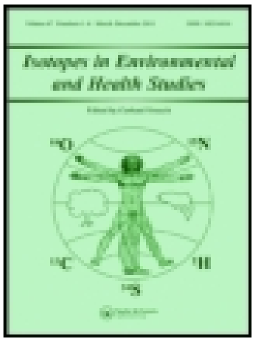

Isotopes in Environmental and Health Studies

ISSN: 1025-6016 (Print) 1477-2639 (Online) Journal homepage: https://www.tandfonline.com/loi/gieh20

Stable H and O isotope-based investigation of moisture sources and their role in river and groundwater recharge in the NE Carpathian Mountains, East-Central Europe

Carmen-Andreea Bădăluță, Aurel Perșoiu, Monica Ionita, Viorica Nagavciuc & Petruț-Ionel Bistricean

ISOTOPES IN ENVIRONMENTAL AND HEALTH STUDIES
https://doi.org/10.1080/10256016.2019.1588895

Stable H and O isotope-based investigation of moisture sources and their role in river and groundwater recharge in the NE Carpathian Mountains, East-Central Europe†

Carmen-Andreea Bădăluță[a,b,c,d], Aurel Perșoiu[a,e], Monica Ionita[d], Viorica Nagavciuc[a,c,f,g] and Petruț-Ionel Bistricean[b,h]

[a]Stable Isotope Laboratory, Ștefan cel Mare University of Suceava, Suceava, Romania; [b]Department of Geography, Ștefan cel Mare University of Suceava, Suceava, Romania; [c]Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences MTA, Budapest, Hungary; [d]Alfred Wegener Institute, Helmholtz Center for Polar and Marine Research, Bremerhaven, Germany; [e]Emil Racoviță Institute of Speleology, Romanian Academy, Cluj Napoca, Romania; [f]Faculty of Forestry, Ștefan cel Mare University of Suceava, Suceava, Romania; [g]Department of Geography, Johannes Gutenberg University, Mainz, Germany; [h]Regional Meteorological Center of Moldova, Suceava, Romania

ABSTRACT

The region situated between the mountain area and the lowlands in NE Romania (East-Central Europe) is experiencing increased competition for water resources triggered by a growing population, intensification of agriculture, and industrial development. To better understand hydrological cycling processes in the region, a study was conducted using stable isotopes of water and atmospheric trajectory data to characterize regional precipitation and vapour sources derived from the Atlantic Ocean, Mediterranean and Black Seas, as well as recycled continental moisture, and to assess and partition these contributions to recharge of surface and groundwater. Atmospheric moisture in the lowlands is found to be predominantly delivered along easterly trajectories, while mountainous areas appear to be dominated by North Atlantic Ocean sources, with moisture transported along mid-latitude, westerly storm tracks. Large-scale circulation patterns affect moisture delivery, the North Atlantic Oscillation being particularly influential in winter and the East Atlantic pattern in summer. Winter precipitation is the main contributor to river discharge and aquifer recharge. As winter precipitation amounts are projected to decrease over the next decades, and water abstraction is expected to steadily increase, a general reduction in water availability is projected for the region.

ARTICLE HISTORY
Received 28 September 2018
Accepted 22 January 2019

KEYWORDS
Carpathian Mountains; groundwater; hydrogen-2; moisture sources; oxygen-18; precipitation; river; teleconnection patterns

CONTACT Carmen-Andreea Bădăluță carmen.badaluta@usm.ro Stable Isotope Laboratory, Ștefan cel Mare University of Suceava, Suceava, Romania; Aurel Perșoiu aurel.persoiu@gmail.com Stable Isotope Laboratory, Ștefan cel Mare University of Suceava, Suceava, Romania

†'Population on 1 January by age groups and sex–functional urban areas'. Eurostat. (http://ec.europa.eu/eurostat/web/cities/data/database).

Supplemental data for this article can be accessed at doi:10.1080/10256016.2019.1588895.

1. Introduction

Water availability is a major worldwide concern arising from a growing population, intensification of agriculture, and industrial growth [1]. The cumulative impact of these stressors, on the backdrop of ongoing climate changes, exerts an increasing pressure on the availability of water sources, generally leading to competition and/or conflict between users, depletion of resources, and social or economic losses [2]. While numerous studies have addressed these issues in different parts of the world, no comprehensive study has yet been conducted in the wider Carpathian region (Romania, Hungary, Ukraine, Moldavia), a region home to more than 80 million people, and acknowledged as one of the largest agricultural regions of Europe. The region is situated within the Danube River watershed, the second largest European river (after Volga), its tributaries in the area being fed by precipitation derived from both North Atlantic Ocean and Mediterranean Sea vapour sources [3]. The Suceava River, located in NE Romania (East-Central Europe), is one of the major tributaries of the Siret River, which is the largest Carpathian tributary of the Danube River. Surface and groundwater from this watershed is the main water source for more than 1 million people and agriculture in Suceava, Botoșani and Iași counties (Figure 1).

Local populations are competing with agriculture, natural vegetation and industry for water, exerting increasing cumulative pressure on these resources. This problem is exacerbated by increased use of groundwater for irrigation, Romania being the fifth largest exporter of groundwater per capita in the world [5]. The continental climate of the region (with hot and dry summers, and an eastwardly increasing soil moisture deficit) exerts significant constraints on the agricultural use of the land, and, historically, has resulted in catastrophic crop failures. Furthermore, over the past decades, the study region has experienced pronounced winter warming, with average winter temperatures increasing by about 2.5 °C between 1961 and 2007 [6]. Assuming winter precipitation amounts will decrease over the next few decades [7–11], sustainable agricultural yields may necessitate additional demands on rivers, surface and ground water resources. Overall, given contemporary conditions which suggest mounting pressure on already limited water supplies, there is a clear need to improve understanding of water cycling processes, including large-scale atmospheric circulation patterns, to comprehensively evaluate sustainability of these resources while meeting the competing interests of all water users (e.g. [12]).

In hydrology, the stable isotopes of hydrogen and oxygen are established tools for tracing sources of atmospheric moisture, precipitation and recharge sources to surface and ground water [13–15]. Climate-driven patterns in the stable isotope distribution of oxygen and hydrogen in regional air masses across Europe are well understood, and these can be locally applied to distinguish between different moisture sources and tracks, to apportion seasonal contributions of various recharge sources to rivers and/or groundwater [16], and to identify and potentially quantify post-precipitation processes (e.g. evaporation) [17], etc. So far, only two studies have demonstrated this approach in Romania [18,19]. The objectives of the current study are to refine previous isotope-based assessments, and in particular to identify the principal moisture sources feeding rainfall in NE Romania and to understand their role in recharging local aquifers and their impact on potential sustainability of water resources in the region.

