Water stable isotopes distribution in the karst systems from Ocoale Plateau (Apuseni Mountains), Romania

Carmen-Andreea BĂDĂLUŢĂ[1,2,3*]
[1] Department of Geography, Stefan cel Mare University of Suceava, Romania
[2] Stable Isotope Laboratory, Stefan cel Mare University of Suceava, Romania
[3] Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences MTA , Budapest, Hungary

* Correspondence to: Carmen- Andreea Bădăluță, Department of Geography, Stefan cel Mare University of Suceava, Romania E-mail: carmenbadaluta@yahoo.com.

doi: 10.4316/GEOREVIEW.2015.25.1.277

GEOREVIEW

Article history
Received: September 2015
Received in revised form: November 2015
Accepted: November 2015
Available online: December 2015

ABSTRACT: Knowledge of the hydrological processes in the karst areas of the Apuseni Mountains (Romania) are currently hampered by the limited available information. To partly address this issue, we have investigated the dynamics of stable isotopes in waters of the Ocoale Plateau, central Apuseni Mts. We have collected 103 samples from meteoric water, rivers, springs and caves and analyzed them for their isotopic composition. The data indicates that meteoric waters are the main source for all types of water; however, differences in the duration of underground flow, recharge and residence time occur in relation to the characteristics of the cave systems and external hydrological regime.

KEY WORDS: stable isotopes, precipitation, rivers, springs, karst, Ocoale Plateau

1. Introduction

The necessity of studying karst water sources is very important because carbonate rock is an important source of fresh water (Bakalowicz, 2005), between 20 and 25 % of global population drinking water derived from carbonate rocks (Ford and Williams, 2007). The mechanisms of water infiltration and hydrological processes in karst areas are difficult to characterize because these are influenced by a number of factors which can modify the flux and quantity of water input (Fernandez - Cortes et al., 2008). Climate is the major controlling factor determining the quantity of water input and their forms (Fairchild et al., 2007). In karst areas the waters can flow through karst conduit and fractures and the classical hydrological studies are not reasonable for groundwater hydrodynamics (Barbieri, 2005). To define the hydrodynamic processes between surface and underground good indicators are the stable isotope tracers (McGuire K. and McDonnell, 2007). Stable isotopes of water ($\delta^{18}O$ and $\delta^{2}H$) can be used to determine the isotopic signature of rainfall (Clark and Fritz, 1997; Sharp, 2007), evaporation rates, hydrograph separation, recharge rates and source (Jeelani et. al., 2015), water time travel (McGuire K. and McDonnell, 2006).

The aim of the study is the investigation of hydrological processes in the Ocoale Plateau (Apuseni Mountains, Romania), based on the isotopic composition of surface and underground water, collected over two years (2012 and 2014).

2. Study area

The Ocoale Plateau is localized in Bihor Mountains, Romania and is delimited by Ordâncușa Valley (in east and south) and Gârda Seacă Valley in west. In the north the limit is Ghețar Valley, situated between Gârda Seacă Valley and Ocoale Hill (Figure 1).

