https://doi.org/10.5194/essd-2026-212
Preprint. Discussion started: 15 July 2026

Open Access Earth System Science Data Discussions

Spatial and temporal variability of $\delta^{18}O$ and $\delta^{2}H$ in rivers and precipitation in Eastern Europe

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Abstract. The isotopic composition of water is one of the main tools used to track the origin and pathways of moisture from source to precipitation site, and the recharge characteristics of groundwater and surface waters. Further, in order to asses the role of climate and regional physiographic characteristic of the Earth's surface in determining the availability of water resources, dense networks long times series of $\delta^{18}O$ and $\delta^{2}H$ in precipitation and surface water are required. However, in many parts of the world, such data is lacking or has numerous gaps. In this context, we present a database of monthly $\delta^{18}O$ and $\delta^{2}H$ in precipitation (22 stations) and rivers (19 stations) in Romania and Republic of Moldova, spanning the period between January 2015 and December 2017. The dataset covers an area where multiple potential sources of moisture (Atlantic Ocean, Mediterranean, Black and Caspian Seas), complex surface topography and competing large-scale atmospheric circulation patterns result in highly complex conditions leading to precipitation and surface runoff generation. Our data shows that regional differences in the $\delta^{18}O$ and $\delta^{2}H$ of precipitation and rivers are linked to the blocking effect of the Carpathian Mountains and the interactions between different atmospheric circulation patterns: the North Atlantic Oscillation and the Siberian High (in winter), northward expanding Mediterranean cyclones (in autumn and winter), and long-lasting heat waves (in summer). $\delta^{18}O$ and $\delta^{2}H$ in rivers generally follow those in precipitation, but also reflect the strong evaporative conditions in the dry continental climate in summer and the effect of melt water from winter snow in spring. The data can offer a strong support for future studies aimed towards understanding the role of changing rainfall patterns, warming climate and reduced winter snow accumulation on water availability and stress in the region.

1 Introduction

The isotopic composition of precipitation (δ_{prec}) is an essential component of studies aimed at understanding the links between climate and water cycle (Craig, 1961; Dansgaard, 1964; Gat and Gonfiantini, 1981). The temporal and spatial

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variability of $\delta^{18}O$ and $\delta^{2}H$ in precipitation can be linked to weather and climate dynamics and by being registered in sedimentary archives (ice cores, speleothems, biotic products etc.) can further be used to reconstruct past climate changes (Jouzel, 2013; Bradley, 2014). Separately, δ_{prec} is a powerful tool for tracking how water moves through the hydrological cycles, in both natural (Richter, 1987; Sprenger et al., 2016; Masse-Dufresne et al.; 2021, Vystavna et al., 2021) and anthropogenic (Sánchez-Murillo et al., 2024) systems. Especially important it is to establish links between δ_{prec} and the stable isotopic composition of rivers (δ_{riv}), as these can further help understanding recharge mechanisms and patterns of groundwater (Stumpp et al., 2014; Jasechko et al. 2016; Vystavna et al., 2020).

Ongoing efforts by the International Atomic Energy Agency (IAEA) to collect and systematize such data have provided a wealth of information (Rozanski et al., 1992; Terzer et al., 2013; Halder et al., 2015; IAEA/WMO, 2025), but gaps in spatial and temporal coverage still remain. South Eastern Europe is one of the regions with poor coverage in δ_{prec} and δ_{riv}. Sampling efforts over the past years have started to fill in the gaps in δ_{prec} (Bojar et al., 2009; Holko et al., 2012; Ersek et al., 2018; Vystavna et al., 2018; Badaluta et al., 2019; Fórizs et al., 2020; Czuppon et al., 2021), but systematic data on δ_{riv} is still lacking for most of the region. South Eastern Europe has complex climatic and hydrologic regimes, resulting from the interplay of different atmospheric circulation patterns (the (NAO) Atlantic Oscillation (AO), the East Atlantic-Western Russia Pattern (EA-WR), the Scandinavian Pattern, the Siberian High (SH)), moisture being sourced from seas/oceans with different surface conditions (Atlantic Ocean, Black Sea, Adriatic Sea, Aegean Sea, Caspian Sea) and from its complex topography (the Carpathian Mountains act as a barrier for moisture derived from either of the sea supplying moisture to the region). As such, reliable $\delta^{18}O$ and $\delta^{2}H$ data for the precipitation and surface waters are of paramount importance for better understanding the source of moisture feeding precipitation in the region, for establishing links between precipitation and surface water and, in the end, for better planning of water usage in an uncertain future. The region is experiencing intensification in the frequency and duration of summer heat waves (Ionita et al., 2024), leading to increased stress on scarce water resources, yet whether the precipitation variability (and thus river recharge patterns) will become more or less stable is still unknown (Zhang et al., 2021). Considering that three of the countries in the region (Romania, Republic of Moldova and Bulgaria) are among the ten largest exporters of virtual groundwater per capita worldwide (Dalin et al. 2017), knowing where the water is coming from is a pressing issue.

In this context, we provide here a database of monthly $\delta^{18}O$ and $\delta^{2}H$ in precipitation (22 stations) and rivers (19 stations) in Romania and the Republic of Moldova, spanning the period between January 2015 and December 2017. The stable isotope data are complemented by monthly mean air temperature (°C) and precipitation amount (mm) data (for precipitation stations) and monthly mean discharge ($m^3 s^{-1}$) data (for river stations). Stations for precipitation sampling were positioned to capture moisture derived from different marine sources as well as recycled moisture from continental areas. The network also aimed to assess the role of the Carpathian Mountains in modifying the stable isotopic composition of moisture and precipitation. River stations were located along all major rivers in the region (including the Danube, Europe's second longest river) and on smaller ones, in order to understand how river waters reflect the stable isotopic composition of precipitation.

2 Study site

Romania and the Republic of Moldova are located in East-Central Europe, in the lower basin of the Danube river (Fig. 1). The region has a temperate continental climate, with generally cold winters and dry summers (Dfa and Dfb in the Köppen climate classification, Köppen (1936)).