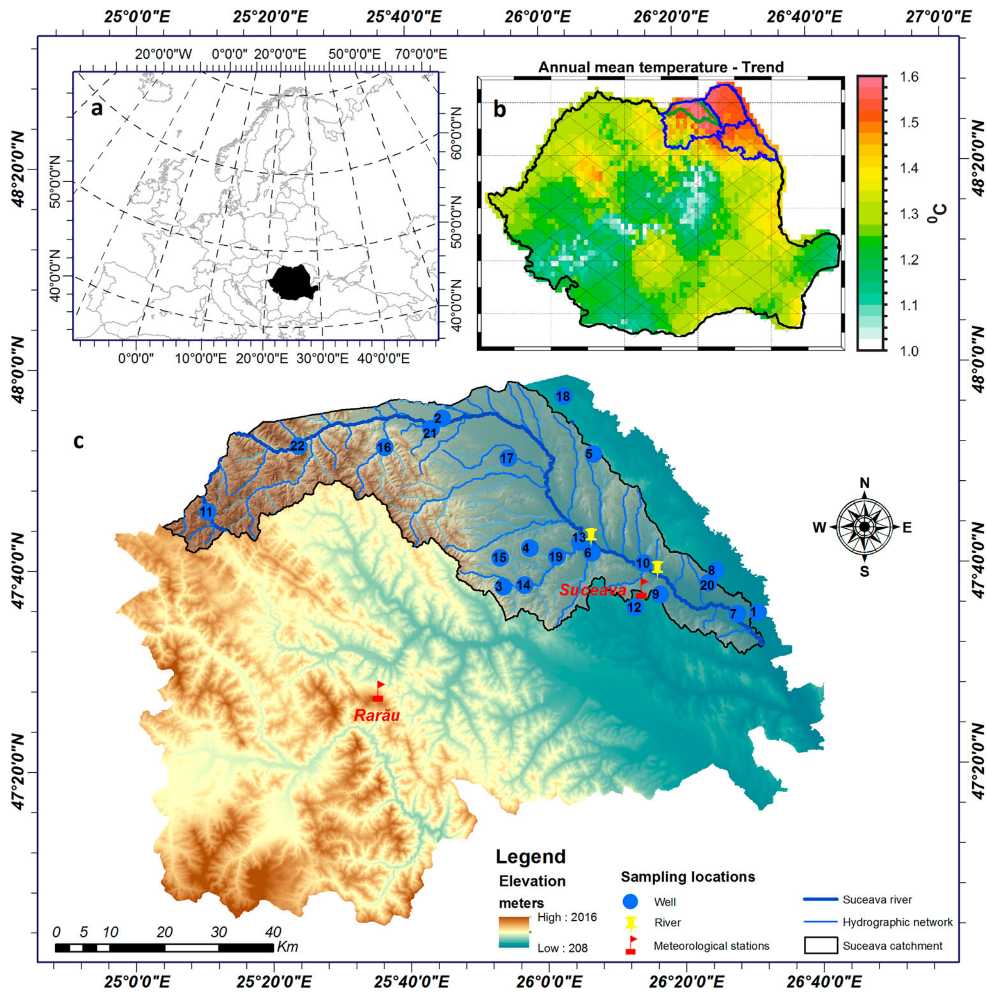

Figure 1. Location of the study site in Europe (a) and Romania (b). The map in (b) shows the annual mean temperature trend over Romania for the period 1961 – 2013 based on ROCADA dataset [4]. Panel (c) shows the location of the studied drainage basin with the sampling points locations.

2. Study area

The Suceava River (170 km long) has its headwaters at 1508 m above sea level (m.a.s.l.), in the Obcina Mestecăniș Mountains. One quarter of the 3800 km^2 drainage basin is comprised of mid-altitude mountains, with the remainder being low-altitude (300–500 m a.s.l.) tableland (Figure 1). The mean annual river discharge is 16.1 m^{3}s^{-1}, varying between 0.94 and 1700 m^{3}s^{-1}, with minima occurring in early autumn, and maxima in early summer, as driven by the precipitation cycle characterized by a June maximum. The Soloneț River (31 km long) is a tributary of Suceava River (210.7 km^2) located on the Suceava Plateau [20], with a mean annual discharge of 1.3 m^{3}s^{-1}, varying between 0.1 and 137 m^{3}s^{-1}, with a regime similar to that of the Suceava River.

The climate in the Suceava River watershed is temperate-continental, with a mean annual temperature of 8 °C, and a minimum occurring in January and a maximum in

July. Slightly lower temperatures are recorded in the western, mountainous sector [21]. Based on data for the 1961–2010 reference period, the mean annual precipitation is 607 mm, being slightly higher to the west (700 mm at Izvoarele Sucevei), and lower to the east (580 mm at Liteni) [22]. 73.5 % of annual precipitation falls between April and September. Evapotranspiration rates in NE Romania are estimated at 600 to 800 mm a^{-1} [23]; which exceeds the precipitation rate. The minima evapotranspiration rates occur in winter (45 to 60 mm) and maxima occur in summer (300 to 400 mm).

3. Data and methods

Monthly precipitation samples were collected between December 2012 and December 2016 at Rarău (RR, 47°27′N, 25°34′E, 1536 m a.s.l.) and Suceava (SV, 47°38′N, 26°14′E, 352 m a.s.l.) stations (Figure 1). River water was collected monthly between November 2014 and December 2016, from Suceava River at Suceava (Figure 1) and from its tributary, Soloneț, ca. 20 km west of Suceava (Figure 1). A total of 84 groundwater samples were collected seasonally in October 2014, February 2015, May 2015 and August 2015 from 21 dug wells (between 3 and 24 m deep – Table S2) spread throughout the Suceava River Basin (Figure 1). Well and river samples were collected as grab samples (30–50 cm below the surface of the water) in 20 mL HDPE scintillation vials. Precipitation water was collected continuously using tube-dip-in 5 L water collectors (IAEA, 2014). At the end of each month, a sample was taken from the container and stored until analyzed at 4 °C in 20 mL HDPE scintillation vials. In winter, snowfall samples were collected in open plastic containers (10 L, 40 cm deep), allowed to melt at room temperature at the end of each month, and stored as per water samples described above.

Water samples were analyzed for stable isotopic composition at the Stable Isotope Laboratory, Ștefan cel Mare University (Suceava), using a Picarro L2130*i* CRDS analyzer coupled to a high precision vaporizing module. Prior to the analyses, all samples were filtered through 0.45 µm nylon membranes. Each sample was manually injected into the vaporization module multiple times, until the standard deviation of the last four injections was less than 0.03‰ for $\delta^{18}O$ and 0.3‰ for $\delta^{2}H$, respectively. The average of these last four injections was normalized on the SMOW-SLAP scale using two internal standards calibrated against VSMOW2 and SLAP2 standards provided by IAEA. A third standard was used to check the long-term stability of the analyzer. The stable isotopic composition of oxygen and hydrogen are reported using standard δ notation, with precision estimated to be better than 0.16 ‰ for $\delta^{18}O$ and 0.7 ‰ for $\delta^{2}H$, respectively, based on repeated measurements of an internal standard.

Daily precipitation amount, air temperature and discharge data were provided by the National Meteorological Administration and the Siret-Bacău Basin Waters Administration, respectively. The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model [24] was used to reconstruct the trajectories of precipitation events higher than 3 mm (contributing >90 % of the total volume of monthly precipitation). The model used the data generated by the Global Data Assimilation System (GDAS) and was set to compute trajectories backwards for 72 h, at 500 m above ground level (m.a.g.l.). We have also calculated trajectories at 1000 and 1500 m.a.g.l, to check for possible changes with increased altitude, but differences were minor. The 500 m.a.g.l. altitude was chosen as it is above local topographic influences and it is also close to the mean value of the cloud base during precipitation events. For the calculation of the precipitation source percentages we have calculated the sum of precipitation amount from one direction for each analyzed month. For this, we used the formula:

$$\mathrm{PSP} = \frac{\sum \mathrm{PS}*100}{\mathrm{Pmonth}}, \tag{1}$$

where PSP is precipitation source percentage, PS is amount of precipitation from one direction and Pmonth represents the total rainfall in a month.

For large-scale atmospheric circulations, we used the monthly means of geopotential height at 500 mb (Z500), the zonal wind (U500) and the meridional wind (V500) at 500 mb level from the Twentieth Century Reanalysis (V2) data set (NCEPv2, [25–27]) on a 2° × 2° grid, for the period 1871–2012.

The spatial variability of stable isotopes in groundwater was mapped using the ordinary kriging method [28]. For the interpolation of the underlying data (see maps in section 5.2), we used the empirical semivariogram of δ^{18}O and *d*-excess residuals, based on multiple regression and ordinary kriging, with the following steps:

(i) build a raster grid of δ^{18}O and *d*-excess variance depicted by the multiple regression model derived from geographic variables (latitude, longitude, altitude and distance);
(ii) create a residual grid (ordinary kriging interpolation) using the theoretical semivariogram based on adjusted residuals from the multiple regression model;
(iii) sum the raster grid variance with residual grid to obtain the final map shown in section 5.2.

The empirical semivariogram was expressed as:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} (Z_i - Z_{i+h})^2, \tag{2}$$

where $\gamma(h)$ is the semivariance of values separated by distance h, Z_i is the values of the variable in coordinate points $x_{i,}$ Z_{i+h} is the values of the variable in the points located at a distance h (by the coordinates x_{i+h}) from the coordinate points x_i and $N(h)$ is the number of points located at a distance h.

