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Stable isotope composition of precipitation events revealed modern climate variability

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Abstract

Event-based sampling of isotopes in precipitation (δ^{18}O and δ^2H) was done in a large European Moscow city (Russian Federation) to understand modern climate variability and isotopic sensitivity to air temperature and precipitation amount. A strong seasonality of δ^{18}O and δ^2H values, with a maximum in summer and a minimum in winter, was a consequence of the temperature effect as expressed by significant correlation ($r = 0.76$). Compared with historical monthly values (Global Network of Isotopes in Precipitation in 1970–1979), event-based stable isotope values in monthly means were lower in March and October and slightly higher in summer due to larger variability in precipitation amount of some events and, particularly, by an increase of the precipitation amount amplitude in last years, relative to the long-term. The isotopic signature of some monthly precipitation values was determined by the predominant role of one or two events, which provide up to 50% of the monthly value. A wide range of d-excess values from -8.7 to $+27.9‰$ for individual events was associated with a frequent change in air masses trajectories moving through Moscow, high mobility of atmospheric transport and cyclonic activity. The low correlation of δ^{18}O values with the North Atlantic Oscillation (NAO) index, absence of the significant relationship between NAO, air temperature and precipitation amount were indicative for a partial effect of the NAO on the precipitation patterns and isotopic composition of precipitation in Moscow. The study provides a first background for understanding of hydrometeorological processes using event based isotopic signature in East European precipitation.

1 Introduction

Understanding of climate variability is mainly based on air temperature and precipitation amount that is available for long-term periods and cover many regions worldwide. However, in the last five decades, stable isotopes ratios in the water molecule (δ^{18}O and δ^2H) have been used to address problems related to the precipitation cycle, including tracing the water vapor source, moisture transportation, and precipitation formation (Dansgaard 1964; Rozanski et al.

1982; Brown et al. 2006; Aggarwal et al. 2016; Vystavna et al. 2020). These isotopic tracers link to hydrological and meteorological conditions and provide important constrains on the effect of local and remote processes on precipitation spatial and seasonal variations, potentially forecasting perturbations in regular precipitation cycles (Rozanski et al. 1982, 1992). Compared to the meteorological parameters, isotopes connect both climate and hydrology and provide understanding of water origin and dynamics through space and time (Dansgaard 1964; Gat et al. 2001; Guo et al. 2019). Owning to this inherent hydroclimate connection, the isotopic composition of meteoric water is often used as a proxy for climatological, hydrological, and paleoclimate studies (Gao et al. 2016; Vystavna et al. 2020, 2021).

In general, variations in the isotope composition of precipitation depend on fixed (latitude, continentality, and altitude) and time-varying (temperature, precipitation amount, and origin) factors (Rozanski et al. 1982; Terzer-Wassmuth et al. 2021; Vystavna et al. 2021). Time-varying climatic factors control the isotope composition in precipitation through the seasonality of temperature and precipitation amount determining the so-called temperature (positive empirical

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relationship of isotopes with surface air temperature) and amount (negative relationship of isotopes with precipitation amount) effects (described for δ^{18}O by Dansgaard (1964)). Therefore, the isotopic signature of precipitation is defined by conditions of evaporation at the moisture source, local meteorological conditions during condensation, and air temperature (Dansgaard 1964; Fricke and O'Neil 1999). This leads to a great variability in the isotope composition of individual precipitation events (Sjostrom and Welker 2009; Klein et al. 2015; Chizhova et al. 2017; Vystavna et al. 2020). Recent studies consider the relationship between the isotope values and the source of moisture defined by back trajectories to trace the location of air mass sources and path of moisture that provides a link of isotopic signature of precipitation with evaporation conditions in the region (Sjostrom and Welker 2009; Vachon et al. 2010; Friedman et al. 2002; Kurita 2011; Aemisegger 2018; Wang et al. 2021). Compared to monthly resolution sampling, event-based sampling can give additional information on the convective processes and moisture sources of precipitation (Klein et al. 2015; Krklec et al. 2018; Heydarizad et al. 2019). However, despite these benefits, such high-resolution sampling is complicated in term of methodology and continued observations and cannot be easily achieved at many sites.

Not only an individual isotopes measurement but also isotope relationship is particularly useful to understand precipitation formation processes in climate studies. Defined as the deuterium excess (or d-excess $= \delta^2$H $- 8\delta^{18}$O), by Dansgaard (1964), this isotopic relationship has shown to be dependent on the humidity conditions in the area of moisture evaporation (Merlivat and Jouzel 1979; Juhlke et al. 2019). According to the theoretical model of isotope fractionation processes during evaporation from the ocean surface, d-excess value in vapor is defined by relative humidity (RH) of the near-surface air with respect to water vapor saturation pressure at the ocean surface, as well as to the ocean surface temperature (Merlivat and Jouzel 1979). Therefore, despite the processes of isotope kinetic fractionation during the formation of snow crystals (Jouzel and Merlivat 1984) and sub-cloud evaporation, d-excess in the precipitation reflects the conditions of temperature and humidity in moisture source (Pfahl and Sodemann 2014).

The main goal of our study was to understand the changes of hydroclimate conditions in a large European city (Moscow, Russian Federation) located in the continental climate using hydrometeorological and isotopic values. The objectives of the research were (i) to evaluate long-term changes in air temperature and precipitation amount; (ii) to compare values of isotopes in precipitation in modern (2018–2019) and past (1970–1979) periods; (iii) to discuss influence of meteorological conditions and atmospheric oscillation on the event-based values; and (iv) to estimate the difference between the monthly average and individual isotope signal

of precipitation. In this paper we present δ^{18}O and δ^2H data of precipitation on individual precipitation events sampled in 2017–2018. New stable isotope data, after a 35-year gap, allows to assess whether the main features of isotopic characteristics of precipitation have changed in recent years due to climate change. The research provides a background for understanding of isotopically evident hydroclimate variations in the continental part of Eastern Europe that is poorly studied and rarely presented in international reviews.

2 Materials and methods

2.1 Sampling site

Precipitation was sampled at the Meteorological Observatory of the Lomonosov Moscow State University in Moscow, Russian Federation (55.707 N, 37.522 E). Long-term (1960–2020), monthly data on precipitation amount and air temperature in Moscow provide annual means of 702 mm and 5.6 °C, respectively. Long-term temperature of the coldest month (January) is – 7.9 °C and the warmest (July) is 19 °C. Half of the annual precipitation amount falls from June to October. The isotopic values for 1970–1979 period were collected from the IAEA (International Atomic Energy Agency)/WMO (World Meteorological Organization) Global Network for Isotopes in Precipitation (GNIP) (access link https://nucleus.iaea.org/wiser). In Moscow, based on monthly precipitation sampling of Hydrometeorological Service Soviet Union, the δ^{18}O and δ^2H data in precipitation were obtained and included to the GNIP database in 1970–1979. In 1980, the sampling program was stopped; but in 2014, stable isotope measurements in precipitation have been resumed as an event-based sampling.

2.2 Samples collection and analysis

The study was based on the data for all individual events, including rain, snowfall, or snow-rain mixture, and was done from the time of precipitation event occurrence till the end of the event on the current or adjacent day. Precipitation was sampled using a vinyl plastic 80×80 cm funnel, located at 2 m above the ground surface. A plastic bucket was placed under the funnel to collect rainwater. In winter, after the end of the snowfall, the snow from the funnel was collected with a plastic scoop into a bucket for thawing at room temperature (24 °C) without additional heating. Samples were stored in small plastic bottles sealed with parafilm. All precipitation events (281 samples) were sampled in 2017–2018, covering two calendar years. Air temperature, amount of precipitation, and its duration were recorded daily.

Oxygen and hydrogen stable isotope analyses were carried out in the stable isotope laboratory of Geography

Faculty, Lomonosov Moscow State University (Russian Federation) using Delta V Plus mass spectrometer (Thermo Co., Germany) combined with the GasBench II option in helium continuous flow regime (CF-IRMS). Hydrogen isotope analysis was carried out by the method of isotopic equilibration with H_2 for 40 min. All $\delta^{18}O$ and δ^2H values were calibrated using three standards to ensure quality control and to cover the entire range of variations: GISP, V-SMOW, and V-SLAP2. The average measurement accuracy was ± 0.1 and $\pm 0.7‰$ for $\delta^{18}O$ and δ^2H, respectively.

