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STABLE ISOTOPES DISTRIBUTION IN THE OLT VALLEY RIVERS

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Abstract
Hydrology studies are an important topic in the current research field due to increased human activity, translated in high demand of resources (fresh water, energy, process water) and pollution. The measurement of oxygen and hydrogen stable isotopes is an essential element in determining the origin, path and history of a water source. The aim of this paper was to obtain an isotopic map of the major water and energy source of Valcea County – the Olt River and it's affluents during autumn season. The isotopic composition of the water samples was determined by continuous-flow isotopic ratio mass spectrometry (CF-IRMS Delta V Plus) coupled with an isotopic equilibration module (GasBench II). The results provide a picture of the stable isotopes distribution in the Olt Valley Rivers. Differences between stable isotopes concentrations give us information about certain hydrological processes that took place.

1. Introduction

^{18}O (oxygen-18) and ^{2}H (deuterium) are the most common and abundant stable isotopes used in characterizing a water source and the physical processes affecting it. The isotope ratios ($^{18}O/^{16}O$ and $^{2}H/^{1}H$) 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 and quality studies, and ultimately as part of the global isotope map [1, 2].

The aim of this paper was to obtain an isotopic map of the Olt Valley hydrological network, in particular the oxygen-18 and deuterium composition of Olt River and its important affluents during autumn.

Olt River is one of the major rivers of Romania that springs from Hasmasu Mare Mountains (Oriental Carpathians). It has a length of 615 km, 30 reservoirs and flows into the Danube (at Islaz, near Turnu Magurele) after passing through Harghita, Covasna, Brasov, Sibiu, Valcea, Olt and Teleorman counties and Miercurea Ciuc, Sfantu Gheorghe, Fagaras, Ramnicu Valcea and Slatina cities [3-6].

Olt Valley begins at Turnu Rosu and ends at Calimanesti, with a lenght of 48km being the longest in the country. The valley caves through Capatanii, Lotrului and Fagarasului Mountains and is sided by Cozia Mountains. The length of Olt River passing through Valcea county is of 130km [3-6].

Surface waters may originate from precipitation or via groundwater discharge, or by some combination of both. The compositional range of surface waters is always liable to exceed that of groundwaters 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. Once these surface waters are exposed to the atmosphere in waterways or lakes, they are potentially subject to modification by evaporative fractionation. 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 [1-2].

Climate conditions in Olt Valley

The climate is continental-temperate, with a mean temperature of 7,5°C. The lowest temperatures are in January (-6 to 4°C) and the highest in August (12-14°C). The humidity is high (80%) almost all the year. Annual precipitation is 800 – 1000 mm, with maximum values in May-June, minimum values in August-September and with an increase in October-November. Large masses of air are channeled through the mountain valley directed north-south and south-south-west [3-7].

Hydrology of Olt Valley

High waters for the rivers are recorded in the May – June period thanks to abundant precipitations and snow melting, in October the flow rate is minimum. January is the month with low levels of water due to freezing phenomena.

The hydrographic network decreases from 0.8-0.9 km/km^2 in the mountain area, to 0.5-0.6 km/km^2 in the subcarpathian area and 0.3-0.5 km/km^2 further south. Olt flow rate is 90 cm/s (multiannual mean) at Rau Vadului and 115 cm/s at Dragasani. The mean descent is 1,5 m/km, bigger in the valley and smaller in the south.

Mountain water input in Olt River is important: the multiannual mean flow of 80 m^3/s (after Cibin) grows to 115 m^3/s at Rm.Valcea, due to Lotru River that has a flow of 20 m^3/s (much bigger than all the southern affluents). Until Dragasani, Olt receives another 15-16 m^3/s from the Babeni area affluents [3-7].

2. Method and samples

The concentration of deuterium and oxygen-18 was determined using isotopic equilibration followed by mass spectrometric analysis. To measure the hydrogen isotopic composition, water samples of 200μl were equilibrated with gaseous hydrogen - H_2. To measure the oxygen isotopic composition, water samples of 500μl were equilibrated with carbon dioxide. The resulting gas was analyzed versus SMOW standard to determine the isotopic ratio of hydrogen $^2H/^1H$ and oxygen $^{18}O/^{16}O$. The isotopic composition is given as a δ value:

$$\delta(‰)_{vs\ SMOW} = \left(\frac{R}{R_S} - 1\right) \cdot 1000$$

where R is the isotopic ratio of the sample and R_S is the isotopic ratio of the SMOW standard (Standard Mean Ocean Water) [8], [9], [10]. The isotopic composition of the water samples was determined with a *DeltaVPlus Thermo* Continuous-Flow Isotopic Ratio Mass Spectrometer (CF-IRMS) coupled with an isotopic equilibration preparation module (GasBench II).