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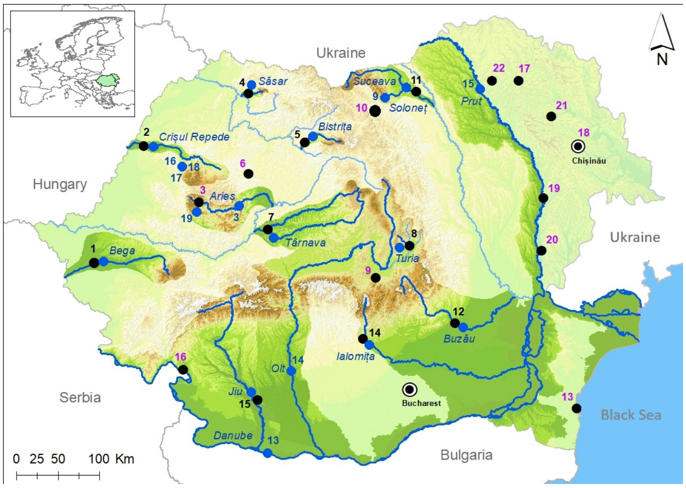

Figure 1: Location of river (blue dots) and precipitation (black dots) sampling sites. Investigated rivers are shown in dark blue and their respective catchments in dark green. Numbers correspond to those given in Tables 1 and 2.

The Carpathian Mountains (Fig. 1) impose regional differences in the temporal and spatial distribution of precipitation, limiting the influence of air masses originating in the Atlantic Ocean to the western and central parts of the country (Ioniţă, 2015). Similarly, outbreaks of northeastern cold winds in winter are blocked east of the Carpathians (Persoiu et al., 2019), while southwesterly Mediterranean cyclones are active only in the SW part of Romania. Consequently, the western and central parts of Romania have a milder climate, with wet winters and summers, while the eastern half and the Republic of Moldova have a strong continental climate, with dry and hot summers and cold winters. Precipitation in SW Romania has two maxima, the first in late spring, linked to the advection of moisture from the Atlantic Ocean, and the second in autumn, generated by northeastward-travelling Mediterranean cyclones. Streamflow variability is governed by topography (*via* snow accumulation in the mountains in winter) and weather and climate patterns. Wet winters result in increased winter streamflow, while cold winters lead to high flow in spring (Ionita et al., 2014). Summer streamflow accounts for 15-30 % of the total discharge (Ionita et al., 2015), the higher percentage being recorded in SE, where intense summer precipitation events are more common. All rivers are tributaries of the Danube, either directly, or through different large collectors (Siret, Olt and Mureş, Fig. 1).

3 Methods

3.1 Sampling

Water samples were collected monthly between January 2015 and December 2017 at 19 rivers in Romania and at 22 precipitation stations across Romania and the Republic of Moldova (Tables 1 and 2). Sites have been selected according to criteria described as follows. First, we considered the different climatic influences in Romania and their role in determining moisture sources feeding precipitation and river water (e.g., Ionita et al., 2014; Ionita, 2015; Bădăluţă et al., 2019; Birsan, 2015) and subsequently selected rivers from regions with Mediterranean (e.g., Bega, Jiu), Atlantic (Săsar, Crişul Repede) and continental (e.g., Suceava, Soloneţ) climatic influences. Second, we also considered rivers with markedly different discharges, ranging from >5000 $m^3 s^{-1}$ (Danube) to less than 1 $m^3 s^{-1}$ (e.g., Turia). Where possible, we have targeted rivers of different sizes in terms of catchment area and discharge within the same climatic region (e.g., Suceava and Soloneţ in northern Romania, Crişul Repede and Săsar in western Romania). We generally avoided rivers with complex and/or extensive hydropower systems (e.g., Someş, Siret), due to the complexity of processes affecting discharge (and consequently the stable isotopic composition of water). Water from one such river (Olt) was nevertheless collected, for comparative

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purposes. River water samples were collected in the lower section of the drainage basin, with a few exceptions (Fig. 1). Precipitation water was collected at stations belonging to the Romanian Network of Isotopes in Precipitation (Bădăluță et al., 2019; Nagavciuc et al., 2022), continuing a program started in 2012 by our group. Our data from the 17 precipitation stations is completed with data from five stations in Republic of Moldova, available in the GNIP database and partly unpublished. Stable isotope data for four rivers (Ocoale, Deblei, Mniera and Toaia, Table 2) were published before by Feher et al. (2024).

	Precipitation station	Latitude (°)	Longitude (°)	Altitude (m asl)
1	Timişoara	45°44'57.06"N	21°13'55.48"E	90
2	Oradea	47°3'5.00"N	21°58'21.09"E	142
3	Ghețar	46°29'28.45"N	22°49'26.02"E	1101
4	Groși (Baia Mare)	47°39'30.61"N	23°34'14.12"E	284
5	Bistrița	47°7'20.59"N	24°29'25.2"E	400
6	Cluj-Napoca	46°42'41.6"N	23°41'33.5"E	362
7	Blaj	46°10'31.23"N	23°54'10.58"E	257
8	Tg. Secuiesc	46° 0'24.95"N	26° 8'19.42"E	567
9	Brașov	45°38'39,421"N	25°35'48,20"E	553
10	Rarău	47°27'00.0"N	25°33'59.9"E	1600
11	Suceava	47°39'31.27"N	26°15'49.49"E	270
12	Buzău	45°10'18.84"N	26°49'21.83"E	87
13	Constanța	44°8'33.00"N	28°37'17.00"E	35
14	Doicești	44°59'44.53"N	25°23'14.64"E	329
15	Craiova	44°17'41.49"N	23°44'51.54"E	109
16	Drobeta Turnu Severin	44°37'42.87"N	22°39'38.01"E	66
17	Bălți	47°42'0.00"N	27°52'59.88"E	231
18	Chișinău	46°58'0.00"N	28°53'60.00"E	125
19	Leova	46°29'50.00"N	28°18'0.00"E	156
20	Cahul	45°47'60.00"N	28°12'0.00"E	113
21	Bravicea	47°24'00"N	28°29'29.9"E	78
22	Glodeni	47°44'30.37"N	27°43'27.03"E	157

Table 1. Location of precipitation sampling stations used in this study.