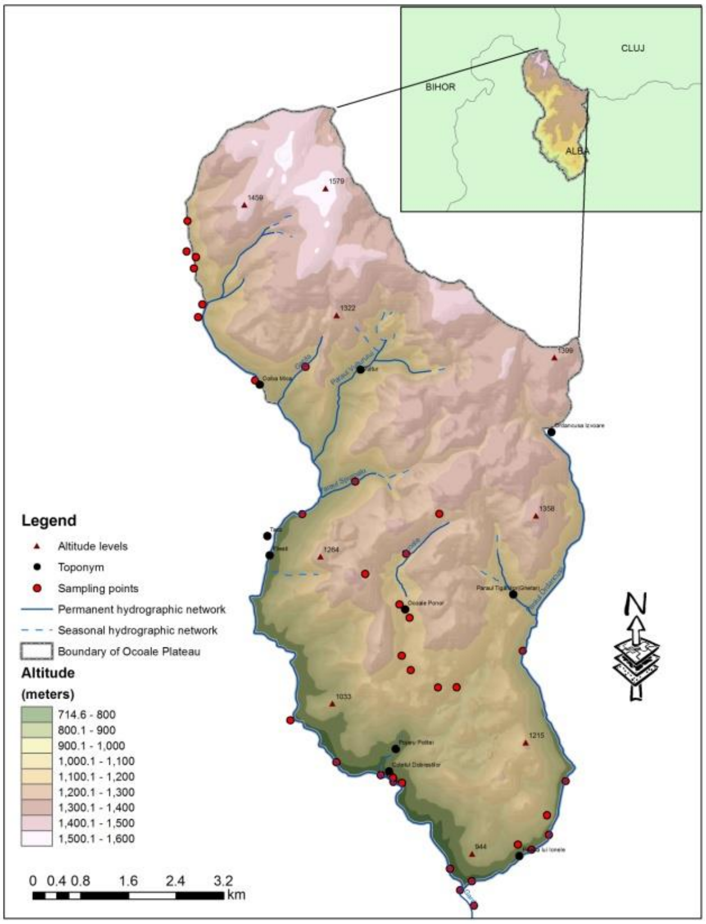


Figure 1 Location map of Ocoale Plateau and sampling points.

The rocks in the area belong to Bihor Autochthonous and the fractured parts of Biharia units (Balintoni, 1997). The most representative formations are sedimentary rocks (limestones) of Triasic - Jurasic (Dimitrescu et al., 1997) age, above which have been deposited a coat of sandstone and red and purple shales alternating with black limestones (Figure 3) of Wetterstain (Bleahu and Dimitrescu, 1957) and Ladinian age. In West, Ocoale Plateau is formed on Permian conglomerates, sandstones, shales and quartzite, the latter belonging to the Gârda Nappe (Damm and Ciubotărescu, 1999).

This study area is strong faulted and fractured (Ianovici et al., 1979). Due to these faults, the tectonic blocks are separated between them and the aquifer systems cannot always communicate (Orășeanu, 2003).

The relief of the investigated area is characteristic for karst zones, with steep slopes, endoreic basins, dolines and underground drainage. The altitudes (Figure 1) are decreasing from north (1559 meters in Bătrâna Peak) towards the south (880 meters at Gârda - Ordâcușa confluence).

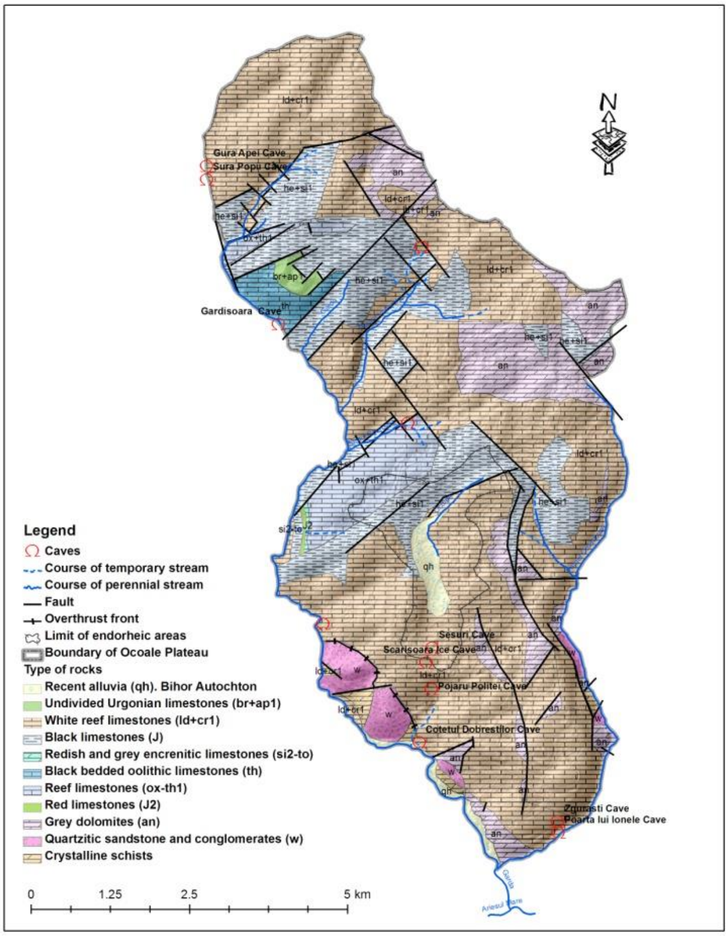


Figure 2 Geological map of Ocoale Plateau.

