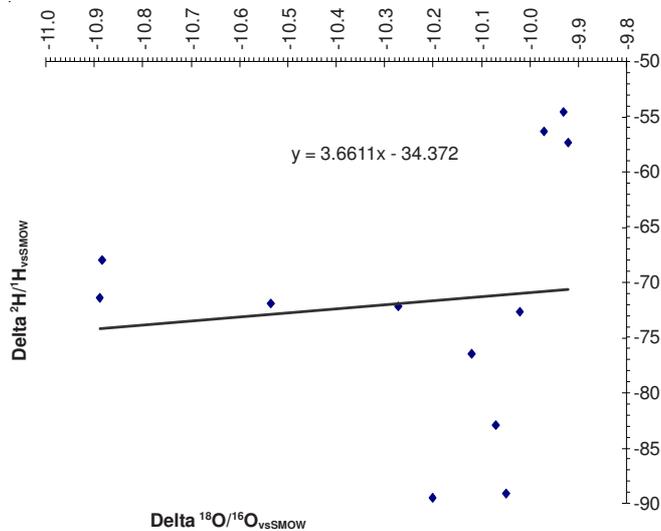


Fig. 3. Correlation of the δ<sup>18</sup>O/<sup>16</sup>O<sub>vsSMOW</sub> (%) versus δ<sup>2</sup>H/<sup>1</sup>H<sub>vsSMOW</sub> (%) values for Nov. 2007 - Oct. 2008

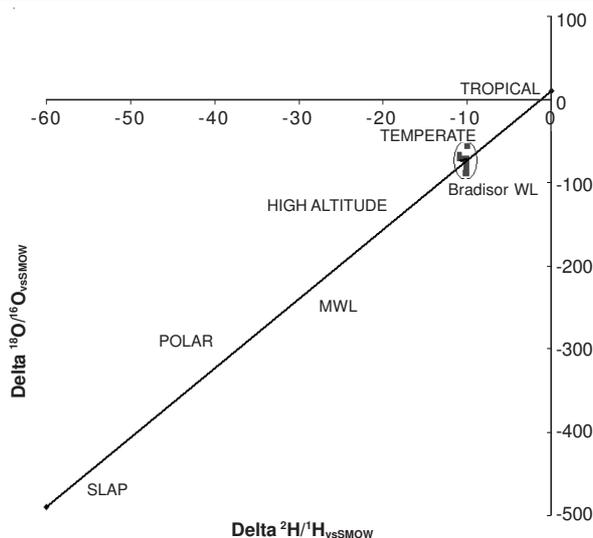


Fig. 4. Bradisor water line's (Bradisor WL) position on the MWL

There can be observed different variation patterns for oxygen-18 and deuterium, explained by d-excess phenomena. For the MWL the deuterium excess (or d-value) is defined as  $d = \delta^2\text{H} - 8\delta^{18}\text{O}$ , where d has a value of 10 ‰. For this particular case  $d = \delta^2\text{H} - 3.66\delta^{18}\text{O}$  and has a value of -34 ‰.

The relationship between the two isotopic ratios changes seasonally (cold and warm seasons), demonstrated by plotting the deuterium excess for each month (Fig. 5). D-values higher than -34 ‰ indicate an enrichment rate for  $^2\text{H}$  greater than that for  $^{18}\text{O}$  (seen for Jan - May period) and values under -34 ‰ show an enrichment rate higher for  $^{18}\text{O}$  (June - Aug period).

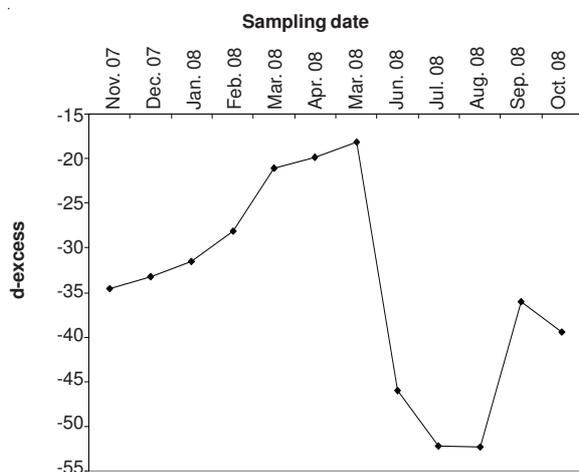


Fig. 5. Deuterium excess for Nov. 2007 - Oct. 2008

Fig. 6 shows the plot of the seasonal isotopic fingerprints, where there can be seen for deuterium extreme values in spring and summer and similar values for autumn and winter; while oxygen-18 presents extreme values in spring and winter and similar ones in summer and autumn.

### Conclusion

For Bradisor water source, a cyclic variation in the deuterium and oxygen-18 contents along one year is observed. The  $\delta^2\text{H}/^1\text{H}$  varies with 45 ‰, between a minimum of -89.49 ‰ (July 2008) and a maximum of -54.57 ‰ (May 2008), with a mean value of -71.85 ‰. The  $\delta^{18}\text{O}/^{16}\text{O}$  varies with 1 ‰,

between a minimum of -10.89 ‰ (January 2008) and a maximum of -9.92 ‰ (March 2008), with a mean value of -10.27 ‰.

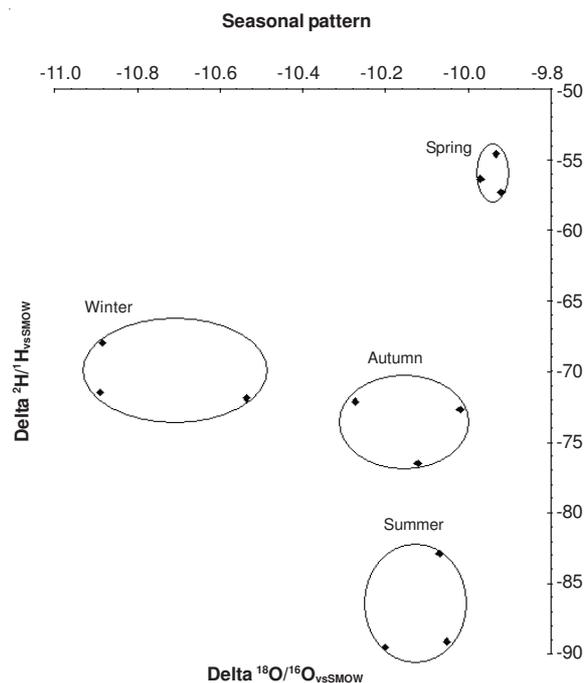


Fig. 6. Isotopic fingerprint and seasonal variations for Bradisor reservoir

The seasonal variations are well correlated with the amount of precipitation and temperatures. For high precipitations the water depletes in deuterium; for high temperatures, increased evaporation and freezing phenomena the water enriches in heavy isotopes.

The aim of the present paper was to obtain an isotopic fingerprint of the major water source of Rm. Valcea area - Bradisor reservoir of Romania and to present the isotopic variations for oxygen-18 and deuterium along one meteoric cycle.

### ACKNOWLEDGEMENTS

The authors thank the Romanian Academy for partially finance and Mihaela Pana from National Water Administration for providing the samples.

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