3. Results and Discussions

The water samples were collected in 17 points from 11 waters in November 2010 (Table 1, Fig. 1). The results for deuterium and oxygen-18 analysis in the water samples are given in Table 1.

The distribution of deuterium and oxygen-18 in Olt Valley can be observed in Fig. 2 and Fig. 3:

- deuterium composition of Olt River is rather low (values under -72‰) with an exception of Rm.Valcea point (-68‰). The low values can be explained by the fact that it is recharged from precipitation with low deuterium content. After receiving Lotru River and Calimanesti/Caciulata Springs the deuterium composition rises from -75.76‰ to -72.61‰.

- Olt affluents have higher deuterium content than Olt River (between -68‰ and -58‰), with the exception of Spring 2 Caciulata (-73.56‰).

- oxygen-18 composition of Olt River (between -10.36‰ and -10.10‰) is lower than that of the affuents (with values between -9.68‰ and -9.23‰), with the exception of the same Spring 2 Caciulata that has the lowest oxygen-18 composition (-10.97‰).

Table 1. Values of the deuterium and oxygen-18 composition of water samples

N^o.	Water source	Location	$\delta^2H/^1H_{vsSMOW}$ (‰)[a]	$\delta^{18}O/^{16}O_{vsSMOW}$ (‰)[b]
1	Olt	Boita	- 74.24	- 10.33
2	Olt	Cainenii Mari	- 75.76	- 10.31
3	Lotru	Brezoi	- 63.78	- 9.67
4	Spring 1	Caciulata	- 58.34	- 9.41
5	Spring 2	Caciulata	-73.58	- 10.97
6	Spring 4	Calimanesti	- 66.41	- 9.68
7	Olt	Calimanesti	- 72.61	- 10.36
8	Olt	Rm.Valcea	- 67.99	- 10.21
9	Olanesti	Rm.Valcea	- 68.94	- 9.59
10	Olt	Priza Olt (industrial area)	- 76.31	- 10.10
11	Govora	Stoenesti	- 66.76	- 9.03
12	30th Dec. Spring	Baile Govora	- 61.68	- 9.44
13	Govora	Babeni	- 62.18	- 9.46
14	Olt	Tatarani (industrial area)	- 75.35	- 10.10
15	Bistrita	Barbatesti (national park area)	- 66.11	- 9.46
16	Luncavat	Otesani	- 66.38	- 9.23
17	Topolog	Galicea	- 68.61	- 9.26