To identify the physical mechanisms responsible for the connection between the winter and summer temperature at Suceava meteorological station and the large-scale atmospheric circulation, we constructed the composite maps of Z500 standardized anomalies for each season by selecting the years when the value of the normalized time series of the winter and summer temperature was >1 standard deviation (high) and <−1 standard deviation (low), respectively. This threshold was chosen as a compromise between the strength of the climate anomalies associated with the temperature anomalies and the number of maps that satisfy this criterion. Further analysis has shown that the results are not sensitive to the exact composite threshold value used (not shown).

4. Results – stable isotopes in precipitation, rivers and groundwaters

The dataset of non-weighted, monthly $\delta^{18}O$ and $\delta^{2}H$ in precipitation at the two stations is shown in Table S1, and plotted in Figure 2 against air temperature and precipitation amount. At Suceava station (SV, 352 m.a.s.l.), the stable isotopic composition of precipitation (δ_{prec}) varies from summer to winter between 1.1 and −27.1 ‰ for $\delta^{18}O$, and between −10 and −205 ‰ for $\delta^{2}H$, with mean values of −10.8 and −77 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively. At Rarău station (RR, 1536 m.a.s.l.) the δ values are found to be fairly similar in winter but much lower in summer than at SV station. Values vary from summer to winter between −4.3 and −21.7 ‰ for $\delta^{18}O$, and between −33 and −163 ‰ for $\delta^{2}H$, with mean values of −11.8 and −84 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively. The maximum deuterium-excess (*d*-excess) values (Table S1) are between 16.9 ‰ (December 2013, SV) and 22.2 ‰ (November 2013, RR), while the minima are −3.6 ‰ (August 2013, RR) and −21 ‰ (February 2016, SV). The stable isotopic composition of precipitation shows a good correlation with air temperature, with maxima in June–August and minima in December–February (Figure 2).

The local meteoric water lines (Figure 3), calculated using the amount-weighted least-square regression, are close to the global meteoric water line (GMWL, defined by the equation $\delta^{2}H = 8.17*\delta^{18}O + 10.35$; [29,30]), showing a stronger influence of evaporation at Suceava ($\delta^{2}H = 7.4*\delta^{18}O + 2.7$), compared with the wetter Rarău station ($\delta^{2}H = 8.1*\delta^{18}O + 12.4$).

Monthly river $\delta^{18}O$ and $\delta^{2}H$ (δ_{river}) values are shown in Table S1 and plotted in Figure 4. The stable isotopic composition of Suceava River water varies between −8.8 and −10.8 ‰ for $\delta^{18}O$, and between −63 and −75 ‰ for $\delta^{2}H$ (in August and February 2015, respectively); while in the Soloneț River, δ values range between −8.2 and −10.7 ‰ for $\delta^{18}O$,

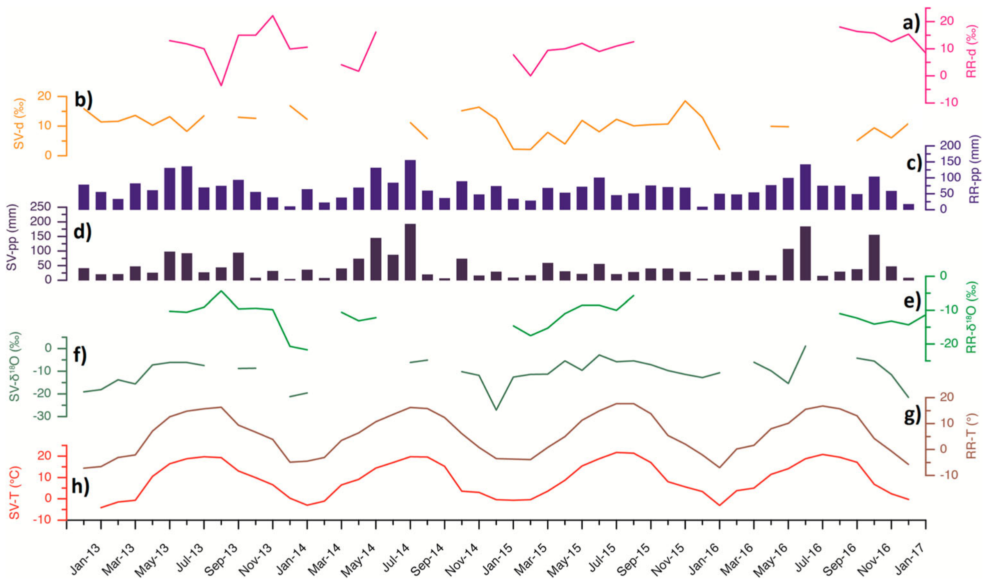

Figure 2. Monthly time series *d*-excess (d) at (a) Rarău station (RR) and (b) Suceava station (SV), precipitation amount (pp) at RR (c) and SV (d), precipitation ($\delta^{18}O$) at RR (e) and SV (f) and air temperature (T) at RR (g) and SV (h).

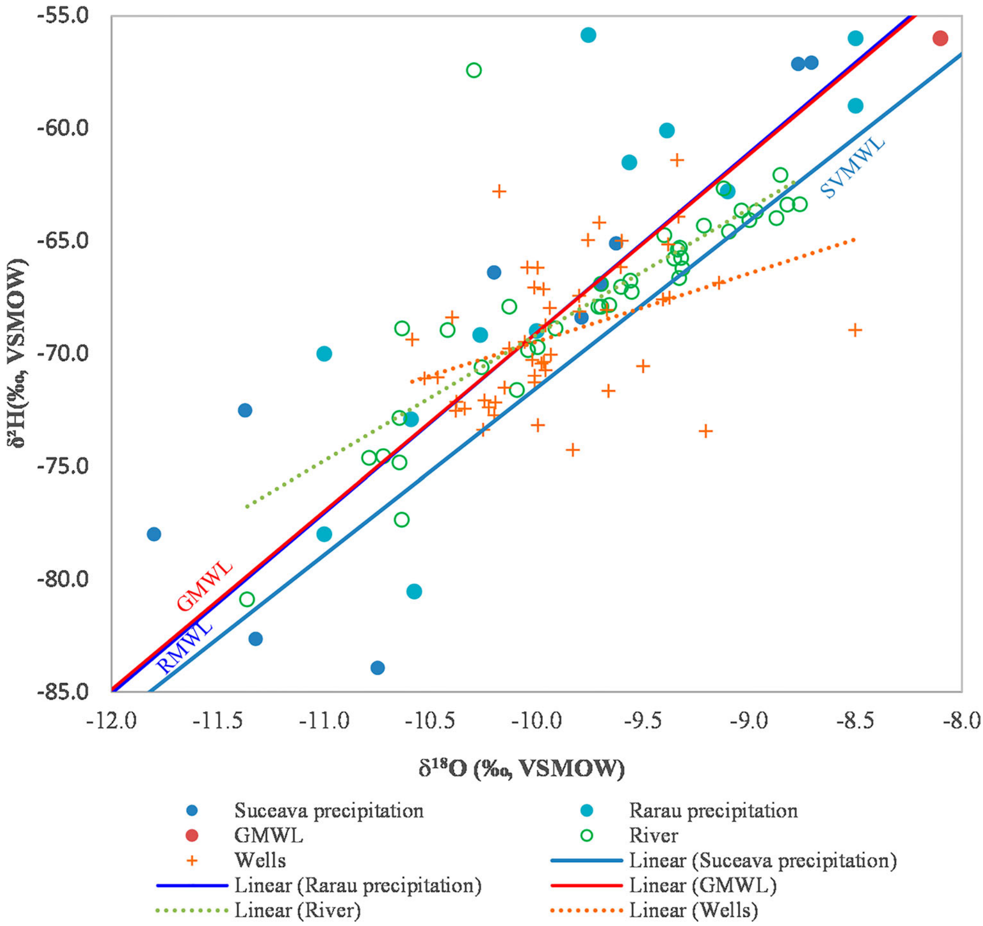

Figure 3. Local Meteoric Water Lines and River Water Lines for precipitation (blue line), surface (green line) and groundwaters (orange line) in the Suceava Watershed.

and between −61 and −75 ‰ for δ^2H (in July 2016 and May 2015, respectively). The average values of δ^{18}O and δ^2H were −9.6 and −67 ‰ for both Suceava, and Soloneț, compared to −10.8 and −77 ‰ in precipitation at Suceava. The regression line between the plotted δ values gives a river water line (RWL) defined by the equations $\delta^2H = 6.2*\delta^{18}O–7.2$ for Suceava and $\delta^2H = 5.8*\delta^{18}O–11.4$ for Soloneț, respectively (Figure 3). Low flow conditions during July through September were characterized by maximum δ values, while during high flow conditions in spring and early summer, streamflow had average δ values. The *d*-excess values in river water ranged from 5.1 to 12.3 ‰ (with minimum in summer), with a mean of 9.9 ‰ for the Suceava River and 9 ‰ for the Soloneț River; both the extremes and means being lower than in precipitation (Table S1).

