Monitoring of stable isotopes (δ^2H, δ^{18}O) in precipitations of Moscow (Russia): Comparison for 2005–2014 and 1970–1979 periods

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The isotopic composition of oxygen (δ^{18}O) and hydrogen (δ^2H) of atmospheric precipitation in Moscow in 2005–2014 was studied by sampling single precipitations (a total of 842 measurements after rejection of unreliable samples). A comparison was made with similar studies carried out by All-Russian Research Institute of Hydrogeology and Engineering Geology and Water Problems Institute of the Russian Academy of Sciences for the IAEA-WMO GNIP network in 1969–1979, when monthly average samples were taken by the accumulation method (61 pair determinations of deuterium and oxygen-18, mainly in 1975–1979). The 2005–2015 series is reduced to a similar form as the 1969–1979 series, recalculated through the data on the volume of precipitation at the nearest meteorological station. It was found that in the last decade there has been a significant change in the equation of the local line of meteoric waters, which for the first period had the form δ^2H $= 6.09 \times \delta^{18}$O $- 23.0$‰ ($R^2 = 0.87$), and is currently described by the relation δ^2H $= 6.93 \times \delta^{18}$O $- 11.3$‰ ($R^2 = 0.944$). There is also a decrease in depletion of the average values of δ^2H and δ^{18}O, compared with the first observation period, which apparently reflects the course of climatic changes. At the same time, within each of the periods, a negative (albeit relatively small) slope of the line of approximation of chronological data is noted. Deuterium excess naturally changes seasonally, with negative values in summer, primarily due to non-equilibrium fractionation during evaporation. In 2005–2014, the temperature dependence of the isotopic composition of precipitation changed significantly in comparison with 1969–1979, which makes it impossible to reconstruct the composition of precipitation in the past from meteorological observations.

Keywords: atmospheric precipitation, isotopic composition of oxygen and hydrogen, climate.

1. Introduction

Contents of deuterium (^{2}H) and oxygen-18 (^{18}O) in precipitation determine the initial isotopic composition of surface and groundwater on the continents, being thus a starting point for reconstructions aimed at clarifying the circumstances of the formation of the

mass balance and chemical composition of water (Dansgaard, 1964; Mook, 2001). A world monitoring network for the observations of deuterium, oxygen-18 and tritium contents began to form in 1961 according to the program Global Network on Isotopes in Precipitation (GNIP), coordinated by IAEA and WMO. The summary database is accessible via the WISER tool on the website of the IAEA (iaea.org, n. d.). Long-term continuous series of measurements (up to 50 years long) of the isotopic composition of precipitation are available for almost all parts of the world, although for a limited number of points. Besides the points with unique long measurement series, periodic observations with a duration of 1–5 years were carried out at several hundred stations. The observations made it possible to estimate annual and long-term variability of the ^{2}H and ^{18}O contents, their spatial distribution and relation to air temperature, and also the dependence on global climate indicators, e. g., North Atlantic oscillation index and El Niño (Mook, 2001).

The validity of interpretations and correct usage of the stable isotope data depend on the duration and nature of observations of deuterium and oxygen-18 contents in precipitation. For example, in Vienna, the average monthly precipitation was monitored starting in 1968, and in 2001–2003 a study of each case of rainfall was carried out (Hager and Foelsche, 2015). A significant difference in the statistical evaluation of the isotopic composition of precipitation was obtained for these observation methods, which highlighted the need to increase the density of the GNIP network and to harmonize the interregional sampling techniques used. Increase of the observation density is also necessary due to the fact that the data on spatial and temporal distribution of deuterium and oxygen-18 are increasingly used for verification and calibration of global and regional climate models (West et al., 2010). However, the available information is not sufficient to solve these problems on the territory of Northern Eurasia, especially within Russia, where there is insufficient isotope information.

In the Soviet Union, long-term average monthly rainfall monitoring was carried out at about 30 locations from 1969 till 1990. Maps of the isotopic composition of precipitation on the European territory of Russia were created for separate years (Brezgunov et al., 1987). After 1983, the amount of systematic observations significantly decreased, and from 1991 to 2005, the study of precipitation happened sporadically. At present, the monitoring of the isotopic composition of precipitation in Russia is carried out as some research projects or as the initiative of individual groups of scientists, so the potential for linking initial data in a single system is not available. The aim of the present study was to clarify the nature of the δ^2H and δ^{18}O distribution in meteoric waters of the central part of European Russia. In 2005–2014 each event of rain and snowfall in Moscow was sampled, and their comparisons with previously obtained data were conducted.