The Ocoale Plateau, between Garda and Ordancusa valleys, is divided in two parts: in north (between Poiana Călineasa and the lineament Spurcat stream- Ordâncușa River) is a temporary inhabited region, with water used only for watering the livestock; in south (between lineament Spurcat stream- Ordâncușa River – Gârda river), the area is permanently inhabited, and the drinking water can be found only in few springs. Three large karst aquifers are present (Orășeanu, 2003):

1. Ocoale - Ghețar - Cotețul Dobreştilor (Rusu, 1992) was created by the Ocoale brook and includes 3 stages of karstification: I - first level, fossil, represented by the Scărişoara Ice Cave and Pojarul Poliţei Cave, II - middle stage, temporary active, represented by Avenul

din Șesuri and Izbucul Poliţei, III - stage, lower, inaccessible and active, with a series of ponors swallowing the waters of Ocoale river which resurface through the Coteţul Dobreşti Cave (Orăşeanu, 2003) (Figure 6B).

2. Zgurăști - Poarta lui Ionele karst system, with a permanent spring at Poarta lui Ionele, the waters coming from infiltration occurring in dolines in the Mununa Hill and possibly Hănăsești village area.
3. Ordâncușa (Moara lui Ivan) - Cotețul Dobreștilor a hydrological connection between the Ordâncușa stream partly going underground in the Moara lui Ivan area and resurfacing in Coteţul Dobreştilor.

2. Methods

2.1. Collection of samples

Water samples were collected at different times during the year in order to capture the influence of atmospheric dynamics and topography, which are the main factors influencing the spatial and temporal distribution of stable isotope composition of water. Precipitation was collected monthly between April 2012 - March 2014, using a 5l plastic bottle in which a funnel was placed. In the bottle collector we introduced paraffin oil, acting against evaporation. Water from rivers and springs were collected in the same period, but the collection was made seasonally (wet and dry) in 20 ml bottles. The spring samples were collected directly at the outlets while those from rivers were collected from the riverbed (Figure 1).

2.2. Measurements and instruments

The first step in the analysis of stable isotopes composition of water was filtering the sample with a 0.45µm filter (White Nylon Membranes). Analysis of samples was done by manually injecting, with a syringe type SGC Analytical Science, 1.3 µl of water in the vaporizng unit of a Picarro L2130i CRds. This was analyzed by the spectrometer PICARRO L2130 them for 6 minutes. The precision of analyses was better than 0.03 for δ18O and 0.3 for δ2H.

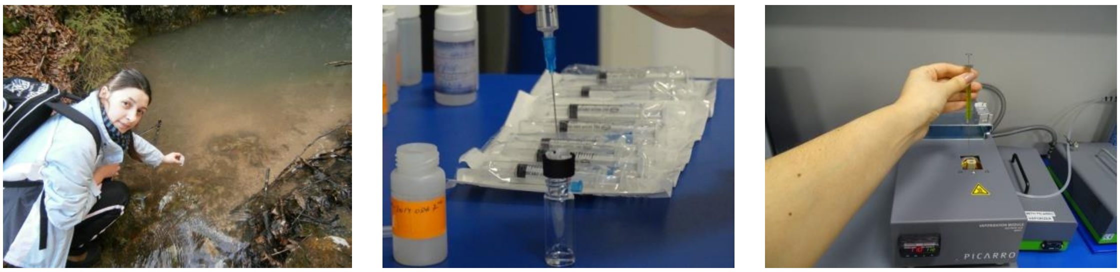


Figure 3 Collection, filtering and analyses of the samples.

2.3. Interpretation of data / results

Interpretation of the data was performed using Microsoft Office tools packages and cartographic material was represented with ArcMap 9.2 software. For drawing up cartographic material representation of spatial data we used 1:25000 topographic maps, satellite images from 2012 (source INIS), 1:50000 geological map, geographic coordinates obtained with GARMIN GPS.

3. Results and discussions

3.1. Variations of stable isotopic composition in precipitation, river and karst springs

We have collected and analyzed 103 water samples from rivers (samples collected at regular intervals), 37 samples of springs and 28 samples of meteoric water. Table 1 shows the maximum, minimum and mean values for δ18O and δ2H and d-excess for precipitation, rivers and karst springs.

Table 1 Stable isotopic composition in different water of Ocoale Plateau between April 2012 - March 2014

No.	Water sources	$\delta^{18}O$ (‰)			$\delta^{2}H$ (‰)			d-excess
		Min	Max	Mean	Min	Max	Mean	(‰)
1.	Precipitation	-17.8	-3.6	-9.1	-125	-22	-62	10.8
2.	Rivers	-23.1	-4.2	-10.8	-165	-27	-73	13.4
3.	Springs	-12.0	-10.9	-11.0	-82	-75	-75	13

Analyzing Figure 4 we can observe a relatively uniform distribution of rainfall along the LMWL, the slope being 7.49, with 0.5 lower than the global average (GMWL). Studies by Kern et al. and Forizs et al. (2004) obtained similar values thereof.