2.3 Moisture source tracking

To assess the possible influence of long-range transport on the isotopic composition of Moscow precipitation, the method of computing back trajectories by the hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) model was used to track a moisture source (access link NOAA, https://ready.arl.noaa.gov). It is assumed that the movement of air particles corresponds to the global transfer of air mass, including water vapor. It was previously presumed that the residence time of water vapor in the air is 5 days. However, recent studies show that the residence time can reach 8–10 days (van der Ent and Tuinenburg 2017) and has led to calculation trajectories 240 h back (10 days) in the latest works on isotope meteorology (Aemisegger 2018; Bailey et al. 2019). In our study, we use 144-h back trajectories, which cover an excessive time interval for moisture source tracking. Depending on the conditions of RH and the height of the air particle relative to the boundary layer height, a partial condensation or additional evaporation occurs during air movement along the trajectory (Sodemann et al. 2008). In most cases, the back trajectories are too long and located over the ocean, likely being fed by moisture from several sources. Therefore, the constructed back trajectories rather schematically indicate the geographical position of the main source region of moisture. The moisture source region and the distance of air mass transfer were diagnosed by air parcel back-trajectories HYSPLIT, using the GDAS $1° \times 1°$ meteorological dataset (Draxler and Rolph 2011; Stein et al. 2015; Rolph et al. 2017). The trajectories were calculated for each day of precipitation with endpoints at 3000 m at 12:00 UTC.

2.4 Additional data collection and calculations

Long-term meteorological data for Moscow was retrieved from databases of Federal Service for Hydrometeorology and Environmental Monitoring (access link www.aisori.ru). The normality of the data was verified using the Kolmogorov–Smirnov test. Nonparametric regression modeling based on an analysis of model residuals was used to define non-linear trends (Vystavna et al. 2020). Methods included locally weighted regression and smoothed scatterplots (LOWESS).

Kernel functions were used to weight the observations. The nonparametric regression modeling maximized the statistical coefficient of explanation (determination) by performing a test of significance. Mann–Kendall seasonal test was used to detected trends in precipitation and air temperature. Shift and trends decomposition were done to understand the time variation in meteorological data. Calculations were done using R software v.3.6.3.

Previous observations of isotopes composition in Moscow precipitation were obtained from the GNIP Database (access link https://nucleus.iaea.org/) for the period of January 1969 to December 1983. Index NAO was retrieved from the NOAA Climate Prediction Center (access link https://www.cpc.ncep.noaa.gov). An ordinary least square regression model of the relation between δ^2H and $\delta^{18}O$ was used to establish a local meteoric water line and significance was determined using Spearman's correlation coefficient.

The calculation of the amount weighted monthly values of δ^2H and $\delta^{18}O$ of precipitation was carried out as following:

$$X = \Sigma(Xi \times Ai/A) \tag{1}$$

where X is the amount of weighted monthly values of δ^2H and $\delta^{18}O$; X_i—value of δ^2H or $\delta^{18}O$ of the ith precipitation event; A_i is the amount of precipitation of the ith event in mm, and A is the total amount of precipitation of the month in mm.

The $\delta^{18}O$ dependency on the temperature (given per 1 °C of air temperature) was calculated as follows:

$$\delta18Ot = \Delta\delta18O/\Delta T \tag{2}$$

where Δ $\delta^{18}O$ and ΔT are the difference between the monthly highest and lowest $\delta^{18}O$ values, and the recorded highest and lowest monthly air temperature, respectively.

3 Results and discussion

3.1 Isotopes values in precipitation events, its relation to air temperature and precipitation amount

Long-term (1960–2020) monthly data on air temperature at the Moscow station displayed a significant increasing trend (Fig. 1) that was confirmed by results of the Mann-Kendall seasonal trend (tau = 0.195, 2-sided p value = 0.00001). Moving average trend indicated a pronounced increase in air temperature since end of the 1980th (Fig. SI-1), particularly, in an increase of temperature minima.

Analysis of breaking points in the time series indicated 1988 as a year, when the temperature trend significantly changed (increased). Nonparametric regression revealed significant air temperature growth trends in summer and
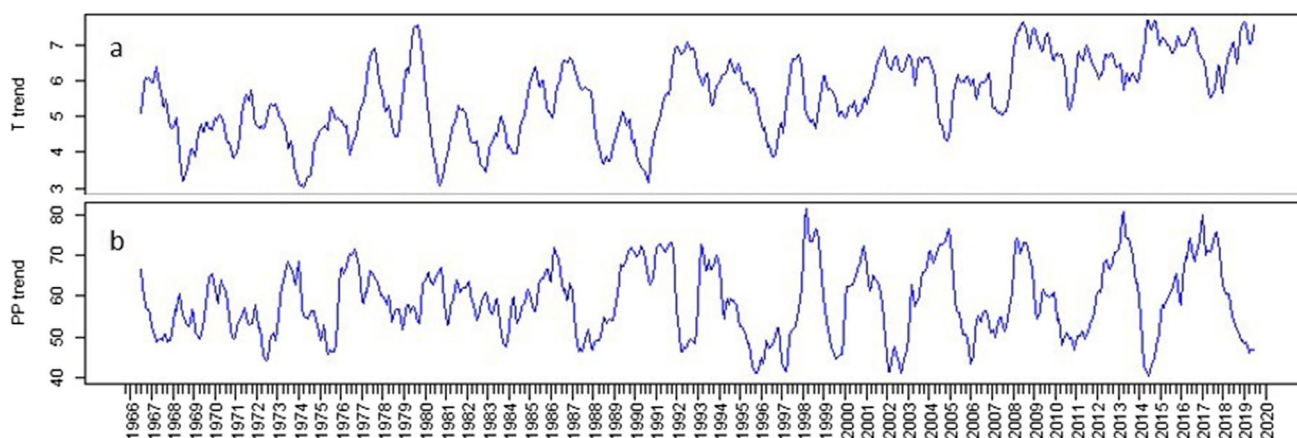
Fig. 1 Time series of the estimated moving average trend of air temperature (T) (**a**) and precipitation amount (PP) (**b**) in Moscow

winter (Fig. SI-1). While no significant trend was found for precipitation amount, still we can observe an increase of the precipitation amount amplitude (as difference between minimum and maximum values) since 1995 (Fig. 1). These results suggest a change of the precipitation regime, with a higher frequency of months with extreme low and extreme high precipitation amounts. Breaking points analysis indicated a shift of the precipitation regime in 1991. This shift well corresponds to similar shifts in hydroclimate conditions observed in the Northern Hemisphere (Vystavna et al. 2017, 2020) and likely attributed to changes in North Atlantic Oscillation (Baldini et al. 2008). This is discussed in detail below.

Stable isotope signature of precipitation reveals a strong seasonality, with a maximum in summer and a minimum in winter (Fig. 2). The high values of $\delta^{18}O$ (from -1.59 to $-4.9‰$) and δ^2H (from -8 to $-34‰$) were obtained for rain samples, which fell in June and August 2017, and May and July 2018. The lowest values were obtained for mixing snow-rain events on 31 October 2017 ($\delta^{18}O = -30.2‰$, $\delta^2H = -228‰$) and for snow in January 2018 ($\delta^{18}O = -23.1‰$, $\delta^2H = -181‰$).

The isotopic seasonality is a consequence of the temperature effect, which is expressed by a linear relationship with a significant correlation coefficient (Fig. 3). The Spearman's correlation coefficient for all events was 0.76, which indicates a high significance of temperature for $\delta^{18}O$ values of precipitation. Such seasonality and strong relationship between isotopes and air temperature is typical for many continental stations located in the Northern Hemisphere, including most of Europe stations and Greenland. The $\delta^{18}O$ dependency on temperature ($\delta^{18}Ot$) is 0.45‰/°C for precipitation amount-weighted monthly mean and 0.5‰/°C for arithmetic mean. Established $\delta^{18}Ot$ was close to that for 2014 (0.5‰/°C ($\delta^{18}O = 0.5t - 15.34$, $R^2 = 0.92$ for monthly amount-weighted averages) (Chizhova et al.