	River	Location of stations along rivers	Latitude	Longitude	Altitude (m asl)	Average discharge ($m^{-3} s^{-1}$)	Length (km)	Drainage area (km^2)
1	Bega	Timişoara	45°44'57.06"N	21°13'55.48"E	90	22	170	2362
2	Crişul Repede	Oradea	47°3'5.00"N	21°58'21.09"E	142	25.4	909	9119
3	Arieş	Moldoveneşti	46°30'41.81"N	23°39'41.80"E	408	19	166	3005
4	Săsar	Grosi	47°39'30.61"N	23°34'14.12"E	284	<1		
5	Bistrița	Bistrița	47°7'20.59"N	24°29'25.2"E	400	7	67	650
6	Tărnava	Blaj	46°10'31.23"N	23°54'10.58"E	257	27	246	6253
7	Turia	Tg. Secuiesc	46° 0'24.95"N	26° 8'19.42"E	567	<0.5		
8	Suceava	Suceava	47°39'31.27"N	26°15'49.49"E	270	20	173	2298
9	Soloneț	Părhăuți	47°42'40.81"N	26° 5'33.76"E	303	<1	36	206
10	Buzău	Buzău	45°10'18.84"N	26°49'21.83"E	87	25	302	5264
11	Ialomița	Doicești	44°59'44.53"N	25°23'14.64"E	329	45	417	10350
12	Jiu	Craiova	44°17'41.49"N	23°44'51.54"E	109	86	339	10080
13	Danube	Bechet	43°44'55.32"N	23°57'15.52"E	29	6400	2860	817000
14	Olt	Slatina	44°25'14.49"N	24°20'30.31"E	105	174	615	24050
15	Prut	Balatina	47°40'52.09"N	27°17'44.96"E	61	110	953	27500
16	Mniera	Potriva	46°59'59.95"N	22°22'17.98"E	374	<0.3	<5 km	<10
17	Deblei	Gălăşeni	46°59'20.20"N	22°26'15.92"E	403	<0.3	<5 km	<10
18	Toaia	Damiş	46°52'21.78"N	22°32'34.97"E	690	<0.3	<5 km	<10
19	Ocoale	Ocoale	46°30'14.23"N	22°48'46.17"E	1168	<0.3	<5 km	<10

Table 2. Location of river sampling stations used in this study.

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3.1.1 Precipitation water sampling

Precipitation water was collected using self-built collectors based on IAEA specifications (IAEA, 2002) and commercially sourced Palmex collectors (Gröning et al., 2012). The collectors were placed between 20 and 120 cm above ground, at a minimum distance of 15 m from buildings and other structures that could have prevented undisturbed direct input of rainfall water. No oil was used in the collectors, as our previous long-term monitoring studies (Bădăluță et al., 2019; Feher et al., 2021) showed no systematic change in the stable isotopic composition of water in the collectors in the absence of oil. At the end of each month, a 22 ml aliquot was transferred to HDPE scintillation vials (with no headspace), which were sealed and kept at 4 °C before shipment to the laboratory. The collectors were cleaned monthly to remove algal growth (occurring as a thin greenish film coating the walls of the collect in summer months) that could have affected the original $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios. In winter, snow was collected in open plastic containers, each between 10 and 20 cm wide and 40-60 cm deep. At the end of each month, the containers were covered and placed indoors at temperatures not exceeding 10 °C to allow melting of snow and ice. The resulting melt water was thoroughly mixed, sediment (both from dry and wet deposition in the open containers) was allowed to settle and subsequently a water aliquot was collected and treated as described above. We did not use Palmex (or similar) collectors in winter, for several reasons: 1) heavy snowfall events quickly filled-up the funnels, resulting in subsequent loss of snow due to wind scouring; 2) freezing of water at the bottom of funnel led to quick filling of the funnel with snow and water subjected to evaporation, sublimation and exchange with atmospheric vapor, all potentially leading to alteration of the original stable isotope ratios; 3) cumbersome operation at (very) low temperatures (below -20 °C).

Every three to six months, the samples were transported to the laboratory and stored in fridges, at ~4 °C, prior to analysis. The elapsed time between sampling and analysis was generally less than nine months.

3.1.2 River water sampling

River water was collected at the end of each month from the main river flow path, usually from bridges. Where no bridge was present, water was collected at points where the main flow was directed towards the shore. Sampling from standing water was always avoided, in order to minimize the risk of collecting evaporated water. Sampling was done by dipping buckets between 20 and 100 cm below surface and transferring the water into 22 ml HDPE scintillation vials. Samples were treated similarly to those from precipitation (see section 3.1.1 above). No filtering was carried out in the field.

3.2 Laboratory analysis

Following removal from the fridge, the vials holding the water were checked for the presence of ice (as samples kept close to the refrigerating unit at the back of the fridge sometimes did partly freeze). Partial freezing of water is accompanied by strong kinetic fractionation, the remaining water being strongly depleted in ^{2}H and ^{18}O isotopes, which are preferentially concentrated in the ice (e.g., Persoiu et al., 2011). After removal from the fridge, the vials were kept at room temperature for ~1 hour, vigorously shaken (not stirred) and as particles settled at the bottom, water was drawn from each vials with single use syringes and filtered through 0.45 µm nylon filters into 1.5 or 2 ml borosilicate glass vials. In several instances (especially river samples), in which high amount of particulate matter was visible, 0.22 µm filters were used. The measurements of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios and $\delta^{18}O$ and $\delta^{2}H$ determination were performed on a Picarro L2130-*i* CRDS using the "High precision" setting. 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 (Bădăluță et al., 2019). The average value of the last four injections was used as the raw value for subsequent data processing. These raw values were normalized (two fixed-point calibration) to the SMOW-SLAP scale (Craig, 1961) using two internal standards calibrated against the VSMOW2 and SLAP2 standards provided by the IAEA (Bădăluță et al., 2019; Persoiu et al., 2023).

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The δ values of the two internal standards are 0.12 ‰ and -0.68 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively (”Kona Deep”™ still water, “heavy” standard); and -33.15 ‰ and -254.44 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively (Greenland Summit snow, ”light” standard). A third standard (”Borsec”™ still water, -10.77 ‰ and -74.35 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively) was run with each batch of samples and was used for data validation. The standards were kept in flame-sealed glass ampoules at ambient temperature in the dark (10 ml of water in 20 ml vials, half-filled only, to prevent potential evaporation during flame sealing). From each ampoule we filled four 2-ml borosilicate glass vials and used one vial per week for analysis, discarding one vial per week. Between analyses, the vials were kept at 4 °C. Standards for normalization were run at the beginning, middle and end of each sequence (each consisting of 10 to 20 samples), while the validation standard was run at the middle of the sequence (Bădăluță et al., 2019). The isotopic compositions of precipitation and river water are reported in the standard δ notation (deviations of a sample $^{18}O/^{16}O$ or $^{2}H/^{1}H$ ratios relative to those of reference water – SMOW), calculated (Gonfiantini, 1981) using Eq. (1).

$$\delta = \left(\frac{R_{sample}}{R_{SMOW}} - 1\right) * 1000\ (‰), \quad (1)$$

where R is the either the $^{18}O/^{16}O$ or the $^{2}H/^{1}H$ ratio. The precision (1 σ) of the reported values is better than 0.16 ‰ for $\delta^{18}O$ and 0.7 ‰ for $\delta^{2}H$, respectively (based on repeated measurements of the internal standard (Bădăluță et al. (2019)).