The stable isotopic composition of groundwater (δ_{ground}, Table S2) shows muted variability compared to precipitation and river water, ranging between −8.5 and −10.6 ‰ for δ^{18}O, and −61 and −74 ‰ for δ^2H, respectively. Groundwater δ^{18}O and δ^2H values are rather stable throughout the year at most stations, with the exception of Cacica, Poieni Solca and Pârteștii de Jos. Groundwater *d*-excess values are also less variable than in

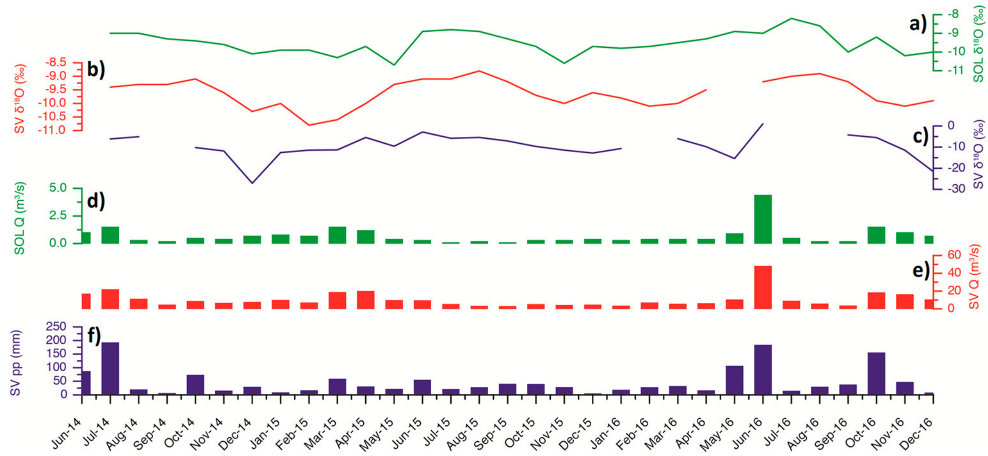

Figure 4. Monthly time series of river δ[18]O of (a) Soloneț River (SOL) and (b) Suceava River (SV) δ[18]O in precipitation at Suceva station (c), river discharge (Q) of SOL (d) and SV (e) rivers and precipitation amount (pp) at Suceava station (f).

precipitation in rivers, ranging from 6.6 to 11.5 ‰, with a minimum in February, a maximum in August, and a mean value of 9.8 ‰ (see section 5.2).

5. Discussion

5.1. Links between the stable isotopic composition of precipitation water and regional air temperature, large-scale atmospheric circulation and moisture sources

A 1100 m elevation difference between Suceava and Rarău stations results in only a limited difference in the δ^{18}O and δ^{2}H values of precipitation. There are differences close to 3 ‰ for δ^{18}O (−8.6 and −11.6 ‰ averages at SV and RR, respectively) and ~21 ‰ for δ^{2}H, (−61.4 and −82.4 ‰ averages at SV and RR, respectively) for the concurrent study periods (May 2013–May 2014 and January–August 2015). We estimate an average altitude gradient of 0.27 ‰/100 m for δ^{18}O, similar to the average worldwide gradient of 0.26 ‰/100 m calculated by Poage and Chamberlain [31], and in agreement with values of 0.21 ‰/100 m in the nearby Carpathian Mountains of Slovakia [32].

Analysis of the stable isotope *versus* temperature relationship shows a high correlation at both Suceava station ($r = 0.73$) and Rarău station ($r = 0.81$), while the correlation between δ_{prec} and precipitation amount is less pronounced ($r = 0.41$ for Suceava, $r = 0.34$ for Rarău). However, dissimilar patterns are noted during summer when δ_{prec} and precipitation amount are positively correlated only at Suceava ($r = 0.47$), whereas the correlation at Rarău is insignificant ($r = -0.06$). Overall, this suggests that amount effects during heavy summer convective rains play an important role in determining δ_{prec}.

Air temperature variability in the study region is known to be controlled by complex interplay between the various large-scale modes of climate variability controlling moisture delivery to the precipitation site [6]. Analyses of correlation between air temperature and the main teleconnection indices show a positive relationship with North Atlantic

Oscillation (NAO), the East Atlantic pattern (EA), the East Atlantic/Western Russia pattern (EA/WR), the Atlantic Multidecadal Oscillation (AMO) and the Arctic Oscillation (AO) and negative correlations with the Polar/Eurasia pattern (POL) and the Scandinavian pattern (SCA) (Table 1). In winter, the climatic conditions in the Central and Eastern part of Romania (CEE) are influenced by the NAO, the main mode of climatic variability in the northern hemisphere [33,34], which in turn is influenced by the EA pattern that has an important role in the location and strength of NAO dipole [35]. The positive phase of NAO (when the atmospheric pressure is below average in Iceland and above it in the Azores) is associated with higher than normal temperatures in CEE and Southern Europe and the precipitation source is predominantly Atlantic. Conversely, the negative phase of the NAO is linked to low temperatures in CEE and a southward displacement of the westerlies, carrying moisture from North Atlantic towards CEE and the Mediterranean Sea. This can be also observed when looking at the composite maps between the winter temperature at Suceava station (located in the north-eastern part of Romania) and the winter geopotential height at 500 mb. Positive temperature anomalies are associated with a dipole like structure in the Z500 field, that projects onto the positive phase of NAO (Figure 5(a)), but a little bit shifted towards Europe. This dipole-like structure, characterized by positive Z500 anomalies over the central North Atlantic Ocean extending up to the eastern part of Europe and negative Z500 anomalies centered on Iceland, favors the advection of warm and moist air over the analyzed region. Negative temperature anomalies in the north-eastern part of Romania, are associated with a center of positive Z500 anomalies around Iceland and a center of negative Z500 anomalies over the

Table 1. Precipitation sources calculated based on HYSPLIT trajectory model at 500 m agl. The percentages are calculated for rainfall events larger than 3 mm/day (hence the TP values is less than 100 %).

Year	Season	*d*-excess (‰)	ATL	MED	CONT	BS	AR	TP
2013	Winter	13.0	0.0	18.4	24.7	9.6	0.0	52.7
	Spring	12.4	19.5	8.8	48.8	0.0	0.0	77.1
	Summer	10.9	20.8	0.0	62.4	0.0	0.0	83.2
	Autumn	12.8	9.4	0.0	45.9	0.0	28.4	83.6
	Annual	**12.3**	**12.4**	**6.8**	**45.5**	**2.4**	**7.1**	**74.2**
2014	Winter	14.6	19.5	0.0	23.9	0.0	0.0	43.5
	Spring	4.0	30.1	12.1	33.7	0.0	9.4	85.2
	Summer	8.4	49.9	0.0	22.4	2.4	12.8	87.5
	Autumn	15.8	4.2	0.0	33.7	0.0	40.3	78.2
	Annual	**10.7**	**25.9**	**3.0**	**28.4**	**0.6**	**15.6**	**73.6**
2015	Winter	5.6	22.3	24.0	20.1	0.0	0.0	66.4
	Spring	7.9	34.4	0.0	40.6	5.1	0.0	80.2
	Summer	10.1	37.7	0.0	28.6	0.0	14.6	81.0
	Autumn	13.2	15.9	14.8	47.5	0.0	0.0	78.2
	Annual	**9.2**	**27.6**	**9.7**	**34.2**	**1.3**	**3.7**	**76.4**
2016	Winter	7.5	30.9	4.1	9.7	0.0	0.0	44.8
	Spring	9.9	22.8	0.0	47.7	11.2	0.0	81.7
	Summer	–	24.1	3.4	27.0	23.0	0.0	77.5
	Autumn	**6.8**	**12.7**	**0.0**	**59.3**	**0.0**	**13.2**	**85.1**
	Annual	**8.1**	**22.6**	**1.9**	**35.9**	**8.6**	**3.3**	**72.3**
Average 2013–2016	**Winter**	**10.2**	**18.2**	**11.6**	**19.6**	**2.4**	**0.0**	**51.8**
	Spring	**8.6**	**26.7**	**5.2**	**42.7**	**4.1**	**2.3**	**81.1**
	Summer	**9.8**	**33.1**	**0.9**	**35.1**	**6.4**	**6.9**	**82.3**
	Autumn	**12.2**	**10.5**	**3.7**	**46.6**	**0.0**	**20.5**	**81.3**

ATL – Atlantic Ocean, MED – Mediterranean Sea, CONT – Continental sources, BS – Black Sea, AR – Arctic Ocean, TP – Total percentage of precipitation sources.