The isotopic composition of precipitation water from Gheţar is between -3.6 - - 17.8 ‰ for $\delta^{18}O$ and from -22 to -125 ‰ for $\delta^{2}H$. The minimum is recorded in December and the maximum in June 2012, air temperature being the main factor controlling these parameters.

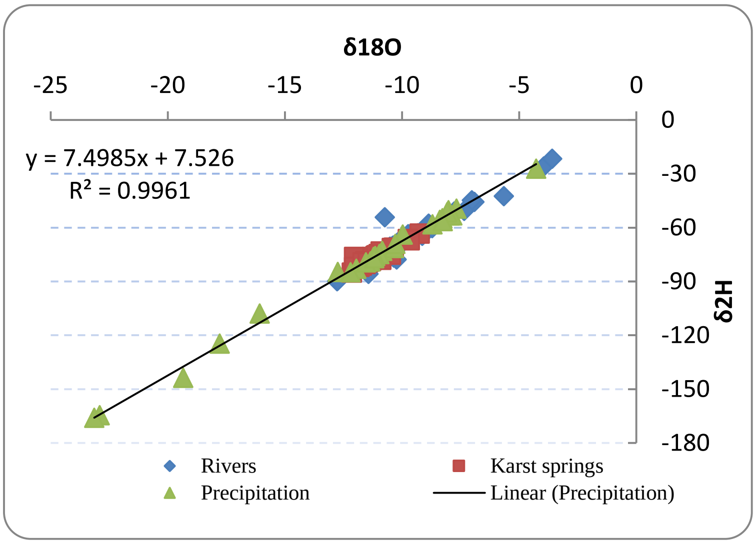


Figure 4 Stable isotopic composition of water from different sources and relation between $\delta^{18}O$ and $\delta^{2}H$.

In surface water, the values of $\delta^{18}O$ are between -4,2‰ and -23,1‰, and between -27 ‰ and -165‰ for δ2H. These values are explained based on of the season in which they were collected, and air temperature. The highest values can be explained by the process of evaporation (-4.28 ‰

in July) and the lowest value based on the condensing process water and deposited as snow (-23.1‰).

Debitor caves have isotopic composition between -10,9 ‰ (Poarta lui Ionele Cave) and -12,0‰ (No name Cave) for $\delta^{18}O$ and -75 - -82‰ for $\delta^{2}H$, the maximum was recorded in July 2012 and the minimum in June 2013.

3.2. Seasonal stable isotopes distribution in Ocoale Plateau waters

Data in Figure 5 shows variable values of stable isotopic composition of river and groundwaters on the plateau, due to strong fracturing and presence of several fault lines (Figure 2). If we look at the distribution of $\delta^{18}O$ in all four seasons (Figure 5), we observe a seasonal trend whit of minimum in June 2013 and the maximum in July 2012.

Thus, during the period July 2012 - March 2014, the isotopic composition of waters presented major fluctuations in spatial distribution, with a maximum in the summer of 2012 (-9.3 ‰ for $\delta^{18}O$ and -61 ‰ for $\delta^{2}H$) and a minimum in the same season in 2013 (-12‰ for $\delta^{18}O$ and -82‰ for $\delta^{2}H$). These variations in the isotopic composition in the same period could be due to the higher temperatures in 2012, with a monthly average to 18,2˚C compared with 2013, when they recorded a monthly average to 14,3˚C (Figure 5).