3.3 Post-analysis quality control

All data was analyzed offline. Data from samples potentially contaminated with volatile organic compounds (VOCs) were analyzed using the ChemCorrect™ software provided together with the analyzer by Picarro, Inc. After replacing the weekly vials of internal standards with new ones, one aliquot from each discarded standard was analyzed as “unknown”. Our long-term (10+ years) observations showed that in the absence of headspace, no change occurs in the isotopic composition of water kept for a week or less in glass vials at 4 °C and opened several times.

For precipitation samples, we calculated the deuterium-excess (d-excess, d) parameter (Dansgaard, 1964) using Eq. (2):

$$d = \delta^{2}H - 8 * \delta^{18}O \quad (2)$$

and used it as a secondary control on the quality of data (by expressing caution when discussing data obtained from samples with negative d-excess values, as post-precipitation evaporation in the rainfall collector was suspected). Nevertheless, all data is reported in this paper but readers are asked to exercise caution when using such data. Measurement of river samples did not yield negative d-excess values.

The long-term inspection of analytical results showed that no memory and linearity (drift) errors occurred; hence no correction was applied. Generally, when long storage time was anticipated, a vial similar to those in which the samples were kept and containing the third standard (see above) was stored and analyzed together with the samples. No change exceeding 0.17 ‰ for $\delta^{18}O$ and 0.7 ‰ for $\delta^{2}H$, respectively, was observed in samples kept up to nine months.

3.4 Meteorological and hydrological data

Meteorological (monthly mean air temperature and precipitation amount) and hydrological (monthly average river discharge at the gauging station nearest to the sampling points) was provided by the Romanian Meteorological Administration and the ”Romanian Waters” National Administration, respectively. Data from the Republic of Moldova were obtained from the GNIP database (IAEA/WMO, 2026).

3.5 Local Meteoric Water Line

We determined Local Meteoric Water Lines (LMWL, defined as $\delta^{2}H = a*\delta^{18}O + b$, IAEA (1992)) for all stations, combining data from this study with previously published data by our group (Nagavciuc et al., 2022). The time series used for determining the LMWLs cover the period 2012-2017. The LMWLs (Table 3) were determined using both the *Ordinary*

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Least Squares Regression (OLSR) method (IAEA, 1992), and the *Precipitation Amount Weighted Least Squares Regression* (PWLSR) method (Hughes and Crawford, 2012). For three stations (Glodeni, Rarău and Brasov) we determined the LMWLs using only the OLSR method, as no precipitation amount data was available.

4. Results and discussions

4.1 Stable isotopes in precipitation

The data from this study is available from Persoiu (2026), and their main characteristics are presented in Figs. 2 and 3 and further discussed below. The minima of individual δ^{18}O (δ^2H) precipitation time series are ranging between -13.4 (-96) ‰ and -21.6 (-166) ‰, and the maxima between -1.4 (-9.7) ‰ -5.7 (-33) ‰. The lowest minima are registered in Tg. Secuiesc and Rarău, the former being located in an intramountain basin with strong thermal inversions during autumn and winter months (Badea, 1983), while the latter being the highest station (1600 m asl) in our database. The time series maxima calculated across all stations have much lower spatial variability (absolute range of 3.4. ‰ and 23 ‰ for δ^{18}O and δ^2H, respectively) than the minima (absolute range of 8.2 and 69 ‰ for ^{18}O and δ^2, respectively, Fig. 2).

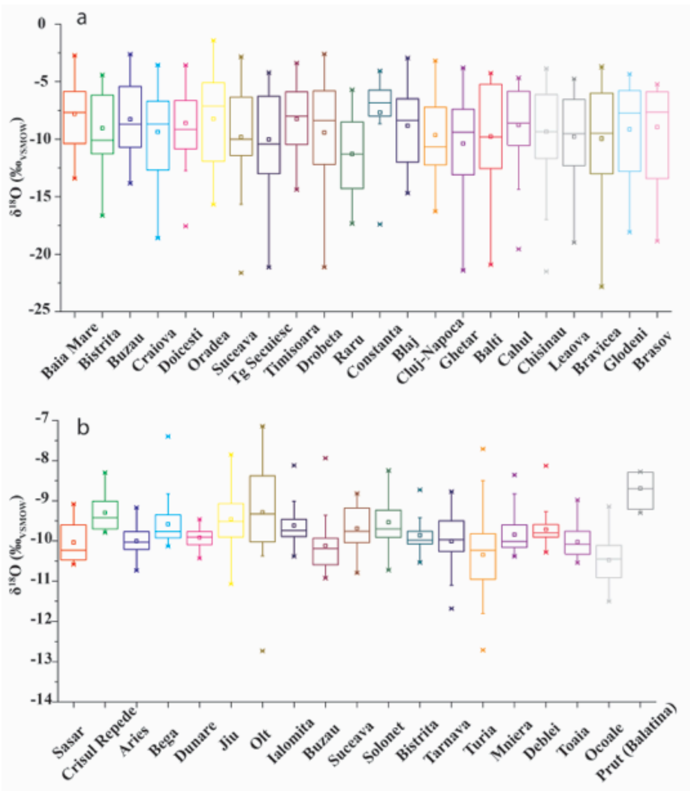

Figure 2. Boxplots of δ^{18}O in precipitation (a) and rivers (b) in Romania and the Republic of Moldova.

The higher spatial variability of the minima is likely the result of regional differences induced by outbreaks of cold air linked to the southward expansion of high-pressure systems under the influence of the Siberian High (Cohen et al., 2001; Persoiu et al., 2019). These outbreaks of cold air are limited to the eastern part of the Romania (and to the whole of Republic of Moldova), the presence of the Carpathian Mountains limiting their extension southward and westwards (Badaluta et al., 2019; Nagavciuc et al., 2021; Nagavciuc et al., 2022). As a result, winter time δ^{18}O and δ^2H are much lower in north and

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east, and higher in south and west, leading to the aforementioned regional differences. The relatively uniform values of summer maxima across the entire region and during the entire study period, suggest a supra-regional influence. Altitude and latitude do not seem to be playing a role and the fact that in winter the differences are much larger suggests a summer-time only mechanisms. In summer, the entire region is affected by extensive heat waves in a pattern that is not affected by the Carpathian Mountains (Ionita et al., 2024). This spatially uniform pattern of heat waves is likely responsible for the relatively homogenous summer maxima in $\delta^{18}O$ and $\delta^{2}H$. Deuterium-excess also displays a clear seasonal variability, with minima in summer and maxima in autumn (Fig. 3). These autumnal maxima of d-excess are higher in SW Romania (Fig. 4), where Mediterranean cyclones (Flaounas et al., 2022, Forray et al., 2024) bring a higher proportion of moisture derived from highly evaporated surface waters of the Eastern Mediterranean (Adriatic and Aegean Seas), with distinctively high d-excess (Gat et al., 2003). Similarly to the situation in winter months, the Carpathian Mountains are blocking these cyclones from reaching northern and eastern Romania and the Republic of Moldova, regions in which d-excess values are consequently lower.