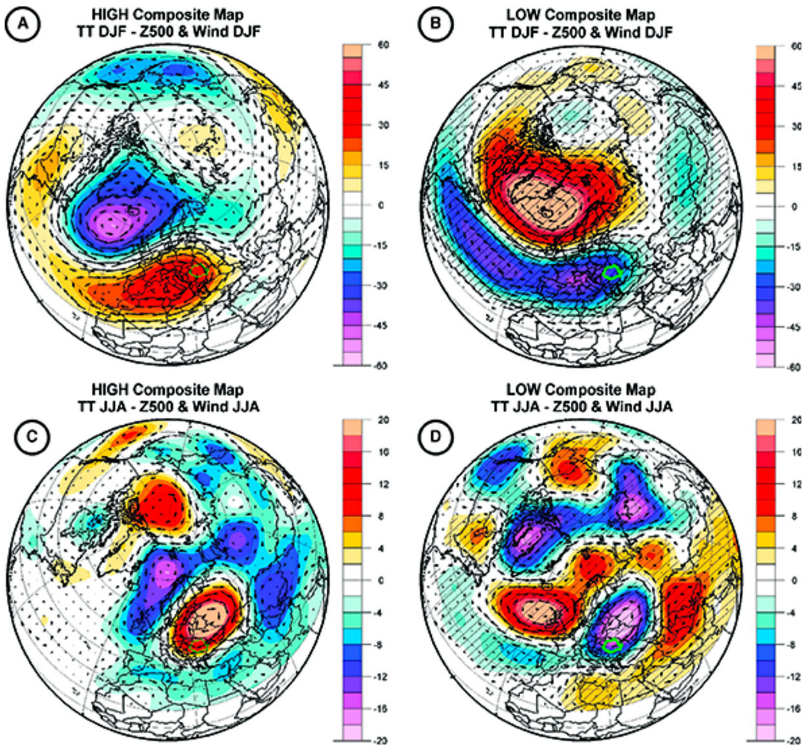

Figure 5. (a) The high (TT >1 standard deviation) composite map between winter mean temperature (TT) at Suceava station and winter (DJF) geopotential height at 500 mb (Z500 – shaded areas) and winter 500 mb wind vectors (arrows); (b) low (TT >0.75 standard deviation) composite map between winter mean temperature (TT) at Suceava station and winter geopotential height at 500 mb (Z500 – shaded areas) and winter 500 mb wind vectors (arrows); (c) as in (a) but for summer TT and summer Z500 and (d) as in (b), but for summer TT and summer Z500.

whole central North Atlantic Ocean extending until the eastern part of Europe. This dipole-like structure, associated with negative temperature anomalies over the analyzed region, projects well onto the negative phase of NAO (Figure 5(b)).

In summer, the action of atmospheric pressure centers on temperature and moisture sources is more complex than in winter, due to blocking structures and highly dynamic Rossby waves meandering over Europe [36–38]. High temperatures are associated with a stationary anticyclonal structure over CEE in which the Rossby waves act in the convergence areas and the moisture sources is predominantly from the eastern part of Europe [37]. These modes of climate variability are affecting the δ_{prec} differently, with the EA, NAO and AO pattern having a stronger influence during winter (Figure 6), while during summer, δ_{prec} shows a strong correlation with the AMO and EA. Positive temperature anomalies, over the north-eastern part of Romania, are associated with a classic 'omega' blocking pattern [39] characterized by a high pressure system over the whole eastern part of Europe (Figure 5(d)) and flanked by a low pressure system on the left and right. In general, these kind of blocking situations are associated with heatwaves and droughts over the eastern part of Europe, like the exceptionally dry and warm summer of 2010 [40]. Positive temperature anomalies tend to occur near the centre of the block, where

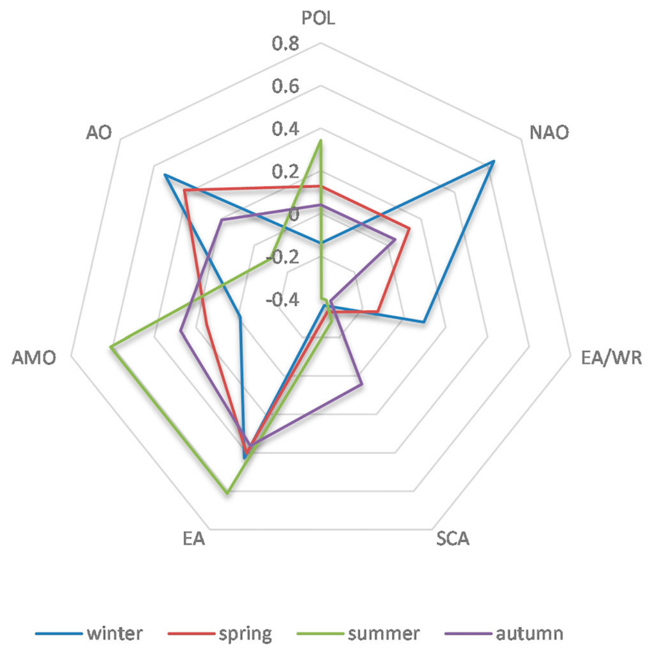

Figure 6. Correlation coefficient between air temperature at Suceava station and teleconnection patterns for winter (blue line), spring (red line), summer (green line) and autumn (purple line) seasons for the period 1961 - 2016. Teleconnection patterns abbreviations: NAO – North Atlantic Oscillation, EA/WR – East Atlantic/Western Russia, SCA – Scandinavian, EA – East Atlantic, AMO – Atlantic Multidecadal Oscillation, AO – Arctic Oscillation, POL – Polar/Eurasia.

northward displaced subtropical air, descending air motions and reduced cloudiness contribute to abnormally warm surface temperatures (Figure 5(c)). Negative summer temperature anomalies, over the north-eastern part of Romania, are associated with a wave-train in the Z500 field, with positive Z500 anomalies over the central North Atlantic Ocean and the British Isles and negative Z500 anomalies over the eastern part of Europe. This kind of pattern favours the advection of cold air from the north towards the southern and eastern part of Europe (Figure 5(d)).