2017). Globally, for monthly mean values, the $\delta^{18}Ot$ varies from 0.7‰/°C at high latitudes to 0‰/°C at low latitudes (Dansgaard 1964; Gat et al. 2001). For Europe, $\delta^{18}Ot$ of 0.58‰/°C was earlier defined by Rozanski et al. (1992) and 0.11–0.47‰/°C for Central Europe (Salamalikis et al. 2016). For Krakow (Poland) precipitation (observation period is 1975–2018), the $\delta^{18}Ot$ was 0.57‰/°C and 0.42‰/°C for arithmetic and precipitation amount-weighted annual mean, respectively (Duliński et al. 2019). The $\delta^{18}Ot$ ratio for weighted values in Austria varies from 0.31‰/°C in Salzburg to 0.62‰/°C in Langenfeld and was 0.35‰/°C ($\delta^{18}O = 0.35$ t $- 13.43$) in Vienna (data from Austrian GNIP stations). For all precipitation in Austria, the resulting $\delta^{18}Ot$ is 0.39‰/°C with $R^2 = 0.85$ (Hager and Foelsche 2015). Therefore, $\delta^{18}Ot$ ratio established for Moscow precipitation in 2017–2018 is close to that for European stations. However, the use of arithmetic mean $\delta^{18}O$ values in some studies complicates a direct comparison with amount-weighted means (Rozanski et al. 1992). A significant difference between the amount-weighted and arithmetic means of $\delta^{18}O$ values of precipitation in Moscow (Table 1) can be explained by high variability of monthly precipitation amount.

The amount-weighted mean is important as an isotopic signature of precipitation for river runoff and groundwater studies where balance calculations are used. However, the arithmetic mean is an indicator of the stability/instability of the precipitation pattern and shows the isotopic signature of the prevailing precipitation. It also reflects the dependence on the condensation temperature since the relationship with temperature in this case is not affected by precipitation amount.

In our data for 2017–2018, a slight difference in the isotope-temperature relationship was found between the amount-weighted and arithmetic means of $\delta^{18}O$ values (Fig. 3). No significant correlation was observed between
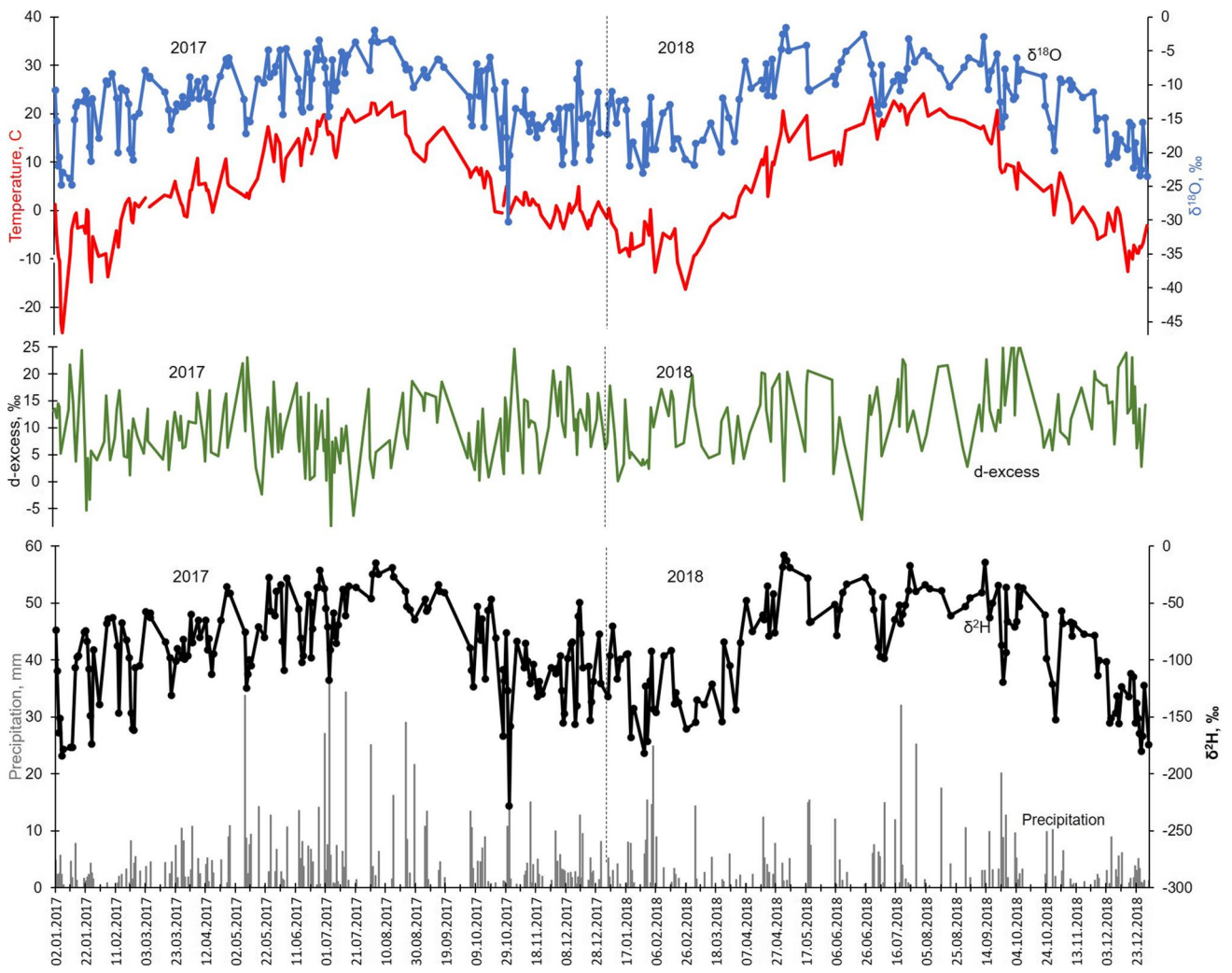
Fig. 2 δ^{18}O, δ^2H, and d-excess values of all precipitation events in 2017–2018

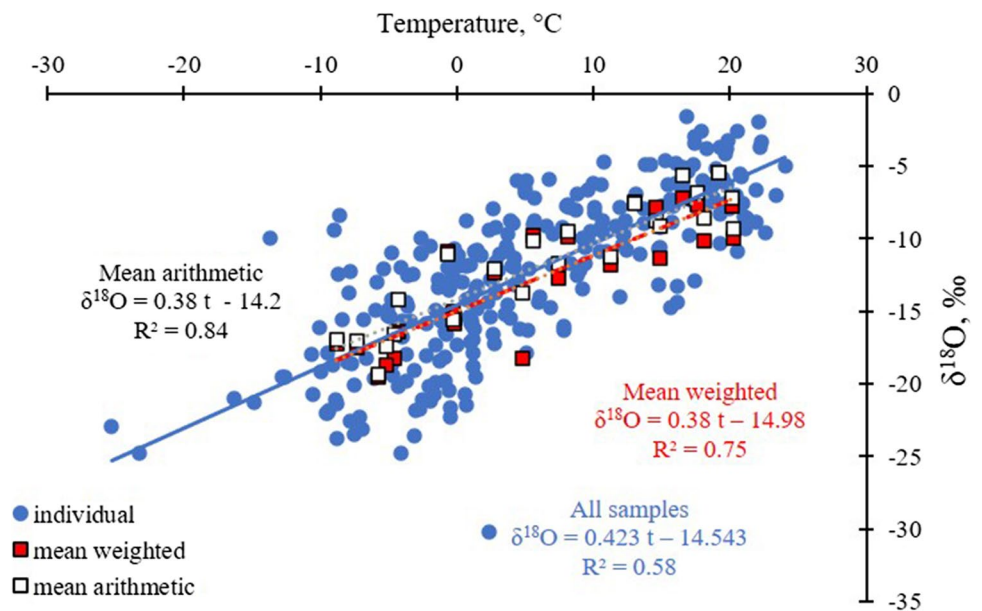**Fig. 3** The δ^{18}O-temperature relationship for Moscow precipitation