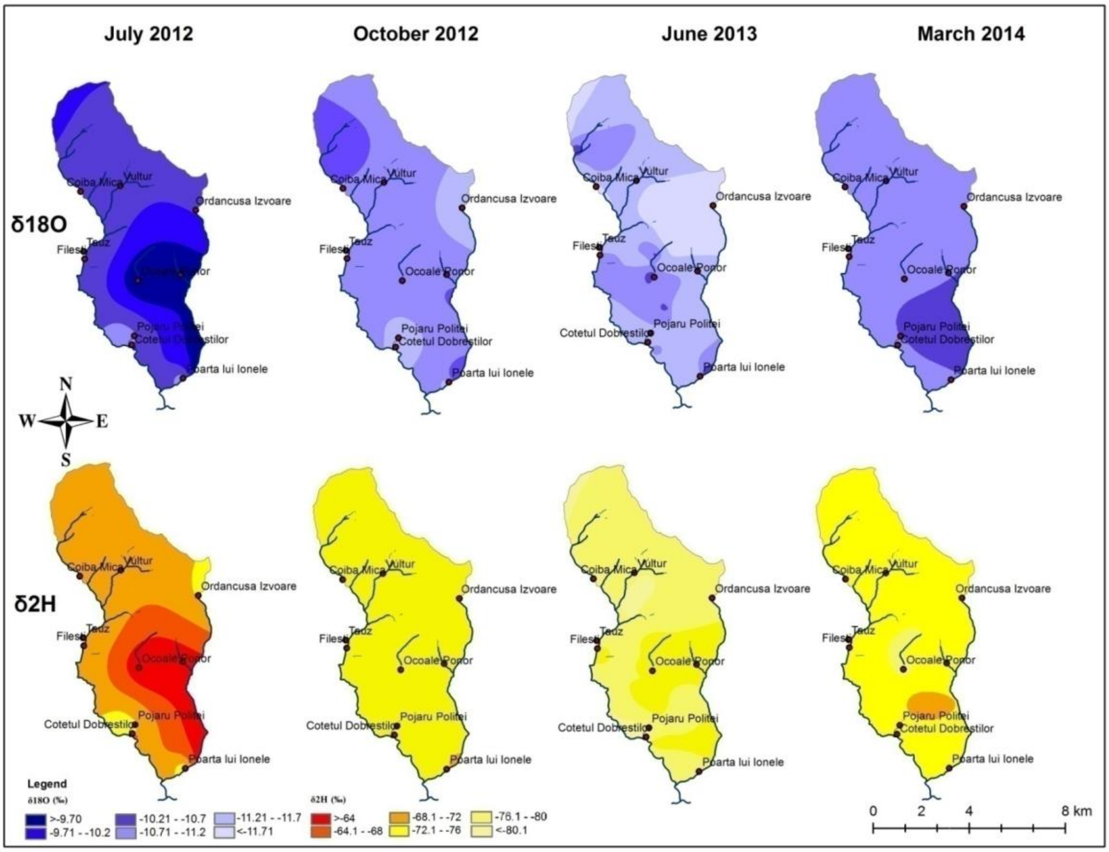
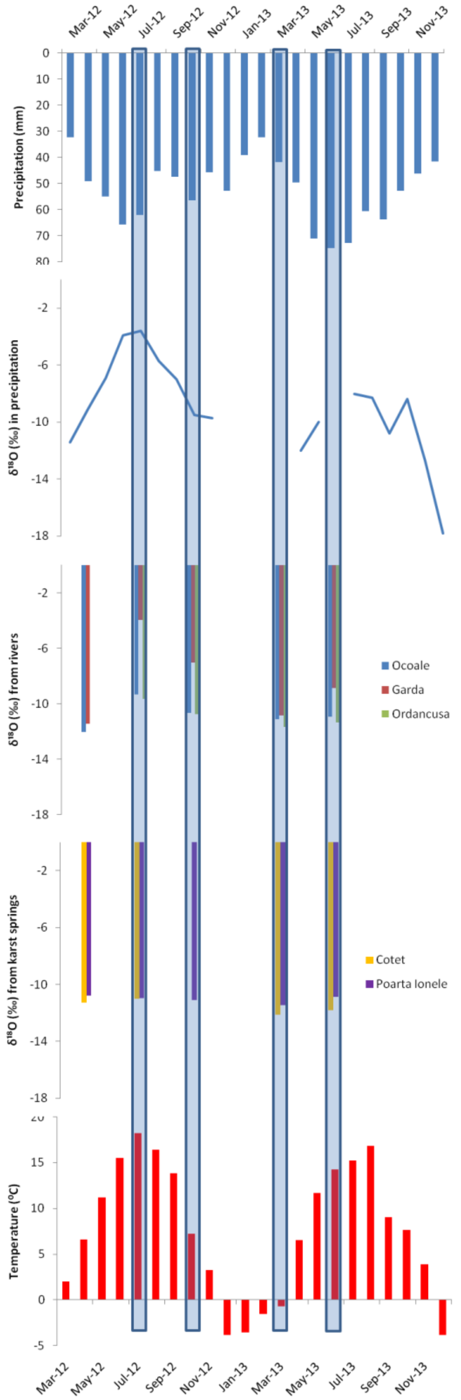
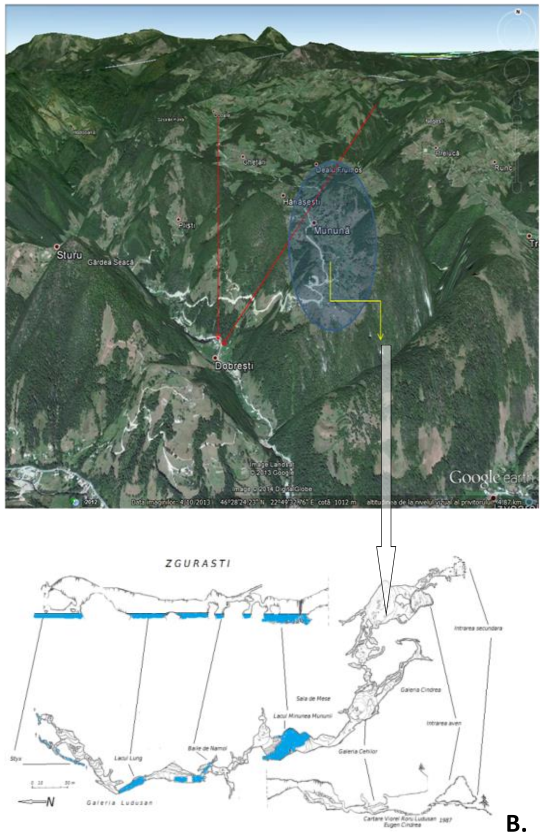