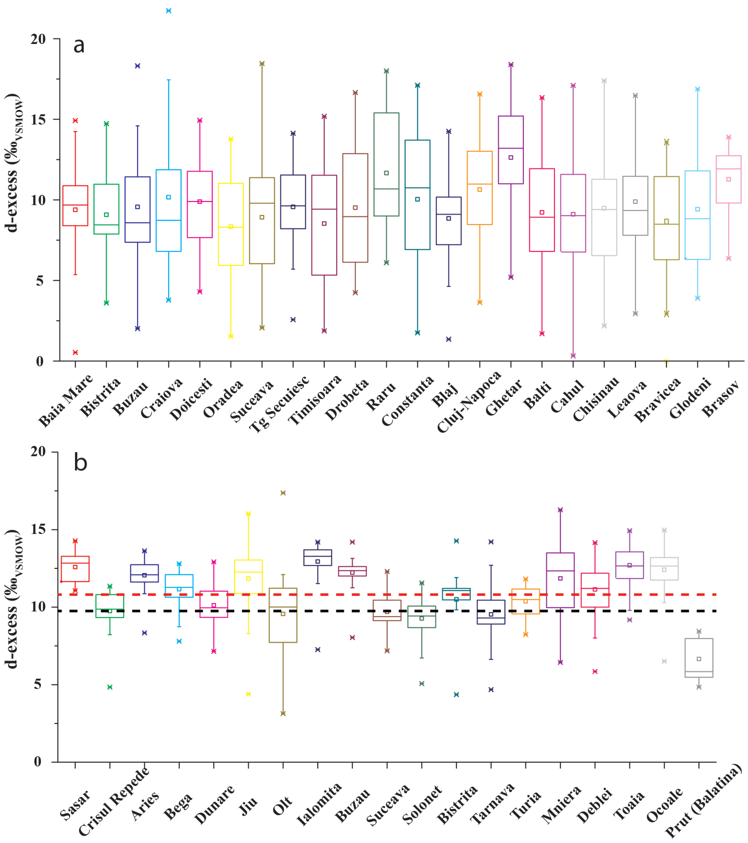

Figure 3. Boxplots of deuterium excess in precipitation (top panel) and rivers (bottom panel) in Romania and the Republic of Moldova. The dashed lines in panel b show the average d-excess values for rivers (black) and precipitation (red).

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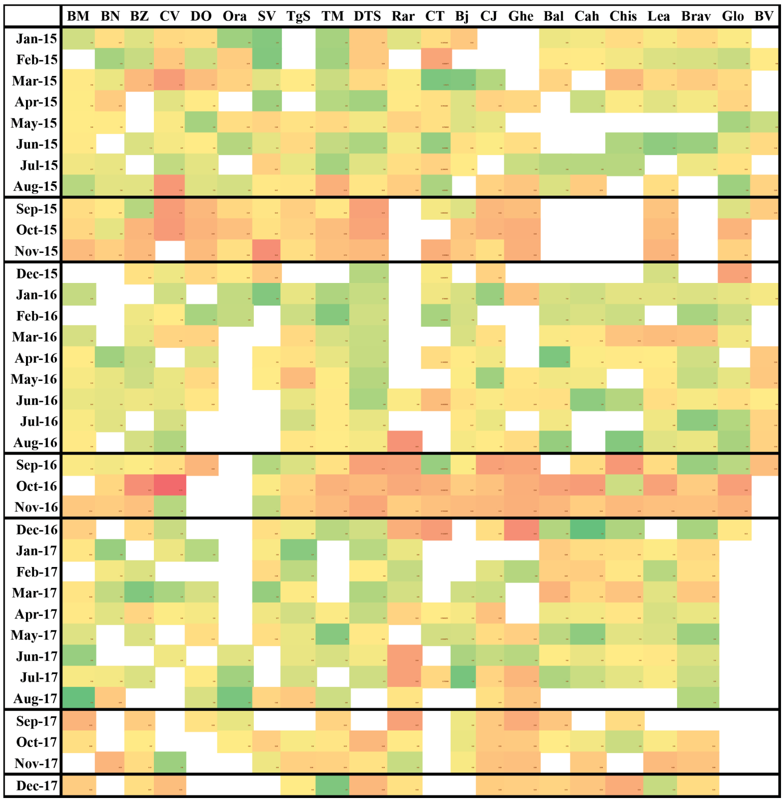

Figure 4. D-excess in precipitation at stations in Romania and Republic of Moldova.

The Local Meteoric Water Lines (LMWL, Table 3) reflect both the seasonal and regional distribution of $\delta^{18}O$ and $\delta^{2}H$. In general, the slopes of the LMWL determined with the PWLSR method are higher (13 out of 19) or marginally lower (5 out of 19) than those determined with the OLSR method, whereas the intercepts are slightly more variable, with 8 (out of 19) being lower in the case of PWLSR method. These differences indicate the role of sub-cloud evaporation of raindrops through the dry atmosphere in summer, as well as the depletion of precipitation in the heavy ^{18}O and ^{2}H isotopes during prolonged or intense rain events (mainly in summer). All LWMLs are generally close to the Global Meteoric Water Line (GMWL, defined either as $\delta^{2}H = 8 * \delta^{18}O + 10$ by Craig (1961) or as $\delta^{2}H = 8.2 * \delta^{18}O + 11.27$ by Rozanski et al. (1992). The LMWLs of the stations in eastern and Southern Romania and in the Republic of Moldova have lower slopes, likely reflecting the more evaporative conditions in summer and possibly the influence of Mediterranean influx of moisture in autumn (Nagavciuc et al., 2022).