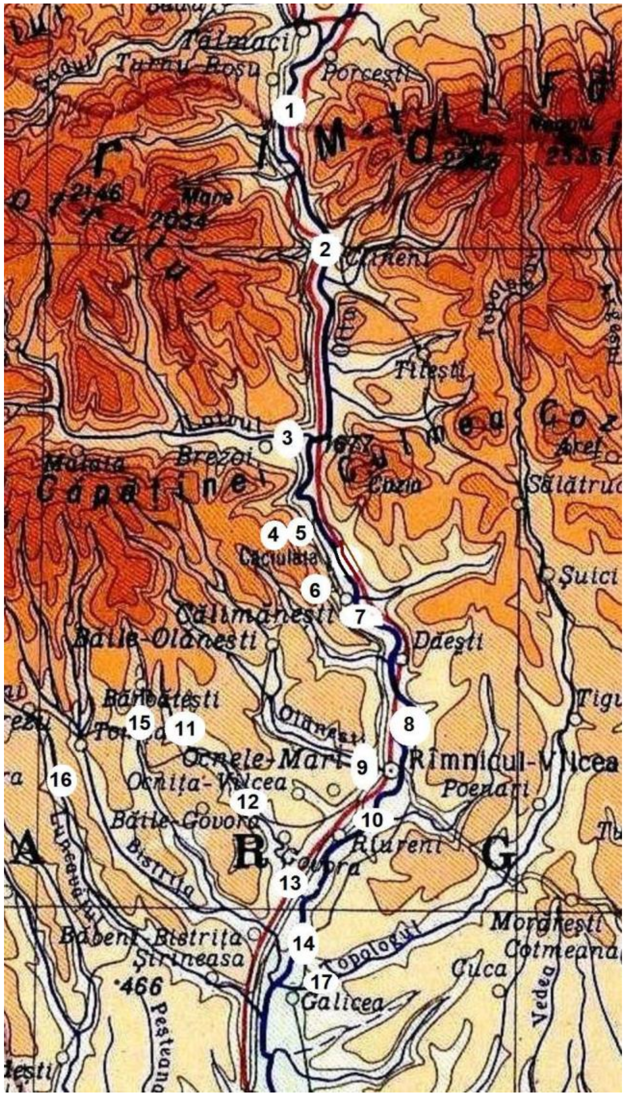

Figure 1. Physical map of Olt Valley with the sampling points.

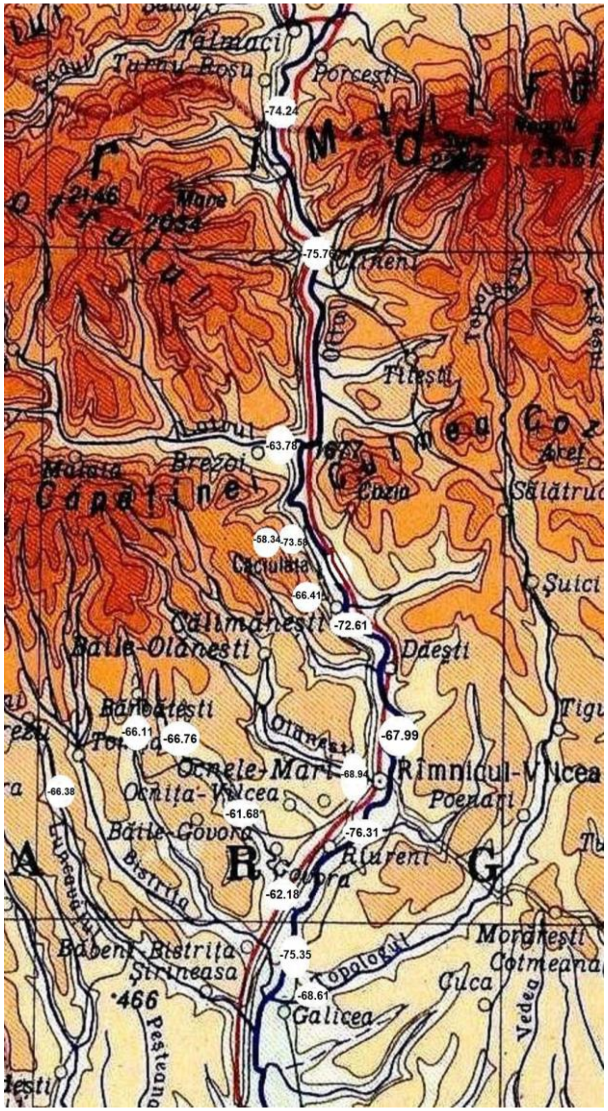

Figure 2. Deuterium isotope map of Olt Valley.