Figure 5 Seasonal and temporal stable isotopes distribution in the hydrographic system of Ocoale Plateau.

July 2012 (Figure 6) appears to be the month with highest value an isotopic composition of $\delta^{18}O$ and $\delta^{2}H$. The highest values are found in the southeastern part of the plateau, respectively in the Ocoale and Ordancușa (Moara lui Ivan area) rivers and Zgurasti – Poarta lui Ionele karst system. In October and March (in autumn and in the spring) the values of $\delta^{18}O$ are between -12 and -10,7‰, and for $\delta^{2}H$ between -71 and -76‰ throughout the plateau.



A.



B.

Figure 6 Correlation between precipitation (mm), air temperature (°C) from Ghețar village and $\delta^{18}O$ from precipitation, Ocoale, Gârda and Ordâncușa rivers and Coteț and Poarta lui Ionele spring (**A**). In right is represented the karst systems between Ocoale - Ordâncușa - Cotețul Dobreștilor (red lines) and Ocoale system (blue circle) - Zgurași Lake (yellow line and schematic reprezentation) - Poarta lui Ionele Cave (**B**).

The results suggest that a strong correlation exists between the local mean temperature and mean isotopic composition of rainfall (Figure 4) and these can be observed in the three karst systems (Figure 6). The differences in time and space between springs and rivers could give new details about the flowpaths at local level of groundwaters (Barbieri, 2005); however, more data is needed to have a consistent image.

Table 2 The value of $\delta^{18}O$ and $\delta^{2}H$ and correlation between river and springs

Period of collection	30.07.12		15.10.12		11.06.13		19.03.14	
Name of sample	**δ18O**	**δ2H**	**δ18O**	**δ2H**	**δ18O**	**δ2H**	**δ18O**	**δ2H**
Ordâncușa spring	-10.3	-73	-11.2	-76			-10.8	-74
Ordâncușa at Moara lui Ivan	-9.7	-64	-10.7	-72	-11.7	-81	-10.8	-74
Ocoale river	-9.3	-63	-10.7	-72	-11.1	-76	-11.1	-76
Cotetul Dobreștilor spring	-11.0	-75	-11.3	-76	-11.7	-81	-10.9	-75
Poarta lui Ionele spring	-10.9	-75	-11.1	-75	-11.4	-79	-10.8	-75
Gârda Seacă river	-10.7	-72	-10.9	-73	-11.6	-79	-11.1	-74

These large differences between the isotopic composition of water in the karts systems could be due to the variable time residence of water in the underground. In the karst systems Ocoale - Cotețul Dobreștilor and Ordâncușa - Cotețul Dobreștilor (Figure 6), the residence time of water is lower compared to Zgurăști - Poarta lui Ionele, because Zgurăști lake is the biggest underground lake of Romania, and mutes the external isotopic signal.

3.3. Deuterium excess

Deuterium excess (d-excess) is another parameter used in climatological and hydrological studies, to determine the vapor water sources (Peng et al., 2004). D-excess is defined by relationship between $\delta^{18}O$ and $\delta^{2}H$ and is calculated using the formula $d = \delta^{2}H - 8^{*} \delta^{18}O$ (Dansgaard, 1964) and has a value of about 10 at global level (Craig, 1961). In groundwaters, d-excess can be influenced by evaporation (before infiltration) processes and mixing of different types of waters (Jellani et al., 2015).