2. Methods

Precipitation in Moscow Oblast was regularly sampled during two campaigns. The first stage was implemented in 1970–1979 by VSEGINGEO and IWP RAS (Moscow). The average monthly rainfall was monitored according to the program of the IAEA and WMO in Zelyony village (Noginsk district, Moscow Oblast, Fig. 1 (Ferronsky and Polyakov, 2012)). Measurements were carried out using two mass spectrometers: ^{18}O — after equilibration of water samples with CO_2, and ^{2}H — after the decomposition of water on hot zinc. The laboratory reference samples bound to SMOW and SLAP were used as a
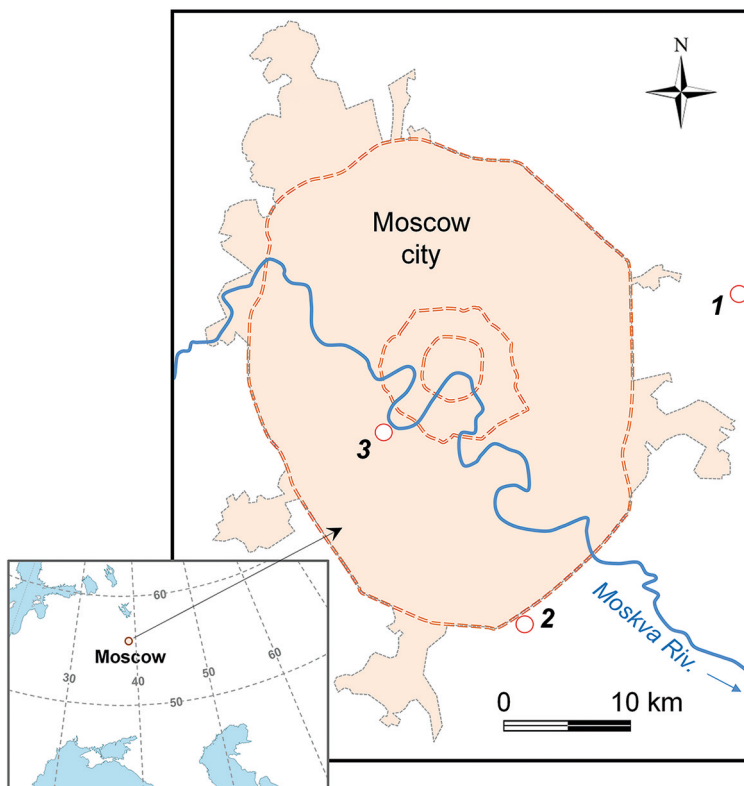
Fig. 1. Location of sampling points

1 — IAEA monitoring site in 1970–1979; *2* — the point used in this work 2005–2014; *3* — point of observation of only $\delta^{18}O$ in 2014 (Chizhova et al., 2017).

standard. From 1970 to 1975, δ^2H was measured in 59 and $\delta^{18}O$ — in 11 average monthly samples; and from 1975 to 1979, in 54 and 50 samples, respectively. Along with isotope sampling, the average monthly precipitation and temperatures were measured (WISER tool on the website of the IAEA (iaea.org, n. d.).

From 2005 to the present, the authors took samples of each event on the site with co-ordinates 55°35′35″N, 37°44′29″E (point 2 on Fig. 1; the data obtained through mid-2014 are presented in this paper). Along with isotope sampling, the air and water temperatures were measured. Liquid precipitation was collected through a funnel into a thick-walled 9–20 ml plastic bottle. Snow was collected on a tray and melted in an airtight container at room temperature. In case of long rain- or snowfalls, a series of samples were taken every 2 or 4 hours. At the end of the precipitation, but not later than several hours after, the obtained samples were poured into a sealed plastic Eppendorf tube with a volume of 2 ml. The containers were filled completely to minimize air bubbles; before transportation to the laboratory, the samples were stored in a cool, dark place or in the fridge upside down. In some cases, evaporation (loss of the water volume in the vials) occurred during storage; such samples were rejected.