Mean arithmetic
δ^{18}O = 0.38 t - 14.2
R^2 = 0.84

Mean weighted
δ^{18}O = 0.38 t – 14.98
R^2 = 0.75

All samples
δ^{18}O = 0.423 t – 14.543
R^2 = 0.58

● individual
■ mean weighted
□ mean arithmetic

Table 1 Arithmetic and amount-weighted mean values of $\delta^{18}O$, δ^2H, and d-excess of precipitation in Moscow for 2017–2018

| Month | n | Average | | | Amount-weighted mean | | | |
| | | $\delta^{18}O$, ‰ | δ^2H, ‰ | d-excess | 2017 | | 2018 | |
					$\delta^{18}O$, ‰	δ^2H, ‰	$\delta^{18}O$, ‰	δ^2H, ‰
January	31	-16.8 ± 4.7	-126.1 ± 38.4	8.5 ± 6.8	-17.5	-129.0	-18.3	-139.5
February	23	-15.4 ± 4.2	-113.6 ± 33.5	9.5 ± 4.9	-16.4	-121.9	-17.2	-127.2
March	20	-14.2 ± 3.8	-104.9 ± 30.2	8.9 ± 4.6	-12.4	-90.7	-18.7	-136.0
April	22	-9.9 ± 2.6	-67.5 ± 20.8	11.5 ± 5.1	-9.8	-68.3	-9.8	-63.7
May	18	-9.1 ± 4.7	-59.7 ± 36.2	12.9 ± 8.0	-11.8	-78.2	-7.2	-43.3
June	23	-8.2 ± 3.5	-57.1 ± 27.1	8.5 ± 6.7	-7.9	-51.6	-7.7	-47.7
July	27	-8.9 ± 3.0	-61.7 ± 23.6	9.8 ± 7.7	-10.1	-74.5	-10.0	-66.0
August	14	-6.1 ± 2.6	-39.2 ± 16.1	9.6 ± 7.0	-6.8	-42.4	-7.8	-46.2
September	17	-8.6 ± 3.4	-54.4 ± 25.7	14.7 ± 5.6	-7.5	-48.7	-11.3	-74.0
October	25	-13.0 ± 5.6	-93.8 ± 45.0	10.4 ± 7.9	-18.2	-136.1	-12.8	-85.9
November	20	-13.7 ± 3.2	-98.6 ± 26.5	10.9 ± 5.9	-15.9	-115.8	-10.9	-74.4
December	40	-17.4 ± 4.0	-125.0 ± 31.6	14.0 ± 5.2	-15.0	-106.0	-19.6	-141.7

$\delta^{18}O$ values and precipitation amount for individual precipitation event and for monthly means.

In the framework of the GNIP program in 1970–1979, the isotope signature of precipitation was established monthly, i.e., the monthly composite samples, which represented all precipitation that fell during the calendar month. Thus, these samples had already a precipitation amount-weighted monthly isotopic signature. The monthly $\delta^{18}O$ values for 2017–2018 differ from those (Fig. 4). Figure 3a illustrates that $\delta^{18}O$ values of some months were constant between years and in the long-term. A larger annual variability in monthly mean $\delta^{18}O$ values derived from differences in meteorological conditions of a particular year such as air temperature and amount of individual precipitation events (Fig. 5).

A significant difference (~5 ‰) in relation to long-term monthly mean was found in March 2018 and May and October 2017. The amount-weighted mean $\delta^{18}O$ value of precipitation in March 2018 was significantly lower (by 6‰) than in 2017 and lower than the long-term mean. March 2018 was characterized by lower air temperatures with the mean monthly temperature of $-5.2\ °C$, compared to March 2017, when the mean monthly air temperature was $+2.7\ °C$. In March 2017, 70% of precipitation had $\delta^{18}O$ values from -11 to $-15‰$, and 30% of precipitation had $\delta^{18}O$ value $> -11‰$. However, in March 2018, 50% of precipitation had $\delta^{18}O$ values from -11 to $-15‰$ and the other 50% of precipitation had values of two precipitation events occurring on the 4th and 22nd of March, -21.8 and $-19.9‰$, respectively, indicating a dominant effect of these two events on the monthly isotopic composition. We suggest that the extreme values of isotopes in precipitation in March 2018 were associated with the temperature effect in relation to air temperature difference between 2017 and 2018. However, during March 2018, precipitation had a correlation coefficient with temperature of $r=0.6$; the $\delta^{18}O$ values varied from -12 to $-21.8‰$ while the air temperature on these days varied from -0.7 to $-9.4\ °C$. The $\delta^{18}O$ values for March 2018 were lower compare to the recorded temperatures and correspond to the winter season (such values are typical for January and February). The arithmetic mean $\delta^{18}O$ for March corresponds to the range of $\delta^{18}O$ for precipitation in January 2017, but the air temperatures in March 2018 were higher than in January 2017. In January 2017, the correlation coefficient between $\delta^{18}O$ and air temperature was 0.78 indicating a high correlation. Considering that only eight precipitation events occurred were during March, a significant deviation from the long-term average is expressed for the arithmetic mean values as well. In March 2018, back trajectories indicate the North Atlantic, Greenland, and southern regions of Europe as moisture sources, which is typical for winter and spring seasons. Possible reason for unusual isotope-temperature signatures of precipitation is a combination of two factors: (i) the different moisture sources of precipitation and (ii) local meteorological conditions such as temperature gradients in the troposphere of Moscow. The atmosphere of Moscow is characterized by frequent changes in the magnitude of temperature gradients and unstable atmosphere, especially in winter and spring–autumn seasons (Kadygrov et al. 2002).

In October 2017, precipitation was characterized by very low monthly weighted $\delta^{18}O$ value ($-18.2‰$). We found that this low isotopic value was caused by the contribution of one precipitation event on 31 October (28 mm that equals to 30% of the monthly precipitation), with a $\delta^{18}O$ value of $-30.2‰$. It was a mixture of snow and rain falling at an air temperature of $+2.4\ °C$. Most likely, mixed precipitation was the result of the partial melting of snow crystals in a warm lower atmosphere. These meteorological features also describe
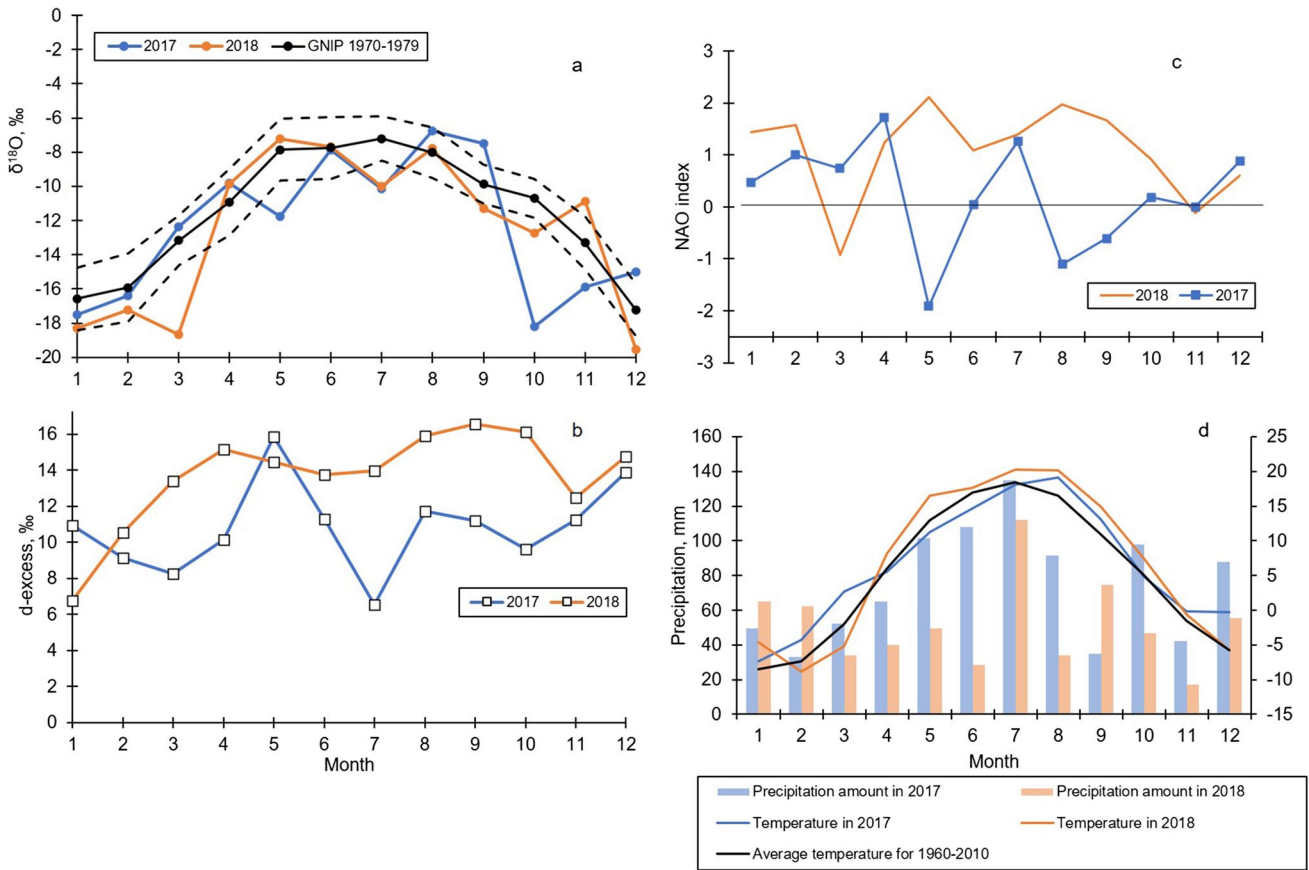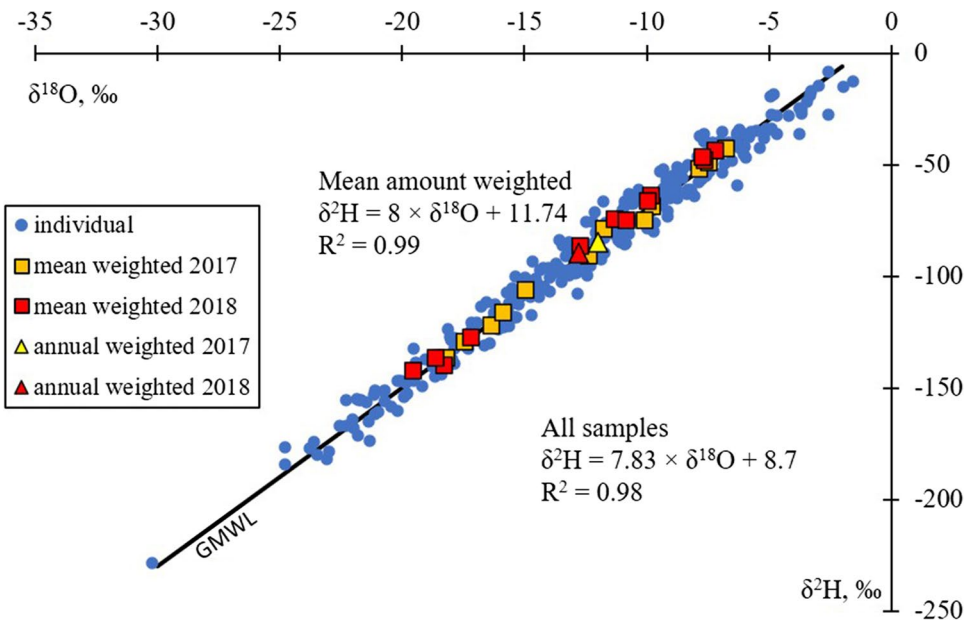
Fig. 4 Monthly amount-weighted mean values of $\delta^{18}O$ (**a**), d-excess (**b**), and NAO-index (**c**) of precipitation (**d**) for 2017–2018. The standard deviations from the monthly means 1970–1979 shown by dotted lines in (**a**)