Across all stations, the stable isotopic composition of precipitation is positively correlated with air temperature ($r^2 = 0.54$ for $\delta^{18}O$) and negatively with altitude ($r^2 = 0.56$ for $\delta^{18}O$). The overall altitude gradient of $\delta^{18}O$ is 0.24 ‰/100 m, similar to regional (between 0.21 and 0.27 ‰/100 m, Holko et al. (2012); Bădăluță et al. (2019)) and global gradients (0.26 ‰/100 m, Poage & Chamberlain, 2001). The good numerical correlation between δ_{prec} and altitude is mainly driven by the outlying two high-altitude sites (Rarău, 1600 m asl and Ghețar, 1100 m asl), with stations at lower altitudes (between 35 and 567 m asl) showing no correlation between the two ($r^2 = 0.14$). However, the correlation between air temperature and altitude is maintained both with ($r^2 = 0.85$) and without ($r^2 = 0.71$) including the high altitude sites, suggesting that altitude (and hence altitude dependent air temperature gradient) is not the main driver of δ_{prec} variability. On seasonal scales, the correlation between δ_{prec} and air temperature is stronger in spring and autumn and weakest in summer, further lending support to the

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hypothesis that large scale atmospheric circulation patterns (including summer heat waves) have a strong impact on $\delta^{18}O$ and δ^2H in precipitation. On monthly scales, $\delta^{18}O$ and δ^2H variability varies with air temperature (high values in summer and low values in winter), but the variability between stations is lower in summer, further reflecting the more variable sources of moisture in winter (Badaluta et al., 2019, Nagavciuc et al., 2022) and more uniform conditions in summer, when regional heat waves block moisture advection and enhance local recycling.

	Station name	LMWL (OLSR)	LMWL (PWLSR)
1	Baia Mare	$\delta^2H = \delta^{18}O * (7.64 \pm 0.12) + (6.78 \pm 0.37)$	$\delta^2H = \delta^{18}O * (7.67 \pm 0.12) + (7.42 \pm 1.04)$
2	Bistrița	$\delta^2H = \delta^{18}O * (7.98 \pm 0.13) + (8.77 \pm 0.39)$	$\delta^2H = \delta^{18}O * (7.93 \pm 0.13) + (8.62 \pm 1.34)$
3	Buzău	$\delta^2H = \delta^{18}O * (7.85 \pm 0.20) + (8.96 \pm 0.45)$	$\delta^2H = \delta^{18}O * (7.61 \pm 0.19) + (7.22 \pm 1.50)$
4	Craiova	$\delta^2H = \delta^{18}O * (7.75 \pm 0.16) + (7.71 \pm 0.38)$	$\delta^2H = \delta^{18}O * (7.69 \pm 0.19) + (8.00 \pm 1.82)$
5	Doicești	$\delta^2H = \delta^{18}O * (7.81 \pm 0.21) + (8.60 \pm 0.58)$	$\delta^2H = \delta^{18}O * (7.79 \pm 0.21) + (9.24 \pm 1.87)$
6	Oradea	$\delta^2H = \delta^{18}O * (7.77 \pm 0.18) + (6.49 \pm 0.52)$	$\delta^2H = \delta^{18}O * (7.74 \pm 0.22) + (6.04 \pm 1.84)$
7	Suceava	$\delta^2H = \delta^{18}O * (7.75 \pm 0.11) + (7.52 \pm 0.34)$	$\delta^2H = \delta^{18}O * (7.79 \pm 0.10) + (8.28 \pm 1.09)$
8	Tg. Secuiesc	$\delta^2H = \delta^{18}O * (8.00 \pm 0.12) + (9.57 \pm 0.45)$	$\delta^2H = \delta^{18}O * (7.85 \pm 0.13) + (8.84 \pm 1.15)$
9	Timișoara	$\delta^2H = \delta^{18}O * (7.78 \pm 0.11) + (7.37 \pm 0.32)$	$\delta^2H = \delta^{18}O * (7.80 \pm 0.11) + (8.09 \pm 1.10)$
10	DTS	$\delta^2H = \delta^{18}O * (7.87 \pm 0.11) + (8.30 \pm 0.29)$	$\delta^2H = \delta^{18}O * (7.90 \pm 0.12) + (9.45 \pm 1.19)$
11	Blaj	$\delta^2H = \delta^{18}O * (7.70 \pm 0.08) + (5.98 \pm 0.31)$	$\delta^2H = \delta^{18}O * (7.52 \pm 0.13) + (5.22 \pm 1.02)$
12	Ghețar	$\delta^2H = \delta^{18}O * (7.64 \pm 0.14) + (8.38 \pm 0.42)$	$\delta^2H = \delta^{18}O * (7.80 \pm 0.14) + (10.56 \pm 1.50)$
13	Cluj-Napoca	$\delta^2H = \delta^{18}O * (7.90 \pm 0.14) + (9.28 \pm 0.43)$	$\delta^2H = \delta^{18}O * (7.86 \pm 0.13) + (8.99 \pm 1.27)$
14	Rarău	$\delta^2H = \delta^{18}O * (8.45 \pm 0.20) + (16.73 \pm 0.56)$	
15	Constanța	$\delta^2H = \delta^{18}O * (7.75 \pm 0.24) + (8.13 \pm 0.49)$	$\delta^2H = \delta^{18}O * (7.36 \pm 0.24) + (5.72 \pm 1.92)$
16	Bălți	$\delta^2H = \delta^{18}O * (7.61 \pm 0.15) + (5.17 \pm 0.44)$	$\delta^2H = \delta^{18}O * (7.36 \pm 0.17) + (3.34 \pm 1.64)$
17	Cahul	$\delta^2H = \delta^{18}O * (7.62 \pm 0.23) + (5.45 \pm 0.53)$	$\delta^2H = \delta^{18}O * (7.41 \pm 0.26) + (4.79 \pm 2.29)$
18	Chișinău	$\delta^2H = \delta^{18}O * (7.73 \pm 0.18) + (6.77 \pm 0.45)$	$\delta^2H = \delta^{18}O * (7.62 \pm 0.17) + (5.64 \pm 1.61)$
19	Leaova	$\delta^2H = \delta^{18}O * (8.03 \pm 0.16) + (10.17 \pm 0.52)$	$\delta^2H = \delta^{18}O * (7.92 \pm 0.20) + (9.73 \pm 2.05)$
20	Bravicea	$\delta^2H = \delta^{18}O * (7.62 \pm 0.13) + (4.82 \pm 0.45)$	$\delta^2H = \delta^{18}O * (7.60 \pm 0.11) + (5.46 \pm 1.07)$
21	Glodeni	$\delta^2H = \delta^{18}O * (7.50 \pm 0.18) + (4.81 \pm 0.53)$	
22	Brașov	$\delta^2H = \delta^{18}O * (7.88 \pm 0.08) + (9.28 \pm 0.38)$	

Table 3. Local Meteoric Water Lines in precipitation for stations in Romania and the Republic of Moldova.