In this study, the seasonal distribution of d-excess during two years is presented, the values ranging between 4.3 and 20.3 ‰ (Figure 7). The highest value is registered in June 2013 (d = 20.3 ‰) and can be explained on the basis of forced (by rapid orographic ascent of water) precipitation events, increase of relative humidity and low air temperatures. The lowest values were registered in the same month in 2013, theses being possible influenced by high temperatures and decreasing relative humidity.

When values of d-excess are smaller than 10 ‰, this can offer information about a secondary evaporation process at the raindrop level that enters into a warm and dry atmosphere (Peng et al., 2007). In cases when d = ≈10 ‰, the origin of water vapors is from western direction, typical of Atlantic air masses (Vreča et al., 2006).

In spring and autumn months, the values of d-excess in precipitation are between 10 – 14 ‰, being maximum in winter and minimum in summer (Froehlich et al., 2002). Maximum values of d-excess in rivers are recorded in Cotetul Dobrestilor spring and Ordancusa River in October, June and March and the similar values in these could be explained by the underground hydrological connectivity of the two.

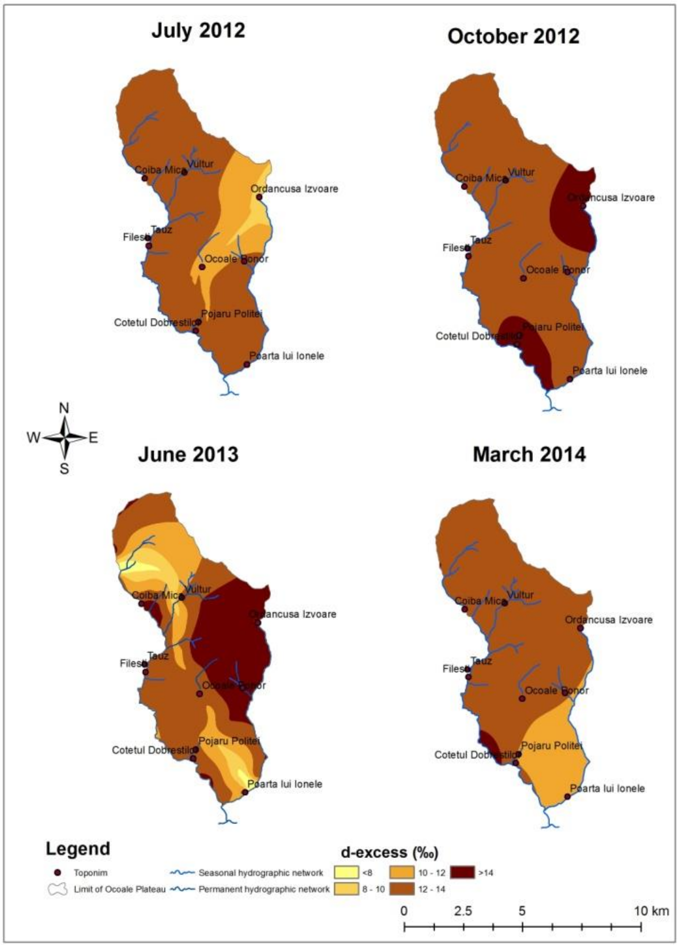


Figure 7 Temporal and seasonal distribution of d-excess in Ocoale Plateau.

In general, the d-excess coefficient has the smallest values in winter, but in this later case these low values are registered in June, indicating that the precipitation is coming mostly from continental sources, undergoing evaporation and recycling.

4. Conclusions

The rapid transfer of precipitation water in the underground supports the high degree of secondary permeability of the rocks in the investigated area, indicating a young to mature karst. In the higher area of the plateau we have identified a number of non-karst aquifers, clustered in detritical rocks with a very short period (weeks) for renewal of the water reserve, but at the same time extremely vulnerable to the effects of droughts. Clustered waters at greater depths in the karst systems have a longer time to renewal, but reduced discharge makes them also vulnerable to droughts, especially on medium or long term.

Acknowledgements
This paper has been prepared with the financial support of the project "Quality European Doctorate - EURODOC", Contract no. POSDRU/187/1.5/S/155450, project co-financed by the European Social Fund through the Sectoral Operational Programme "Human Resources Development" 2007-2013.

References

Bakalowicz M. 2005. Karst groundwater: A challenge for a new resources. *Hydrology Journal* 13: 148-160.

Balintoni J. 1997. *Geotectonica terenurilor metamorfice din România*. Carpatica Ed., 176 p., Cluj-Napoca.