Fig. 5 $\delta^{18}O$-δ^2H plot for all samples of precipitation in Moscow in 2017–2018

Mean amount weighted
$\delta^2H = 8 \times \delta^{18}O + 11.74$
$R^2 = 0.99$

All samples
$\delta^2H = 7.83 \times \delta^{18}O + 8.7$
$R^2 = 0.98$

- individual
- mean weighted 2017
- mean weighted 2018
- annual weighted 2017
- annual weighted 2018

the deviations of the monthly amount-weighted mean values from the long-term average. Generally, all fluctuations of the monthly mean values of $\delta^{18}O$ are mainly connected with temperature and by the difference in the contribution of individual events. The fact that half of the monthly precipitation was associated with one or two events explains the observed increase in the precipitation amount amplitude since 1995 (Fig. 1).

At the annual scale, the amount-weighted mean annual value of $\delta^{18}O$ was $-12.0\permil$ for 2017 and $-12.8\permil$ for 2018. This difference is due to the large contribution of summer precipitation in 2017 (Fig. 4d). In June and August 2017, precipitation amount was 30% higher than long-term amount and dramatically higher than in summer 2018. A total amount of precipitation in 2018 (620 mm) was ~30% lower than in 2017 (900 mm).

The $\delta^{18}O$ and δ^2H values of precipitation in Moscow in 2017–2018 clustered close to the Global meteoric water line and can be approximated by the equation $\delta^2H = 7.83$ $\delta^{18}O + 8.7$ ($R^2 = 0.98$); however, the points of individual precipitation events had some pronounced deviation (Fig. 4).

3.2 Deuterium excess and moisture source origin

The monthly values of d-excess varied from -5 to $25\permil$ without a significant correlation with $\delta^{18}O$ (Fig. 6) indicating a high degree of intra-annual variations with a wide range of d-excess values. The arithmetic mean of d-excess for all precipitation was $10.8\permil$, and the average deviation was $5.4\permil$. Therefore, following Klein et al. (2015), we classified precipitation events with $< 5.4\permil$ as events with low d-excess values and those with $> 16.2\permil$ with high d-excess values. In 2017–2018, 62 events with low d-excess and 63 with high d-excess values were determined. About 60% of precipitation events was characterized by d-excess values lying within range of the calculated mean and its average deviation ($10.8 \pm 5.4\permil$) and 40% of precipitation events was characterized by d-excess values outside of this range.

Low d-excess values were mainly observed in May, June, and July and mostly attributed to partial under-cloud evaporation of rain droplets in conditions of low RH (from 58 to 80%) and high temperatures (above $+15\ °C$) in summer months. However, low d-excess values were also found in January 2017 and December 2018. In winter season, the re-evaporation effect becomes negligible and cannot result in low d-excess values. According to vertical sounding in the suburbs of Moscow (station No. 27713 in the University of Wyoming database access link www.weather.uwyo.edu/upperair/sounding.html), no significant air drying was observed at altitudes of 2000–3000 m a.sl in the winter period. From earlier work of Jouzel and Merlivat (1984), it is known that the influence of the kinetic effect during the formation of snow crystals is not responsible for high d-excess since they are typical both for snow and rainfall. Therefore, we suggest that low and high d-excess values of precipitations were the result of conditions determined by the source of moisture and, possibly, of the air mass trajectories moved into Moscow.

For 2% of precipitation events, the trajectories ended in the high-latitude sector of the Arctic or the Canadian Arctic Archipelago. Precipitation in Moscow is mainly related to the total western transport of air masses, according to back trajectories for each precipitation date. Some precipitation events were also associated with the influx of air masses from the continental and southern regions.

According to the results of the back trajectory analysis, main regional sources of precipitation in Moscow in 2017–2018 were I—the North Atlantic (26% of precipitation events), II—the Atlantic Ocean in the sector from 45 to 40°N (19%), III—the North and Norwegian Seas (5%), IV—the sector of the Arctic Ocean from Svalbard to the Kara Sea (7%), V—the Mediterranean Sea and inland regions of southern Europe (14%), and VI—the sector that includes the Black Sea and the inland areas south of Moscow (27%) (Fig. 7).