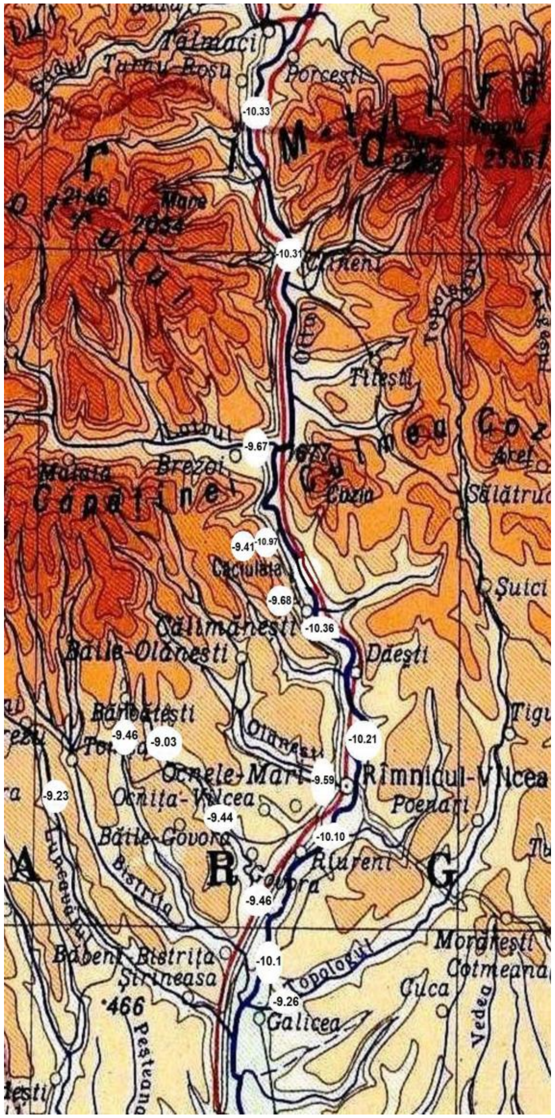

Figure 3. Oxygen-18 isotope map of Olt Valley.

The isotopic values were plotted to give the isotopic fingerprint of Olt Valley (Fig. 4), when it can be observed the following:

- deuterium content varies between a minimum of -76.31‰ and a maximum of -58.34‰, with a mean of -68.53‰. Oxygen-18 content varies between a minimum of -10.97‰ and a maximum of -9.03‰, with a mean of -9.80‰;

- a distinctive **Area 1** can be set for Olt River, where the oxygen-18 content is very specific. Olt River has the smallest values for both isotopes;

- another area (**Area 2**) can be set for the waters sampled at higher altitudes and near the origin. **Area 3** contains two waters that have mountain origins. Areas 2 and 3 can be set for all southern affluents of Olt River, with the exception of Govora River. They have the highest concentrations of oxygen-18 and similar deuterium content.

- the extremes are represented by Spring 1 (point 4) and Spring 2 (point 5) from Caciulata, where Spring 2 (point 5) is behaving atypical both for the oxygen and deuterium contents, showing results similar to Olt River, rather then it's affluents.

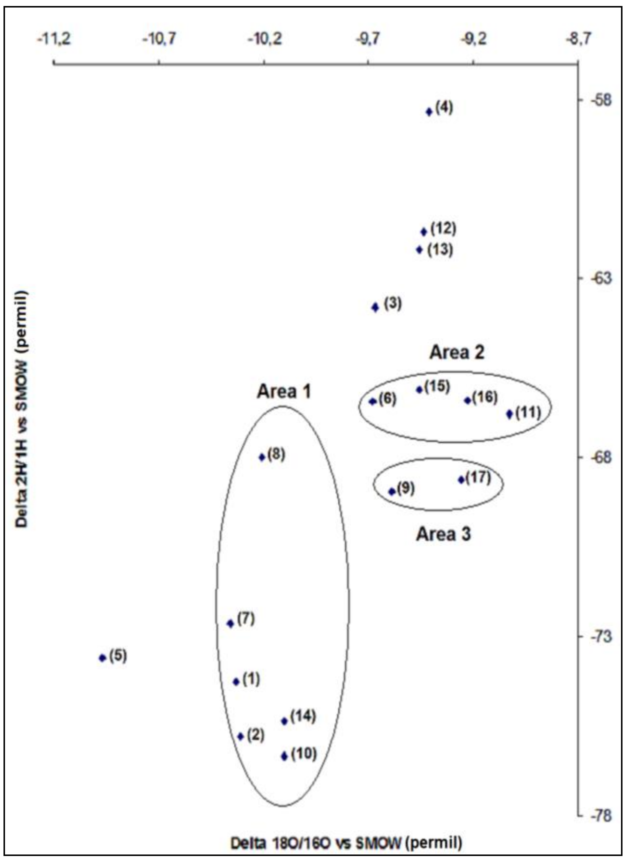

Figure 4. Olt Valley Rivers isotopic fingerprint.

Conclusions

For Olt Valley the deuterium content varies between a minimum of -76.31‰ and a maximum of -58.34‰, with a mean of -68.53‰. Oxygen-18 content varies between a minimum of -10.97‰ and a maximum of -9.03‰, with a mean of -9.80‰.

It can be easily observed an important difference in the isotopic content between Olt River and its affluents, Olt River having the smallest values for both isotopes, indicating a precipitation source for the waters.

The aim of the present paper was to obtain an isotopic fingerprint of the Olt Valley hydrological network during autumn, when there were set one for Olt River and one for the southern affluents (Olanesti, Govora, Bistrita, Luncavat and Topologul).

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