These differences are clearly discernible when identifying the moisture sources based on the analysis of *d*-excess values of precipitation water. *d*-excess values in precipitation are an indication of changes in conditions at the moisture sources (or changes of the moisture sources), recycling processes along the moisture tracks [41] or reorganization of the atmospheric circulation [42]. Analyses of the mean *d*-excess value show small differences between Rarău (11 ‰) and Suceava (10.3 ‰) stations, close to the average global value of 10 ‰. The maximum values of *d*-excess (between 12 and 18 ‰) are recorded in autumn at both stations, and minimum values (between 2 and 8 ‰) are found in winter (January–February) and spring. For a better interpretation of *d*-excess values, we analyzed the trajectories of the air masses delivering moisture to the study site, using the HYSPLIT back-trajectory model [24]. Between 2013 and 2016, 166 individual trajectories were computed (Figure 7 and Table 1). Our data show that during spring and autumn most of the moisture at our site is coming along eastern trajectories or is

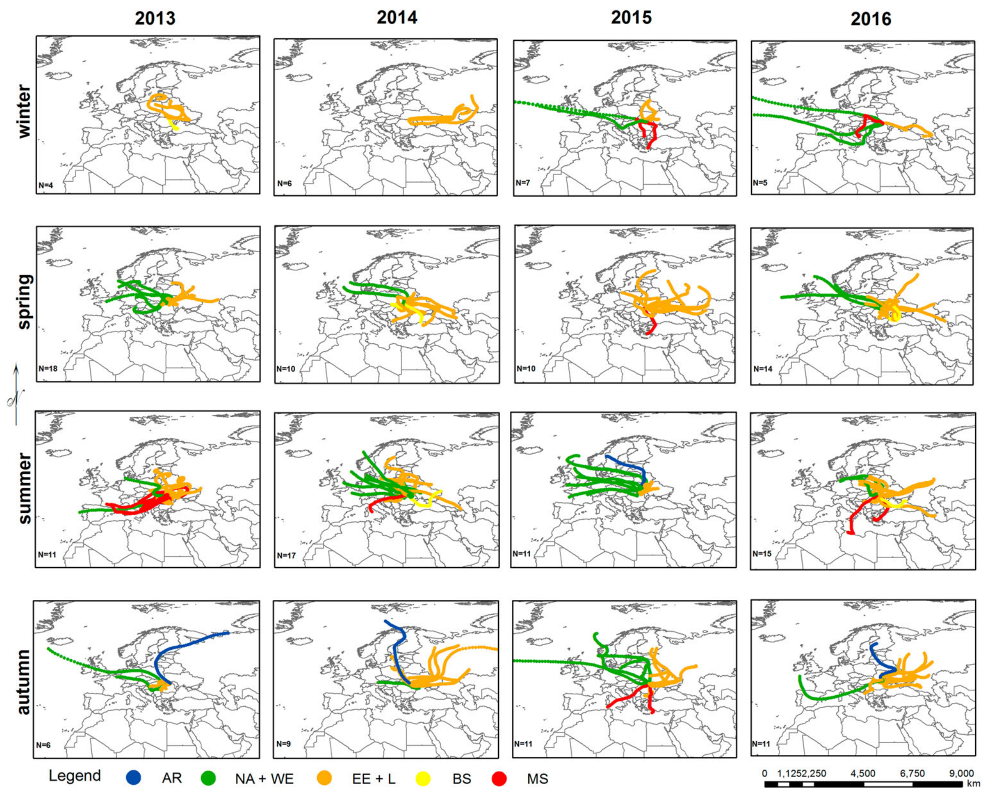

Figure 7. Modeled trajectories for single precipitation events (2013 – first panel, 2014 – second panel, 2015–third panel and 2016 – last panel) at Suceava station based on the HYSPLIT model at 500 m agl. The codes shown in the legend are modelled trajectories from: AR – Artic, NA + WE – North Atlantic and Western Europe, EE + L – Eastern Europe and Local, BS – Black Sea and MS – Mediterranean Sea.

locally recycled (42.7 and 46.6 % of the total moisture delivered between 2013 and 2016, respectively), with the Atlantic Ocean contributing significantly during spring (26.7 %) and summer (33.1 %). The Mediterranean and Black Seas are less important as moisture sources, with the highest percentage influence during winter and spring as mobile cyclones penetrate farther north. Relatively low contributions of Atlantic Ocean and Mediterranean Sea derived moisture are due to the orographic barrier effect of the Carpathians (Figure 1), with two mountains chains blocking both the Atlantic storm tracks and the Mediterranean cyclones.

Comparatively, stable isotopes studies in W Romania [19,43,44] and Hungary [45] have shown the strong influence of both the Atlantic and the Mediterranean sources for regions located on the western flanks of the mountains. High *d*-excess values in precipitation during autumn (12.2 ‰) are a further indicator of recycled moisture and/or a highly-evaporated source, thus reinforcing the view that continental recycled moisture from the eastern part of Europe is the main source of precipitation east of the Carpathian Mountains chain [46]. In summer and spring, eastern sources of precipitation with high *d-excess* remain significant but they are counterbalanced at this time by more frequent incursions of moist low *d*-excess air from the Atlantic, resulting in intermediate *d*-excess values (Table 1).

5.2. Stable isotopes in surface and groundwaters

The variability of δ_{river} follows a trend similar to that of stable isotopes in precipitation, although strongly muted (Figure 4), with the amplitude of δ_{river} for both Suceava and Soloneț Rivers being roughly one order of magnitude smaller than that of δ_{prec} (2 ‰ as compared to 24 ‰ for $\delta^{18}O$). From year to year, isotopic minima in both rivers are found to either be concurrent with or slightly delayed as compared to precipitation; the latter case being specific to cold winters when most of the precipitation is stored as snow. Peak δ_{river} values occur in summer, but, in contrast to winter, appear to be better correlated with air temperature in summer rather than δ_{prec} (Figure 4). This pattern appears to reflect the influence of evaporative enrichment on the original isotopic composition of river waters during summer. Temporally, the lowest river *d*-excess values (indicators of evaporation) occur in summer during the low flow periods, and *d*-excess is significantly correlated with discharge throughout the year, similar to findings from other regions [12,15]. Spatially, the *d*-excess in the waters of the Soloneț River, with a discharge one order of magnitude lower than that of the Suceava River, shows lower values, especially in summer, indicating a higher susceptibility to evaporation. Evaporative effects in river water are also clearly illustrated in δ^2H–$\delta^{18}O$ space, as rivers samples are found to plot along distinct lines with slopes lower than the LMWL (Figure 3). Lower slopes reflect kinetic effects related to evaporation under low humidity conditions during summer, which are responsible for the enrichment of the surface waters in the heavy ^{18}O and ^2H isotopes [47] and the alignment of the samples along local evaporation lines (LEL, [48]), with their origin at the initial stable isotopic composition prior to evaporation [49]. Higher rates of in-river evaporation (as there is no contribution from evaporated lakes and/or wetlands in the watershed) for the low-discharge Soloneț, compared to Suceava, suggests a higher degree of enrichment in the heavy isotopologues for the former, as well as higher degree of kinetic effects for both O and H (e.g. [50]), resulting in lower slopes for the LEL.

The $\delta^{18}O$ and δ^2H values of groundwaters are uniform between sampling localities, being close to average values noted for precipitation at the lower altitude Suceava station. No clear relationship with altitude and/or position (latitude/longitude) has been found, and very limited seasonal differences were discerned, with samples collected in summer being the most depleted in heavy isotopes (although only by max. 0.5 ‰ for $\delta^{18}O$ and 1.5 ‰ for δ^2H). The *d*-excess values in groundwater were less variable (between 8 and 12 ‰) than in precipitation and surface waters, again being slightly higher in samples collected in summer. All these features point towards recharge of the groundwater by local precipitation and limited exchange between groundwater aquifers and rivers. Interestingly, the registration of minimum δ values for groundwater in summer, when precipitation values are highest, suggests a significant proportion of groundwater containing the ^{18}O and ^2H-depleted imprint of winter precipitation. Similarly, the highest *d*-excess values in groundwater occur in summer, contrary to precipitation, which has the highest values in autumn through winter, thus further suggesting a late autumn through winter recharge. Mapping of the spatial distribution of groundwater $\delta^{18}O$ and *d*-excess values (Figure 8) reveals no clear pattern, except for a slight NW–SE decreasing gradient for $\delta^{18}O$, most evident in the warm months, which we tentatively link to the following processes: (1) delayed recharge by snowmelt and/or (2) slow underground flow in the same direction as the aquifer.