Fig. 6 Variations of d-excess values (d-exc) in Moscow precipitation in 2017–2018
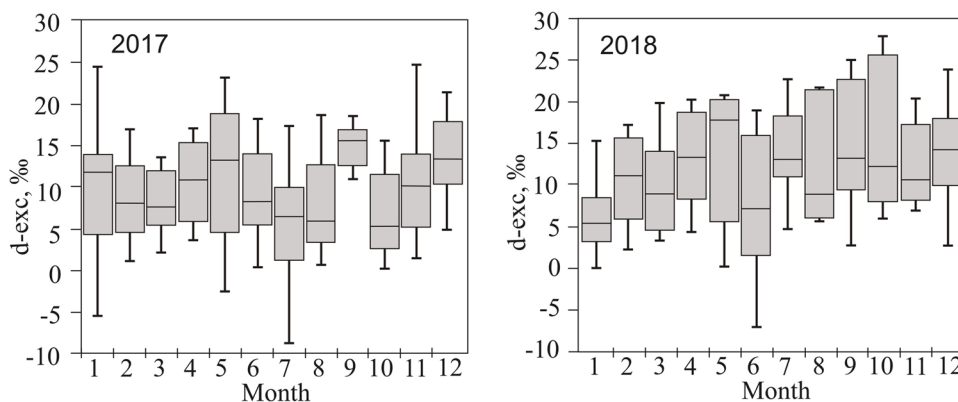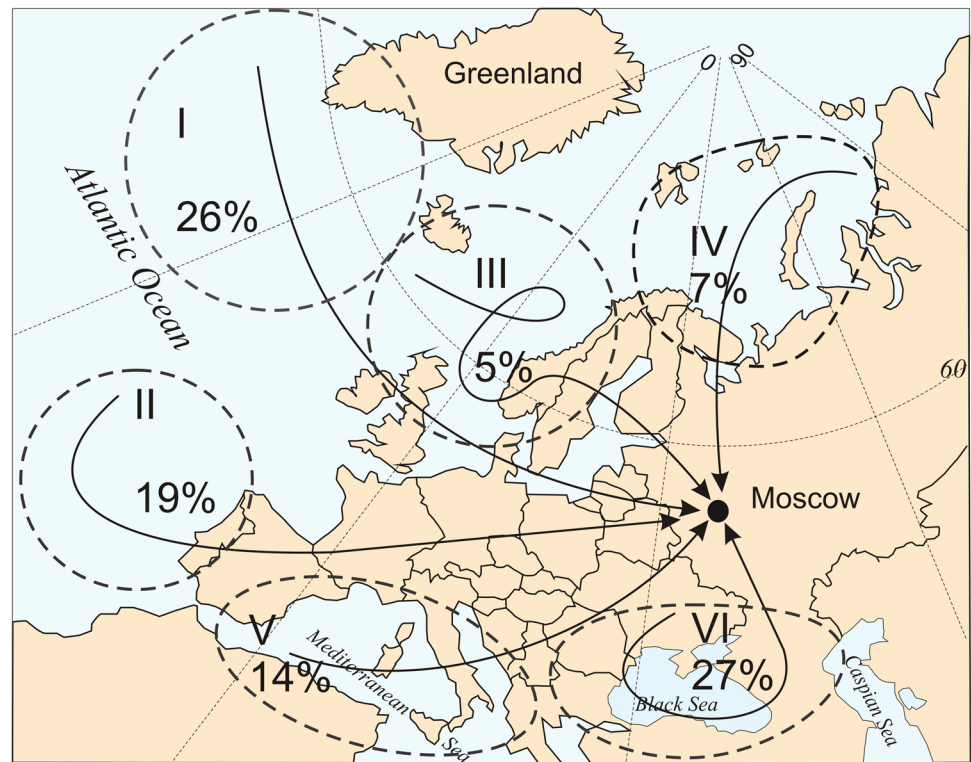
Fig. 7 The main regions of moisture source for Moscow precipitation in 2017–2018

In the winter season, precipitation is mainly associated with the North Atlantic (the southern cape of Greenland), in summer with the southern continental regions and also the Mediterranean Black, and Caspian Seas. This factor is also responsible for the high *d*-excess values in summer precipitation since these seas are sources of moisture with high *d*-excess values (Gat and Carmi 1970; Juhlke et al. 2019). The contribution of re-evaporating moisture from continental areas is also responsible for high *d*-excess values. It is known that the contribution of moisture recycling leads to high *d*-excess values of precipitation (Fröhlich et al. 2008; Terzer-Wassmuth et al. 2021). Thus, high *d*-excess values in summer precipitation could be associated with air inflow from the Mediterranean and Black Seas, as well as from inland regions of Russia and Europe (re-evaporation from freshwater reservoir).

Significant variations in *d*-excess of winter precipitation (including autumn and spring months, i.e., from October to April) are not so obvious. There were 35 events of precipitation with low *d*-excess and 37 events with high *d*-excess from October to April. For precipitation with low d-excess values (from −7 to 5.4‰), the back trajectories indicate the movement of air masses from the North Atlantic (Fig. 7a), from continental Canada, high Arctic, and even from the Kara Sea and continental regions of Western Siberia. The last two sources were quite rare for Moscow.

The *d*-excess values of precipitation primarily reflect the conditions in the moisture source, low *d*-excess values are associated with high values of RH over the ocean surface and vice versa. Earlier, it was shown that high *d*-excess values correspond to a low RH (Jouzel and Merlivat 1982). For winter precipitation in Reykjavik, such a relationship was established as −0.68‰/% (Aemisegger 2018). Recently, it has been shown that *d*-excess values and RH (d-excess $= -0.47\text{RH} + 52.5$, $R^2 = 0.48$) were clearly correlated (Uemura et al. 2008; Sodemann et al. 2008).

Winter precipitation in Moscow with low *d*-excess values is associated with the transport from the Atlantic, but the source is located both in the northern regions (near Greenland) and more southern regions, up to 35°N, as can be seen from the shape of back trajectories (Fig. 8).

In some cases, air masses have moved from the high Arctic or the Canadian Arctic Archipelago, covered with sea ice. The sea ice area was the largest in April 7, 2018, according to NOAA data (access link https://nsidc.org). By this date, the area occupied by sea ice gradually increased from December and reached its maximum. Some of the trajectories end above the ice surface. This cold air blows down to the open water region and removes vapor from the ocean surface.

Studies of the relationship between *d*-excess values and the source of precipitation in Siberia (Kurita 2011) have
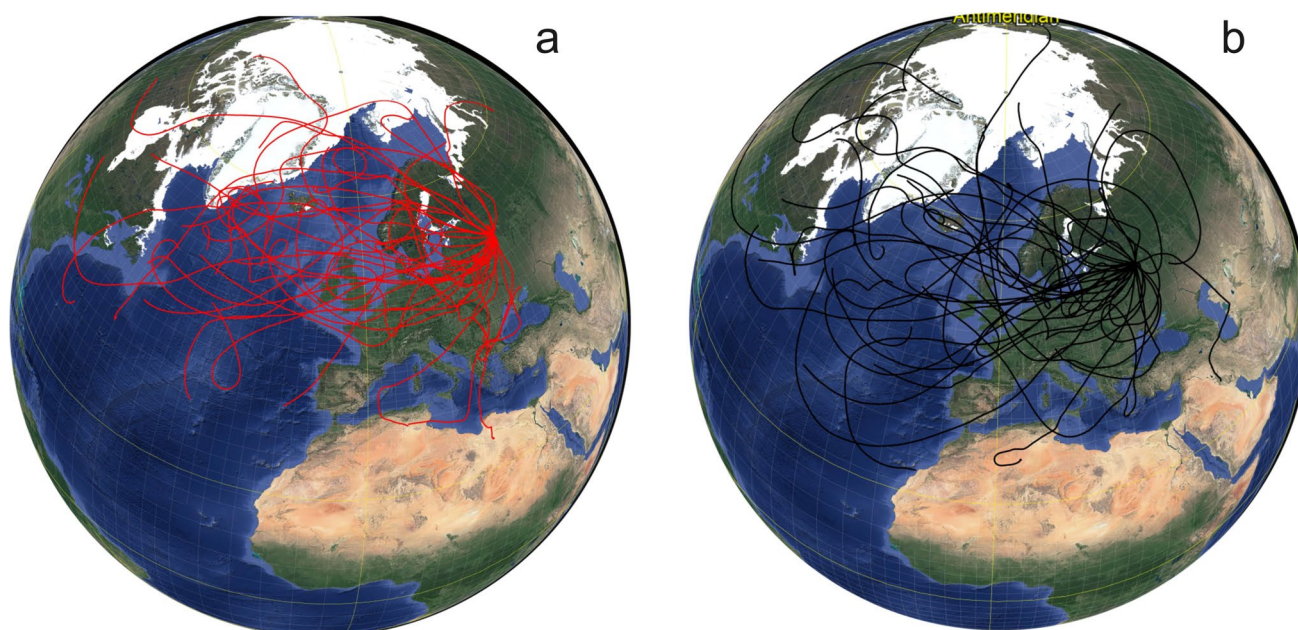
Fig. 8 The shape of back trajectories for events with low *d*-excess values (**a**) and high *d*-excess values (**b**) in Moscow in 2017–2018 from October to April: the trajectories were calculated for each pre- cipitation day with endpoints at 3000 m a.s.l at 12:00 UTC based on GDAS 1° × 1° meteorological dataset

shown that from autumn to winter the main sources were switched. In autumn, air masses with high *d*-excess values (> 20‰) are formed over the Arctic Ocean, not covered by ice under conditions of low RH and a significant tempera- ture gradient between the cold air and the warm sea sur- face. In October, *d*-excess values of air masses originated in the Arctic were clearly higher than those of the continental origin. The contribution of Arctic moisture decreases start- ing in December, but there were similar *d*-excess values of both Arctic and continental types. Thus, the humidity source for Arctic air masses appears to switch from locally driven to moisture transport from lower latitudes in early winter (Kurita 2011).