4.2 Stable isotopes in rivers (δ_{riv})

The stable isotopic composition of river waters is presented in Fig. 2 ($\delta^{18}O$) and Fig. 3 (d-excess), but for simplicity, the discussion focuses on $\delta^{18}O$, as δ^2H has a similar behavior. The range of temporal variability (Fig. 5) for $\delta^{18}O$ is much smaller in rivers (1 σ standard deviation within time series varies between 0.24 and 1.11) than in precipitation (1 σ standard deviation within time series varies between 2.8 and 5), indicating long-term mixing of waters of different origins over the respective drainage basins. In the $\delta^{18}O$-δ^2H crossplots (Fig. 5) river samples align on lines with lower slopes and intercepts than the local LWMLs, indicating the strong evaporation of surface water, both from the watersheds before infiltration and from the rivers themselves. This observation is further supported by the low d-excess values of river waters in summer (Fig. 3), resulting from precipitation depleted in ^{18}O and ^2H and evaporative enrichment of post-precipitation waters.

Generally, d-excess is lower by ~1 ‰ across all rivers (Fig. 3), driven by the strong evaporative conditions during summers. This evaporative trend mainly affects rivers with 1) watersheds developed in the lowlands (e.g., Târnava and Bega), b) smaller discharges (e.g., Bistrița, Soloneț) and c) those with low contribution of winter snowmelt and flowing in areas with strong PE deficit in summer (e.g., Prut). One river, Olt, stands out as having extremely low d-excess values (Fig. 3), resulting from the massive evaporation of the river's waters in the 19 reservoirs located upstream from the sampling site. High d-excess dominates rivers with pluvial regimes in winter (e.g., Koeniger et al., 2022). Compared to precipitation, $\delta^{18}O$ values in rivers are lower (on average by ~ 0.8 ‰), suggesting a higher contribution from wintertime snow to the discharge. However, contrary to this hypothesis, we also note that the precipitation sampling sites were generally positioned in the lower sections of the watersheds, and thus the δ_{prec} were inherently high, thus potentially affecting the accuracy of the above-

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mentioned observation. Both $\delta^{18}O$ (and $\delta^{2}H$) in rivers linearly decrease with altitude, albeit the correlation between the two is weaker than for precipitation (see section 4.1), indicating the mixing of waters sourced from different altitudes within the watersheds. A very good correlation was found between the temporal variability of $\delta^{18}O$ and $\delta^{2}H$ in rivers and precipitation, with clear maxima in summer and minima in winter. The correlation was better for small rivers (e.g., Turia) than for those with large watersheds, affected by different climatic influences (e.g., Tarnava) or with the major part of their watershed extending in mountain regions, where the discharge is dominated by snowmelt (e.g., Ialomita, Fig. 6).

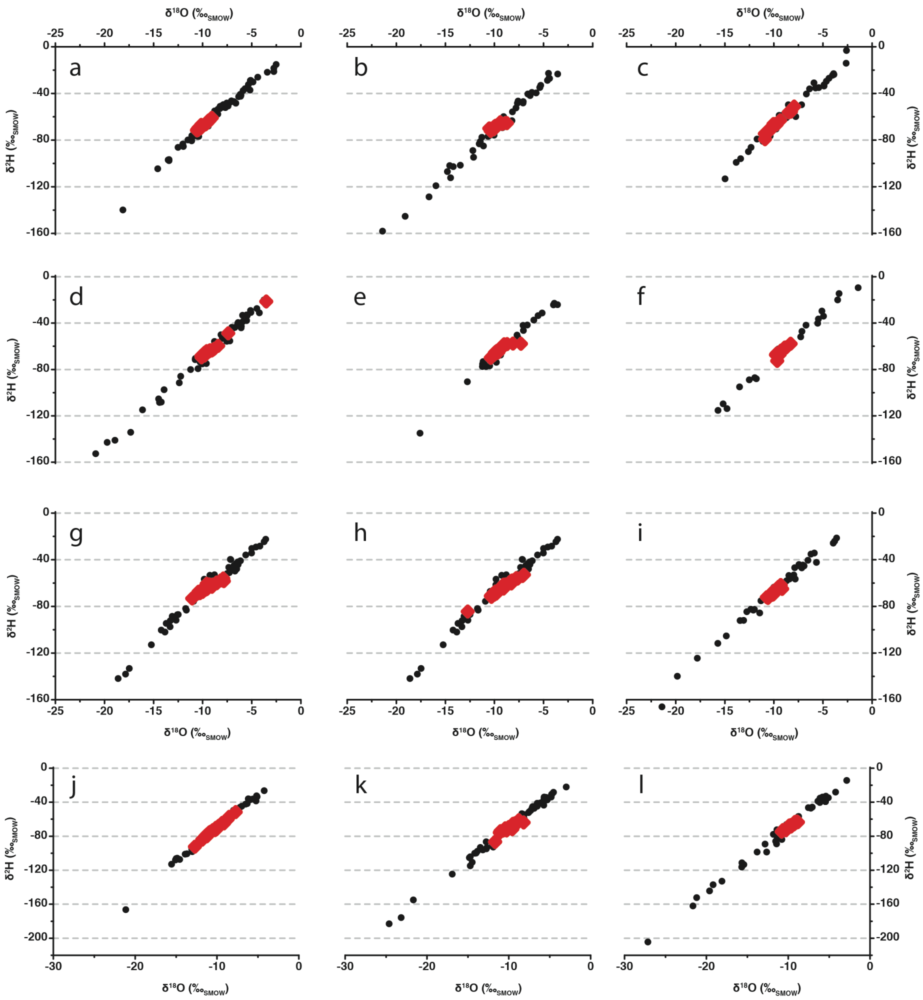

Figure 5. Crossplots of $\delta^{18}O$ and $\delta^{2}H$ for precipitation (black) and river (red) water in Romania: a) Baia Mare (precipitation) and Săsar (river), b) Bistrița (precipitation) and Bistrița (river), c) Buzău (precipitation) and Buzău (river), d) Timișoara (precipitation) and Bega (river), e) Doicești (precipitation) and Ialomița (river), f) Oradea (precipitation) and Crișul Repede (river), g) Craiova (precipitation) and Jiu (river), h) Craiova (precipitation) and Olt (river), i) Gârda (precipitation) and Arieș (river), j) Tg. Secuiesc (precipitation) and Turia (river), k) Blaj (precipitation) and Târnava (river), l) Suceava (precipitation) and Suceava-Soloneț (rivers).