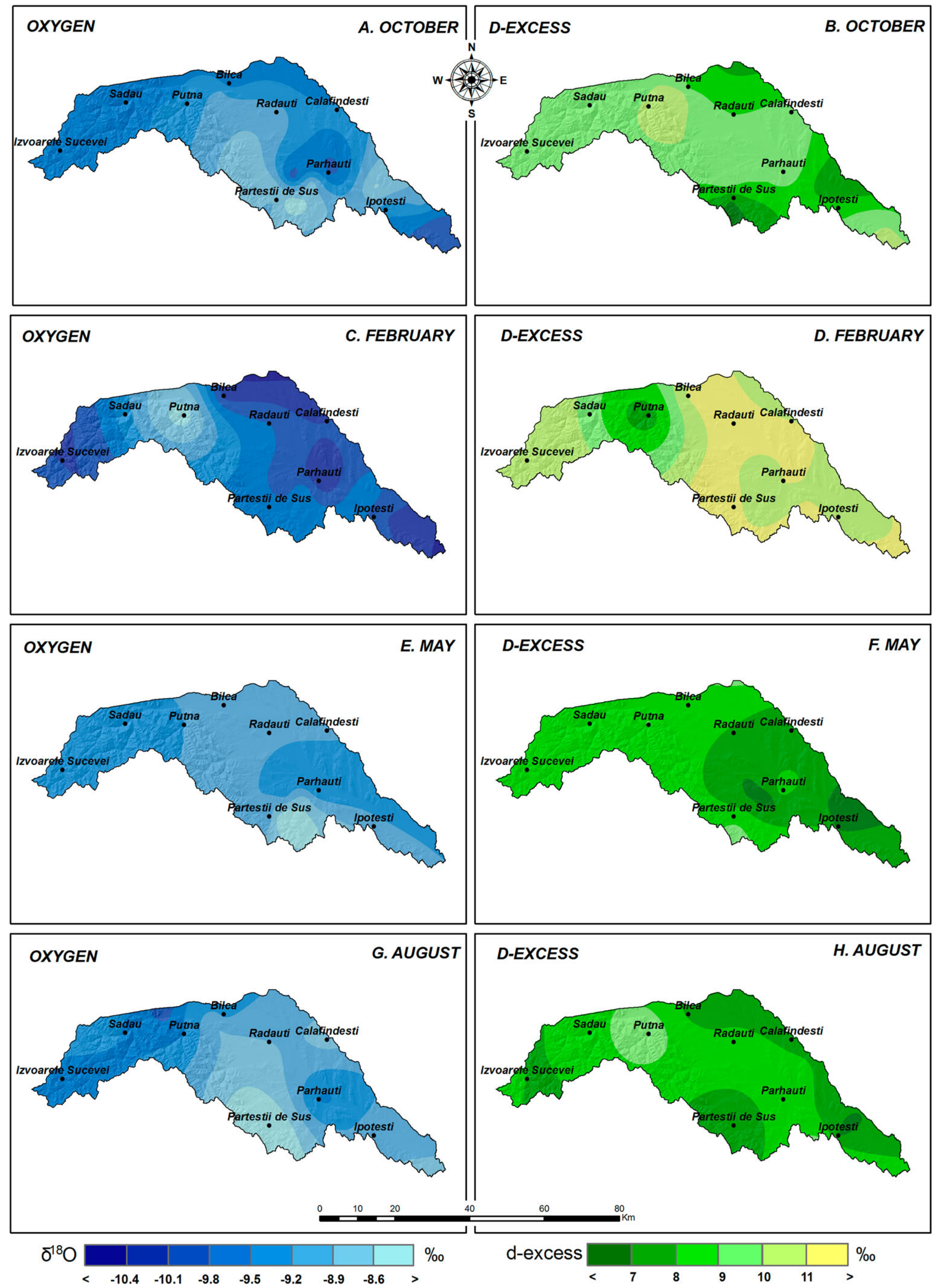

Figure 8. Seasonal distribution of $\delta^{18}O$ (left panel) and *d*-excess (right panel) in groundwater in the Suceava River watershed based on empirical semivariogram [51,52].

6. Conclusions

Stable H and O isotopes in precipitation, surface waters and groundwater have been used to identify the moisture sources, transport mechanisms and hydrological processes responsible for groundwater recharge in NE Romania, a region undergoing increased development pressure and competition for existing water resources. The HYSPLIT-modelled back trajectories, combined with *d*-excess values of precipitation, indicate that the main precipitation sources are located eastward from the sampling site (in the East-European Plain and the Black Sea). At multiannual timescale, the continental sources, including locally recycled moisture contribute approximately 36 % of the total rainfall, with proportions being higher in spring and autumn and lower in winter and summer. The LMWLs at the two precipitation collection stations were found to be somewhat distinct from the GMWL, with visible differences between plateau ($\delta^2H = 7.4*\delta^{18}O + 2.7$) and mountainous ($\delta^2H = 8.1*\delta^{18}O + 12.4$) areas, the former being strongly influenced by evaporation across the watershed, and the latter by generally more humid conditions. Secondarily, evaporation and moisture recycling was found to contribute to the seasonality of the isotopic fingerprints in precipitation. Compared to precipitation, the $\delta^{18}O$ and δ^2H values in surface waters were found to temporally damped, and offset below the LMWLs due to the imprint of evaporative enrichment. While evaporative enrichment is apparent for both investigated rivers, it is clearly more important for the smaller river (Solonet River), with evaporative effects (especially low *d*-excess) being emphasized during periods of low flow for both the Suceava and Soloneț Rivers. Surface water and groundwater are both strongly influenced by winter precipitation and especially snowmelt in cold years, with evidence of bias in isotopic composition of groundwater due to aquifer recharge by winter precipitation. As climate modelling results for the region predict a 40 % decrease in winter and spring precipitation, with a possible increase in summer rainfall over the next two decades [6], we might expect a higher degree of continentality and a possible reduction in water availability in the near future, both at the surface and within the groundwater system. Given concurrent growth in population and water usage in NE Romania, we foresee significant acceleration in competition for a limited water resource. Based on the informative results obtained so far from our study, we recommend continuous use of isotopic diagnostics as a complimentary tool to physical and chemical approaches for understanding the hydrology of watersheds, and as input to developing sustainable water management strategies for the region.

Acknowledgments

We thank the two reviewers and John Gibson for helpful comments that resulted in an improved article.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This project was funded by grants number PN-II-RU-TE-2011-3-0235, PN-II-RU-TE-2014-4-1993, PN-III-P1-1.1-TE-2016-2210 financed by Unitatea Executivă pentru Finanțarea Învățământului Superior, a Cercetării, Dezvoltării și Inovării Romania (UEFISCDI) and RO-18452, RO-22895, financed by the International Atomic Energy Agancy (IAEA), awarded to AP. MI is funded by the Helmholtz Climate Initiative REKLIM. The EEA Financial Mechanism 2009–2014 under the project contract no CLIMFOR18SE funded C-AB and VN. This work was partially supported from contract no. 18PFE/16.10.2018 funded by the Romanian Ministry of Research and Innovation within Program 1 – Development of national research and development system, Subprogram 1.2 – Institutional Performance-RDI excellence funding projects.