In Moscow, in 2017–2018, five out of 35 precipitation events with low *d*-excess values were associated with tra- jectories that ended in the Canadian Arctic Archipelago or the high Arctic above the ice surface (Fig. 8a). In this case, the dominant moisture source represents the open water in the Arctic sector. Arctic moisture has *d*-excess values indica- tive for low sea surface temperature and high RH. However, some events with high *d*-excess values related to trajecto- ries ended above the ice surface (Fig. 8b). Perhaps these air masses represent moisture transport from the more south- ern sector of the Atlantic, but not an Arctic moisture. The trajectories back to 144 h showed a long path (more than 5000 km) to Moscow. This indicates a high rate of (1000 km per day) air mass influx from October to April, a high atmos- pheric transport and high cyclonic activity.

For precipitation falling on adjacent days in Moscow, there is a contrasting change in source regions, which are significantly distant from each other (up to 2000 km). There- fore, we believe that the low and high *d*-excess values in precipitation relate to RH in moisture source. The condi- tions of evaporation in the autumn–winter season at a low RH normalized to temperature of the ocean surface lead to higher *d*-excess values in European precipitation in the autumn–winter season than in the spring–summer season, which also was found in Kharkiv, Vienna, Geneva, and Kra- kow (Fröhlich et al. 2002; Duliński et al. 2019; Diadin and Vystavna 2020). Overall, the European continent is charac- terized by a regular seasonal pattern, with *d*-excess values generally higher from October to January and lower from February to August (the "hysteresis loop"). However, this seasonal pattern is not evident in the Moscow data arith- metic mean and amount-weighted mean of *d*-excess values (Table 1) and the distribution of individual events (Fig. 6). Precipitation in Moscow is likely formed with a large influ- ence of moisture from the southern and continental regions, despite exhibiting a similar $\delta^{18}Ot$ ratio as Europe.

3.3 North Atlantic Oscillation influence on isotopic values and climate patterns

In term of meteorological conditions and isotopic charac- teristics of precipitation, a winter period is near the long- term averages. For the winter months (December, January,

and February), a low correlation ($r = 0.38$) with the NAO index (NOAA/National Weather Service) was observed, indicating only partial influence of processes in the Atlantic on the precipitation in Moscow. NAO dominates winter temperatures over much of the Northern Hemisphere (Baldini et al. 2008). Generally, a strong positive NAO index is associated with temperatures above average in northern Europe and below average temperatures in Greenland and often in southern Europe and the Middle East (Hurrell et al. 2003). A positive NAO index is also associated with heavy rainfalls (above average amount) in northern Europe and Scandinavia in winter and with rainfalls below average amount in southern and central Europe. According to previous studies (Baldini et al. 2008; Comas-Bru et al. 2016), positive correlations were observed between $\delta^{18}O$ values in winter precipitation and NAO index for most GNIP stations. We found that for central Europe, the Spearman coefficient ranged from 0.6 to 1, but no significant correlations were found for moisture originated from southeastern Europe, Ireland, and some stations near the Baltic Sea. This means that the proximity of the seas (Mediterranean, Norwegian, and Baltic) makes a significant contribution to the disruption of NAO impact.

In winter 2017 and 2018, a positive phase of the NAO index was noted, but the Spearman's correlation coefficient between $\delta^{18}O$ and NAO was rather low ($r = 0.38$) and no correlation of NAO with precipitation amount and air temperature was found. In general, for an inland region such as Moscow, the winter influence of NAO on the isotopic composition of precipitation is much lower than for Central Europe. A possible reason for the decrease in the influence of NAO on meteorological conditions and isotopic characteristics of precipitation in Moscow is a frequent change of moisture sources and the contribution of moisture from the Mediterranean Sea.

4 Conclusions

This event-based isotopic signature of precipitation in Moscow city determined for the first time revealed modern hydroclimate variations associated with changes in the moisture source origin, long-term precipitation fluctuation, and air temperature increase. Despite the known seasonal patterns of isotopes in the European stations with enriched summer and depleted winter values, several extreme isotopic values were detected in spring and autumn. A strong temperature effect on isotopes in Moscow precipitation was found with the $\delta^{18}O$ dependence on surface air temperature expressed as 0.45‰/°C, which is close to other inland European stations. However, study of event-based stable isotope values showed that some monthly mean values differ from those previously recorded in the GNIP Program

in 1970–1979, stemming from the greater variability in the amount of precipitation of some events and the increase in the precipitation amount amplitude relative to the long-term. One or two precipitation events, that provide up to 50% of the monthly precipitation amount, can determine the isotopic signature of precipitation in some months. A wide range of observed *d*-excess values (36.6‰) was mainly explained by 1–2 day changes in the main sources of moisture carried by air masses to Moscow. Results of the back-trajectory analysis indicate a high (1000 km/day) movement of air mass from October to April, a high atmosphere mobility and associated transport, and high cyclonic activity.

In contrast to many European stations, a low correlation of $\delta^{18}O$ values with the NAO index and the absence of a relationship between NAO and air temperature as well as precipitation amount was found. These results indicate only a partial effect of the NAO on the precipitation pattern in Moscow. The influence of NAO is traceable on the long-term series of more than 30 years, but it is not evident at the scale of two studied years. In this regard, further studies of the connection between isotope composition of precipitation and meteorological data are necessary to trace current climate changes in the continental part of Eastern Europe.

Future studies would benefit from an increased number of stations that collect event-based precipitation for stable isotope analyses and share these data as an open access (e.g., in GNIP) to address questions on the role of atmospheric oscillations in climate changes.

References

Aemisegger F (2018) On the link between the North Atlantic storm track and precipitation deuterium excess in Reykjavik. Atmos Sci Lett 19(12):e865. https://doi.org/10.1002/asl.865

Aggarwal PK, Romatschke U, Araguás-Araguás L et al (2016) Proportions of convective and stratiform precipitation revealed in water isotope ratios. Nat Geosci 9(8):624–629. https://doi.org/10.1038/ngeo2739

Baldini LM, McDermott F, Foley AM, Baldini JUL (2008) Spatial variability in the European winter precipitation δ^{18}O-NAO relationship: Implications for reconstructing NAO-mode climate variability in the Holocene. Geophys Res Lett 35:L04709. https://doi.org/10.1029/2007GL032027

Bailey HL, Klein ES, Welker JM (2019) Synoptic and mesoscale mechanisms drive winter precipitation δ^{18}O/δ^2H in south-central Alaska. J Geophys Res Atmos 124:4252–4266. https://doi.org/10.1029/2018JD030050

Brown J, Simmonds I, Noone D (2006) Modelling data δ^{18}O in tropical precipitation and the surface ocean for present-day climate. J Geophys Res Atmos 111:D05105

Comas-Bru L, McDermott F, Werner M (2016) The effect of the East Atlantic pattern on the precipitation δ^{18}O-NAO relationship in Europe. J Clim Dyn 47:2059–2069. https://doi.org/10.1007/s00382-015-2950-1

Chizhova JN, Eremina ID, Budantseva NA, Surkova GV, Vasil'chuk YuK (2017) Concentration of ^{18}O in precipitation over Moscow in 2014. Russ Meteorol Hydrol 42(1):54–63

Dansgaard W (1964) Stable isotopes in precipitation. Tellus 16:436–468. https://doi.org/10.1111/j.2153-3490.1964.tb00181.x

Diadin D, Vystavna Y (2020) Long-term meteorological data and isotopic composition in precipitation, surface water and groundwater revealed hydrologic sensitivity to climate change in East Ukraine. Isot Environ Health Stud 56(2):136–148. https://doi.org/10.1080/10256016.2020.1732369

Duliński M, Ryżański K, Pierchała A, Gorczyca Z, Marzec M (2019) Isotopic composition of precipitation in Poland: a 44-year record. Acta Geophys 67:1637–1648

Draxler RR, Rolph GD (2011) HYSPLIT (HYbrid single-particle Lagrangian integrated trajectory). NOAA Air Resources Laboratory, Silver Spring

Fricke HC, O'Neil JR (1999) The correlation between ^{18}O/^{16}O ratios of meteoric water and surface temperature: its use in investigating terrestrial climate change over geologic time. Earth Planet Sci Lett 170(3):181–196. https://doi.org/10.1016/s0012-821x(99)00105-3

Friedman I, Harris JM, Smith GI, Johnson CA (2002) Stable isotope composition of waters in the Great Basin, United States 1. Air-Mass Trajectories J Geophys Res Atmos 107(D19):4400. https://doi.org/10.1029/2001jd000565

Fröhlich K, Kralik W, Papesch W, Rank D, Scheifinger H, Stichler W (2008) Deuterium excess in precipitation of Alpine regions—moisture recycling. Isot Environ Health S 44(1):61–70. 61–70.https://doi.org/10.1080/10256010801887208

Fröhlich K, Gibson JJ, Aggarwal PK (2002) Deuterium excess in precipitation and its climatological significance. Proceedings of the study of environmental change using isotope techniques. International Atomic Energy Agency, Vienna. 54–66pp.