Barbieri M., Boschetti T., Petitta M., Talinni M. 2005. Stable isotope (2 H, 18O and 87Sr/86Sr) and hydrochemistry monitoring for groundwater hydrodynamics analysis in a karst aquifer (Gran Sasso, Central Italy), *Applied Geochemistry* 20, 2063–2081.

Bleahu M., Dimitrescu R. 1957. Stratigrafia și tectonica Munților Apuseni (cu privire specială asupra cristalinului și Mezozoicului), *Anal. Rom.-Sov. (Geol. Geogr.),* Seria a 2-a, 2, 29-42.

Clark I.D., Fritz P. 1997. *Environmental isotopes in hydrogeology*, CRC Press LLC.

Craig H. 1961. Isotopic variation in meteoric waters. *Science* 133, 1702-1703.

Damm P., Lascu V., Ciubotărescu C. 1999. Platoul Ocoale, *Speomond* 4, 14-18.

Dansgaard W. 1964. *Stable isotope in precipitation*. Tellus, 16, 436-438.

Dimitrescu R., Bleahu M., Lupu M. 1997. *Harta geologică a României scara 1:50000, foaia Avram Iancu*, Editura IGR, București.

Fernandez-Cortes A., Calaforra J.M., Sánchez-Martos F. 2008. Hydrogeochemical processes as environmental indicators in drip water: Study of the Cueva del Agua (Southern Spain). *International Journal of Speleology* 37 (1): 41-52.

Fairchild I.J., McMillan E.A. 2007. Speleothems as indicators of wet and dry periods, *International Journal of Speleology* 36 (2) 69-74.

Ford D., William P. 2007. *Karst Geomorphology and Hydrology*. Chapman and Hall, London.

Fórizs I., Kern Z., Szántó Zs., Nagy, B., Palcsu, L., Molnár, M. 2004. Environmental isotopes study on perennial ice in the Focul Viu Ice Cave, Bihor Mountains, Romania. *Theoretical and Applied Karstology* 17, 61-69.

Ianovici V., Borcos M., Bleahu M., Patrulius, D., Lupu M., Dimitrescu, R. and Savu H. 1976. *Geologia Munților Apuseni*. Editura Academiei Republicii Socialiste România, București.

Jeelani Gh., Saravana Kumar U., Bhat Nadeem A., Sharma S., Kuman B. 2015. Variation of $\delta^{18}O$, δD and ^3H in karst springs of south Kasmir, western Himalayas (India). *Hydrological Processes* 29, 522-530.

Kern Z., Forizs I., Nagy B., Kázmér, M., Gál A., Szánto Z., Palcsu L., and Molnar M. 2004. Late Holocene environmental changes recorded at Ghețarul de la Focul Viu, Bihor Mountains, Romania, 1 *Theoretical and Applied Karstology*, 7, 51–60.

McGuire K.J. and McDonnell J.J., 2006. A review and evaluation of catchment transit time modeling, *Journal of Hydrology*, 330, 543-563.

McGuire K.J. and McDonnell J.J. 2007. Stable isotope tracers in watershed hydrology – book chapter from *Stable Isotopes in Ecology and Environmental Science.* Blackwell Publishing, 335-374.

Orășeanu I. 2003. The groundwater and surface water hydrology and geochemistry in the Gârda-Ghețar area (Bihor Mountains*), Proiect Apuseni, Final Report*.

Peng H., Mayer B, Harris S., Krouse H.R., 2004. A 10-yr record of stable isotope ratios of hydrogen and oxygen in precipitation at Calgary, Alberta, Canada. *Tellus* 56B, 147-159.

Perrin J., Jeannin P-Y., Zwahlen F. 2003. Epikarst storage in a karst aquifer: a conceptual model based on isotopic data, Milandre test site, Switzerland, *Journal of Hydrology* 279, 106-124.

Rusu T., Cocean P. 1992. Contribuții la studiul sistemului carstic Ocoale-Ghețar-Dobrești (Munții Bihorului). *Studii și cercetări geografice*, 37-44.

Sharp, Z. 2007. *Principles of stable isotope geochemistry*, Pearson Prentice Hall.

****Topographic map of Romania*, Edition 1985.

****Geological map of Romania*, 1:50000, Poiana Horea Sheet, 1980.

****Geological map of Romania*, 1:50000, Avram Iancu Sheet

****Ortophotoplans by INIS* (http://geoportal.ancpi.ro/geoportal/viewer/index.html)