References

[1] Vörösmarty CJ, Mcintyre PB, Gessner MO, et al. Global threats to human water security and river biodiversity. Nature. 2010;467:555–561.
[2] Jury WA, Vaux HJ. The emerging global water crisis: managing scarcity and conflict between water users. Adv Agron. 2007;95:1–76.
[3] Ciric D, Nieto R, Ramos AM, et al. Wet spells and associated moisture sources anomalies across Danube River basin. Water. 2017;9:615.
[4] Dumitrescu A, Birsan M-V. ROCADA: a gridded daily climatic dataset over Romania (1961–2013) for nine meteorological variables. Nat Hazards. 2015;78(2):1045–1063.
[5] Dalin C, Wada Y, Kastner T, et al. Groundwater depletion embedded in international food trade. Nature. 2017;543:700–704.
[6] Busuioc A, Caian M, Bojariu R, et al. [Climate change scenarios in Romania for 2001–2030]. București (România): National Meteorological Administration. 2012. Romanian.
[7] Busuioc A, Dobrinescu A, Birsan MV, et al. Spatial and temporal variability of climate extremes in Romania and associated large-scale mechanisms. Int J Climatol. 2015;35:1278–1300.
[8] Rimbu N, Stefan S, Necula C. The variability of winter high temperature extremes in Romania and its relationship with large-scale atmospheric circulation. Theor Appl Climatol. 2015;121:121–130.
[9] Birsan MV, Dumitrescu A, Micu DM, et al. Changes in annual temperature extremes in the Carpathians since AD 1961. Nat Hazards. 2014;74:1899–1910.
[10] Cheval S, Busuioc A, Dumitrescu A, et al. Spatiotemporal variability of meteorological drought in Romania using the standardized precipitation index (SPI). Climate Res. 2014;60:235–248.
[11] Ionita M, Scholz P, Chelcea S. Assessment of droughts in Romania using the standardized precipitation index. Nat Hazards. 2016;81:1483–1498.
[12] Wassenaar LI, Athanasopoulos P, Hendry MJ. Isotope hydrology of precipitation, surface and ground waters in the Okanagan Valley, British Columbia, Canada. J Hydrol. 2011;411:37–48.
[13] Bowen GJ. Isoscapes: spatial pattern in isotopic biogeochemistry. Annu Rev Earth Planet Sci. 2010;38:161–187.
[14] Clark I, Fritz P. Environmental isotopes in hydrogeology. Boca Raton (FL): Lewis Publishers; 1997.
[15] Ferguson PR, Weinrauch N, Wassenaar LI, et al. Isotope constraints on water, carbon, and heat fluxes from the northern Great Plains region of North America. Glob Biogeochem Cycl. 2007;21: GB2023.
[16] Dansgaard W. Stable isotopes in precipitation. Tellus. 1964;16:436–468.
[17] Vystavna Y, Holko L, Hejzlar J, et al. Isotopic response of run-off to forest disturbance in small mountain catchments. Hydrol Process. 2018;32:3650–3661.
[18] Bojar AV, Halas S, Bojar HP, et al. Stable isotope hydrology of precipitation and groundwater of a region with high continentality, South Carpathians, Romania. Carpath J Earth Environ Sci. 2017;12:513–524.
[19] Drăgușin V, Balan S, Blamart D, Forray FL, Marin C, Mirea I, Nagavciuc V, Perşoiu A, Tîrlă L, Tudorache A, Vlaicu M. Transfer of environmental signals from the surface to the underground at Ascunsă Cave, Romania. Hydrol Earth Syst Sci. 2017;21:5357–5373.
[20] Bădăluţă C-A, Bistricean PI, Nagavciuc V. Using GIS techniques in the analysis of land use in the Soloneţ river catchment between 1856 and 2011. Georeview. 2013;23(2):23–33.
[21] Brânduș C, Cristea AI. Judeţul Suceava. B Bucureşti (România): Romanian Academy Press; 2013. Romanian.
[22] Cocerhan C. Bazinul râului Suceava pe teritoriul României – valorificarea potenţialului turistic [PhD thesis]. Bucharest: Bucharest University; 2013. Romanian.

[23] Croitoru A, Piticar A, So C, et al. Recent changes in reference evapotranspiration in Romania. Glob Planet Change. 2013;111:127–136.
[24] Stein AF, Draxler RR, Rolph GD, et al. NOAA's HYSPLIT atmospheric transport and dispersion modeling system. Bull Am Meteorol Soc. 2015;96:2059–2077.
[25] Whitaker JS, Compo GP, Wei X, et al. Reanalysis without radiosondes using ensemble data assimilation. Mon Weather Rev. 2004;132:1190–1200.
[26] Compo, G. P, Whitaker JS, Sardeshmukh PD. Feasibility of a 100-year reanalysis using only surface pressure data. Bull Am Meteorol Soc. 2006;87:175–190.
[27] Compo GP, Whitaker JS, Sardeshmukh PD, et al. The twentieth century reanalysis project. Quart J Roy Meteor Soc. 2011;137:1–28.
[28] Nas B, Berktay A. Groundwater quality mapping in urban groundwater using GIS. Environ Monit Assess. 2010;160:215–227.
[29] Craig H. Isotopic variations in meteoric waters. Science. 1961;133:1702–1703.
[30] Rożanski K, Araguás-Araguás L, Gonfiantini R. Isotopic patterns in precipitation. In: Swart PK, Lohmann KC, Mckenzie J, Savin S, editors. Climate change in continental isotopic records. Washington (DC): American Geophysical Union; 1993. p. 1–36. (Geophysical Monograph Series; 78).
[31] Poage MA, Chamberlain CP. Stable isotope composition of precipitation and surface waters: considerations for studies of paleoelevation change. Am J Sci. 2001;301:1–15.
[32] Holko L, Michalko J, Sanda M. Isotopes of oxygen-18 and deuterium in precipitation in Slovakia/Izotopy kyslíka-18 A deutéria v zrážkach na Slovensku. J Hydrol Hydromech. 2012;60:265–276.
[33] Hurrell JW, Kushnir Y, Ottersen G, et al. An overview of the North Atlantic oscillation. In: Hurrell JW, Kushnir Y, Ottersen G, et al. editors. The North Atlantic oscillation. Climatic significance and environmental impact. Washington (DC): American Geophysical Union; 2003. p. 1–35. (Geophysical Monograph Series; 134).
[34] Ionita M, Chelcea S, Rimbu N, et al. Spatial and temporal variability of winter streamflow over Romania and its relationship to large-scale atmospheric circulation. J Hydrol. 2014;519:1339–1349.
[35] Moore GWK, Renfrew IA, Pickart RS. Multidecadal mobility of the North Atlantic Oscillation. J Climate. 2013;26:2453–2466.
[36] Ionita M. Interannual summer streamflow variability over Romania and its connection to large-scale atmospheric circulation. Int J Climatol. 2015;35:4186–4196.
[37] Ionita M, Tallaksen LM, Kingston DG, et al. The European 2015 drought from a climatological perspective. Hydrol Earth Syst Sci. 2017;21:1397–1419.
[38] Schubert SD., Wang H, Koster RD, et al. Northern Eurasian heat waves and droughts. J Climate. 2014;27:3169–3207.
[39] Dole RM, Gordon ND. Persistent anomalies of the extratropical northern hemisphere wintertime circulation: Geographical distribution and regional persistence characteristics. Mon Weather Rev. 1983;111:1567–1586.
[40] Dole R, Hoerling M, Perlwitz J, et al. Was there a basis for anticipating the 2010 Russian heat wave? Geophys Res Lett. 2011;38:L06702.
[41] Jouzel J, Merlivat L. Deuterium and oxygen 18 in precipitation: Modeling of the isotopic effects during snow formation. J Geophys Res. 1984;89:11749–11757.
[42] Steffensen JP, Andersen KK, Bigler M, et al. High-resolution Greenland ice core data show abrupt climate change happens in few years. Science. 2008;321:680–684.
[43] Bojar A, Ottner F, Bojar H, et al. Stable isotope and mineralogical investigations on clays from the late Cretaceous sequences, Haţeg Basin, Romania. Appl Clay Sci. 2009;45:155–163.
[44] Ersek V, Onac BP, Persoiu A. Kinetic processes and stable isotopes in cave dripwaters as indicators of winter severity. Hydrol Process. 2018;32:2856–2862.
[45] Bottyán E, Czuppon G, Weidinger T, et al. Moisture source diagnostics and isotope characteristics for precipitation in east Hungary: implications for their relationship. Hydrol Sci J. 2017;62:2049–2060.

[46] Vystavna Y, Diadin D, Huneau F. Defining a stable water isotope framework for isotope hydrology application in a large trans-boundary watershed (Russian Federation/Ukraine). Isot Environ Health Stud. 2018;54(2):147–167.

[47] Froehlich K, Gonfiantini R, Rozanski K. Isotopes in lake studies: a historical perspective. In: Aggarwal PK, Gat JR, Froehlich KF, editors. Isotopes in the water cycle. Dordrecht: Springer; 2005. p. 139–150.

[48] Gibson JJ, Edwards TWD, Birks SJ, et al. Progress in isotope tracer hydrology in Canada. Hydrol Process. 2005;19:303–327.

[49] Rozanski K, Froehlich K, Mook WG. Surface water. Volume III of: Mook WG. editor, Environmental isotopes in the hydrological cycle: principles and applications. Paris: UNESCO/IAEA; 2001. (IHP-V Technical Documents in Hydrology; No. 39, Vol III).

[50] Gat JR. The isotopic composition of evaporating waters – Review of the historical evolution leading up to the Craig–Gordon model. Isot Environ Health Stud. 2008;44:5–9.

[51] Oliver MA, Webster R. A tutorial guide to geostatistics: Computing and modelling variograms and kriging. Catena. 2014;113:56–69.

[52] Hatvani IG, Leuenberger M, Kohán B, et al. Geostatistical analysis and isoscape of ice core derived water stable isotope records in an Antarctic macro region. Polar Sci. 2017;13:23–32.