Gao J, Risi C, Masson-Delmotte V, He Y, Xu B (2016) Southern Tibetan Plateau ice core δ^{18}O reflects abrupt shifts in atmospheric circulation in the late 1970s. Clim Dyn 46:291–302

Gat JR, Carmi I (1970) Evolution of the isotopic composition of atmospheric waters in the Mediterranean Sea area. J Geophys Res 75:3039–3048

Gat JR, Mook WG, Rozanski K, Fröhlich K (2001) Environmental isotopes in the hydrological cycle: Principles and applications, vol 2. UNESCO, Paris

Guo H, Zhu G, He Y et al (2019) Dynamic characteristics and influencing factors of precipitation δ^{18}O, China. Theor Appl Climatol 138:899–910. https://doi.org/10.1007/s00704-019-02867-z

Hager B, Foelsche U (2015) Stable isotope composition of precipitation in Austria. Austrian Journal of Earth Sciences 108. https://doi.org/10.17738/ajes.2015.0012

Heydarizad M, Raeisi E, Sori R et al (2019) An overview of the atmospheric moisture transport effect on stable isotopes (δ18O, δ2H) and D excess contents of precipitation in Iran. Theor Appl Climatol 138:47–63. https://doi.org/10.1007/s00704-019-02798-9

Hurrell JW, Kushnir Y, Ottersen G, Visbeck M (2003) The North Atlantic Oscillation: Climate Significance and Environmental Impact. Geophysical Monograph Series 134, 279 p.

Jouzel J, Merlivat L, Lorius C (1982) Deuterium excess in an East Antarctic ice core suggests higher relative humidity at the oceanic surface during the last glacial maximum. Nature 299(5885):688–691. https://doi.org/10.1016/j.quascirev.2006.07.015

Jouzel J, Merlivat L (1984) Deuterium and O-18 in precipitation—modeling of the isotopic effects during snow formation. J Geophys Res 89:11749–11757

Juhlke TR, Meier C, van Geldern R, Vanselow KA, Wernicke J, Baidulloeva J, Barth JAC, Weise SM (2019) Assessing moisture sources of precipitation in the Western Pamir Mountains (Tajikistan, Central Asia) using deuterium excess, Tellus B: Chemical and Physical Meteorology, 71:1, 1601987 https://doi.org/10.1080/16000889.2019.1601987

Kadygrov EN, Kuznetsova IN, Golitsyn GS (2002) Urban heat island: new results on the base of remote sensing data. Doklady Earth Science 385(4):541–548

Klein ES, Cherry JE, Young J, Noone D, Leffler AJ, Welker JM (2015) Arctic cyclone water vapor isotopes support past sea ice retreat recorded in Greenland ice. Sci Rep 5(10295):10295

Krklec K, Domínguez-Villar D, Lojen S (2018) The impact of moisture sources on the oxygen isotope composition of precipitation at a continental site in central Europe. J Hydrol 561:810–821. https://doi.org/10.1016/j.jhydrol.2018.04.045

Kurita N (2011) Origin of Arctic water vapor during the ice-growth season. Geophys Res Lett 38(2):L02709. https://doi.org/10.1029/2010GL046064

Merlivat L, Jouzel J (1979) Global climatic interpretation of the deuterium-oxygen 18 relationship for precipitation. J Geophys Res Oceans 84:5029–5033. https://doi.org/10.1029/JC084iC08p05029

Pfahl S, Sodemann H (2014) What controls deuterium excess in global precipitation? Climate of the past 10:771–781. https://doi.org/10.5194/cp-10-771-2014

Rolph G, Stein A, Stunder B (2017) Real-time environmental applications and display system: READY. Environ Model Software 95:210–228. https://doi.org/10.1016/j.envsoft.2017.06.025

Rozanski K, Sonntag C, Munnich KO (1982) Factors controlling stable isotope composition of European precipitation. Tellus 34:142–150. https://doi.org/10.1111/j.2153-3490.1982.tb01801.x

Rozanski K, Araguás-Araguás L, Gonfiantini R (1992) Relation between long-term trends of oxygen-18 isotope composition of precipitation and climate. Science 258:981–985. https://doi.org/10.1126/science.258.5084.981

Salamalikis V, Argiriou A, Dotsika E (2016) Periodicity analysis of δ^{18}O in precipitation over Central Europe: Time–frequency considerations of the isotopic 'temperature' effect. J Hydrol 534:150–163

Sjostrom DJ, Welker JM (2009) The influence of air mass source on the seasonal isotopic composition of precipitation, eastern USA. J Geochem Explor 102(3):103–112. https://doi.org/10.1016/j.gexplo.2009.03.001

Sodemann H, Schwierz C, Wernli H (2008) Interannual variability of Greenland winter precipitation sources: Lagrangian moisture diagnostic and North Atlantic Oscillation influence. J Geophys Res 113(D3):D03107. https://doi.org/10.1029/2007JD008503

Stein AF, Draxler RR, Rolph GD, Stunder BJB, Cohen MD, Ngan F (2015) NOAA's HYSPLIT atmospheric transport and dispersion modeling system. Bull Am Meteorol Soc 96:2059–2077. https://doi.org/10.1175/BAMS-D-14-00110.1

Terzer-Wassmuth S, Wassenaar LI, Welker J, Araguas-Araguas LJ (2021) New high-resolution global and regionalized isoscapes of δ18O, δ2H, and d-excess in precipitation. Hydrol. Process 35(6):e14254

Vachon RW, Welker JM, White JWC, Vaughn BH (2010) Monthly precipitation isoscapes (δ^{18}O) of the United States: connections with surface temperatures, moisture source conditions, and air mass trajectories. J Geophys Res 115:D21126. https://doi.org/10.1029/2010JD014105

van der Ent R, Tuinenburg OA (2017) The residence time of water in the atmosphere revisited. Hydrol Earth Syst Sci 21:779–790. https://doi.org/10.5194/hess-21-779-2017

Vystavna Y, Hejzlar J, Kopáček J (2017) Long-term trends of phosphorus concentrations in an artificial lake: Socio-economic and climate drivers. PLoS One 12(10):e0186917. https://doi.org/10.1371/journal.pone.0186917

Vystavna Y, Matiatos I, Wassenaar LI (2020) 60-year trends of δ18O in global precipitation reveal large scale hydroclimatic variations. Glob Planet Change. 103335https://doi.org/10.1016/j.gloplacha.2020.103335

Vystavna Y, Matiatos I, Wassenaar LI (2021) Temperature and precipitation effects on the isotopic composition of global precipitation reveal long-term climate dynamics. Sci Rep 11:18503. https://doi.org/10.1038/s41598-021-98094-6

Uemura R, Matsui Y, Yoshimura K, Motoyama H, Yoshida N (2008) Evidence of deuterium excess om water vapor as an indicator of ocean surface condition. J Geophys Res 113:D19114. https://doi.org/10.1029/2008JD010209

Wang Y, Tang Y, Xu Y et al (2021) Isotopic dynamics of precipitation and its regional and local drivers in a plateau inland lake basin, Southwest China. Sci Total Environ 763:143043. https://doi.org/10.1016/j.scitotenv.43043