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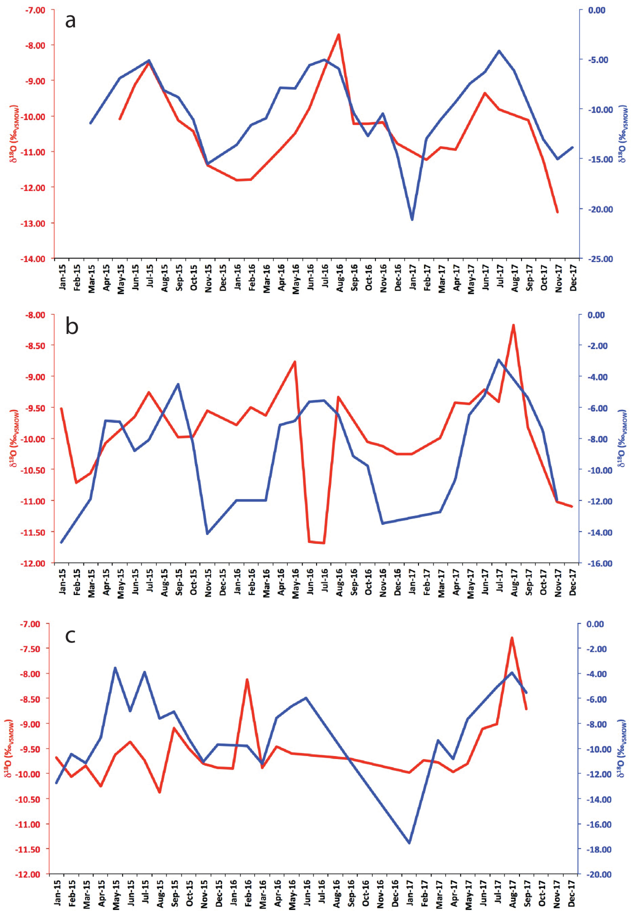

Figure 6. Examples of precipitation (blue) and river (red) δ^{18}O co-variability for Turia (top-panel), Tarnava (middle panel) and Ialomita (bottom panel) rivers.

Overall, the stable isotope data from rivers indicate a dominance of discharge generated by snowmelt in the upper sections of their respective watersheds and strong evaporative conditions in the lowlands. Rivers with catchments mainly in the plains have the weakest winter signal and strongest evaporative one, and are also the least resilient to ongoing changes in regional weather and climate patterns. Recent climate warming in Romania, as expressed by rising air temperatures (Birsan et al., 2019, 2025) increases in frequency of convective precipitation (Manea et al., 2016), and a marked decline in snow cover duration and persistence, particularly below mid-elevations (approximately 1,000-1,500 m) (Micu et al., 2021; Birsan et al., 2024), has reduced the buffering role of seasonal snowmelt on river discharge. As shown by Amihăesei et al. (2024), the shortening and upward shift of the snow season enhance the relative contribution of rainfall and recycled moisture in lowland rivers, leading to more enriched and evaporation-influenced δ^{18}O signatures and increased isotopic sensitivity to summer heatwaves. In addition, Mediterranean cyclones, historically responsible for up to ~50% of cold-season snowfall over Romania, show a declining contribution to snowfall in recent decades, particularly in late winter and spring, reinforcing reduced snow storage and a shift toward rainfall-dominated runoff that further enhances isotopic enrichment signals in lowland rivers (Amihaesei et al., 2026).

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5. Data availability

The data that support the findings of this study are openly available at https://doi.org/10.5281/zenodo.18374497 (Persoiu, 2026).

Conclusions

Oxygen and hydrogen stable isotope data collected at 22 precipitation and 19 river stations in Romania and the Republic of Moldova collected between 2015 and 2017 are reported. The precipitation data show clear spatial trends, with the Carpathian Mountains acting as an orographic barrier, separating three regions: 1) west of the mountains, with oceanic influences, 2) south of the mountains, with a combination of oceanic (Atlantic) and Mediterranean influences and 3) east of the mountains, with strong continental influences, linked to the westward expansion of the Siberian High and winter and strong local moisture recycling in summer. Interactions between atmospheric circulation patterns (NAO, SH and blocking patterns in both summer and winter) play an important role in determining the source of moisture and hence the δ^{18}O and δ^{2}H of precipitation. Time series minima of both δ^{18}O and δ^{2}H show greater spatial variability than maxima, likely reflecting the spatial variability of winter conditions, as opposed to the more uniform summer conditions, influenced by prolonged heat waves acting on large areas. The temporal variability of δ^{18}O and δ^{2}H shows a simple bimodal distribution, with minima in winter and maxima in summer, strongly influenced by air temperature. Deuterium-excess values are higher in SW Romania in autumn, indicating the northwestward penetrations of Mediterranean cyclones, carrying moisture from the highly evaporated surface waters of the Eastern Mediterranean Sea.

The δ^{18}O and δ^{2}H of river water show more nuanced variability, resulting from the complex history of waters originating in areas with different climatic influences. The values show a muted variability, being higher for small rivers, but the temporal dynamics is not linked to changes in liquid discharge. Deuterium-excess values indicate that evaporation plays an important role in the overall water balance, with large rivers and those in the eastern part of the study area showing greater evaporative loss.

Our data set and the brief analyses presented here offer an important source of information in a region where no similar data is available. Considering the rapid pace of changes in moisture sources, rainfall patterns and overall recharge patterns of surface (and ground) waters in the area, it can be used to better asses future availability of water resources and planning of their usage.

Author contributions

AP designed the study and led the writing of the article, with input from all authors. AP, RF, CAB, SB, GM, AO, EP, FZ and OB collected precipitation and river samples; RF, CAB, OB, FLF and AP conducted stable isotope analyses; AP, CAB, OK and CP analyzed the stable isotope data; MVB, DMM, VAA and MB provided and analyzed meteorological and hydrological data.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgements

We thank the numerous people who helped us collect samples in the field and analyze them in the laboratory.

Financial support

This work was supported by two grants of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2016-2210 and PN-III-P4-ID-PCE-2020-2723, within PNCDI III and by the International Atomic

Energy Agency (Coordinated Research Projects F33021, F33025, F33024, F31006 and Regional Technical Cooperation Projects RER7013 and RER7017).

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Preprint. Discussion started: 15 July 2026

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