Analysis was carried out using an infrared laser spectrometer Picarro L-2120i in the Center of X-ray Diffraction Studies at the Research Park of St. Petersburg State Univer-

sity. Standards of V-SMOW2, GISP and SLAP (IAEA), and also USGS-45 and USGS-46 (US Geological Survey) were used as reference material. The measurement error was ±0.1 ‰ for δ^{18}O and ±1 ‰ for δ^2H. The results are presented in per mille in relation to SMOW:

$$\delta^2 H = 1000 \times [((^2H/^1H)_{SAMPLE} / (^2H/^1H)_{SMOW}) - 1]\ ‰,$$

$$\delta^{18} O = 1000 \times [((^{18}O/^{16}O)_{SAMPLE} / (^{18}O/^{16}O)_{SMOW}) - 1]\ ‰,$$

where subscript *SAMPLE* is $^2H/^1H$ or $^{18}O/^{16}O$ ratio, which were measured for analyzed material; and *SMOW* — the same ratios for Standard of Mean Ocean Water $^2H/^1H = (155.76 \pm 0.05) \times 10^{-6}$ and $^{18}O/^{16}O = (2005.20 \pm 0.45) \times 10^{-6}$.

3. Results

Only for 1975–1979 are both δ^2H and δ^{18}O data for the whole year available in the GNIP database (see WISER on IAEA site), and for 1975–1979 the Local Meteoric Water Line (LMWL) for Moscow was described by the following equation (Fig. 2):

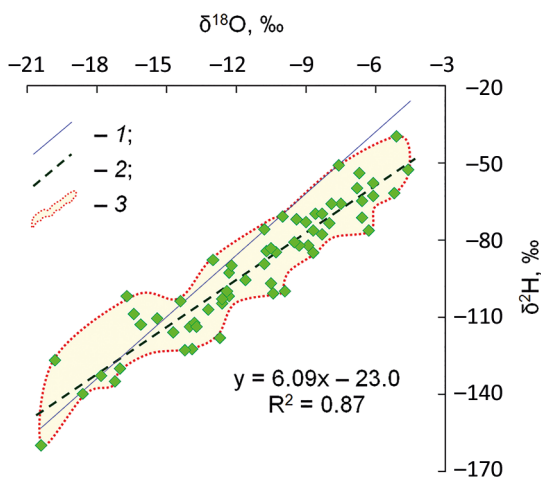$$\delta^2 H = 6.09 \cdot \delta^{18} O - 23.0\ ‰\ (R^2 = 0.87).$$

Fig. 2. The relationship between deuterium and oxygen-18 abundance in precipitation for Moscow (the 1970–1979 average monthly samples)

1 — the Global Meteoric Water Line (GMWL); *2* — the Local Meteoric Water Line (LMWL) (its equation is shown in the diagram); *3* — distribution of isotopic composition of precipitation (to be used in the following figure).

In total 842 samples were analyzed for the period 2005–2014; the relationship for all the 2005–2014 data corresponds to the equation (Fig. 3):

$$\delta^2 H = 6.93 \cdot \delta^{18} O - 11.3\ ‰\ (R^2 = 0.944),$$
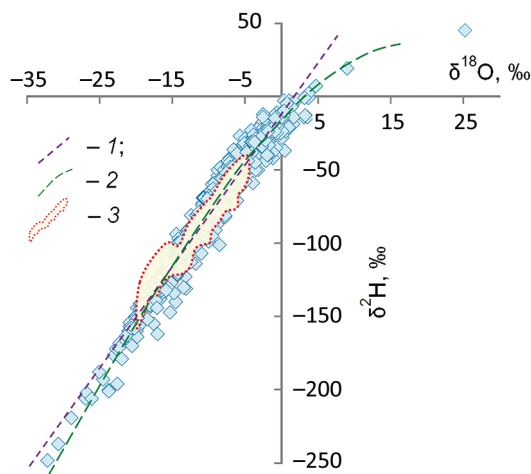
Fig. 3. The relationship between deuterium and oxygen-18 abundance in precipitation for Moscow (sampling the individual events in 2005–2014)

1 — linear approximation, *2* — polynomial approximation (equations are presented in the text); *3* — area of the monthly isotopic composition of precipitation in 1970–1979.

but using the third-degree polynomial gives a still better approximation:

$$\delta^2H = -1.26E\text{-}03 \cdot (\delta^{18}O)^3 - 1.12E\text{-}01 \cdot (\delta^{18}O)^2 + 5.27E + \\ + 00 \cdot \delta^{18}O - 1.48E\text{+}01 \ (R^2 = 0.963),$$

$$\delta^2H = -0.00126 \cdot (\delta^{18}O)^3 - 0.112 \cdot (\delta^{18}O)^2 + 5.27 \cdot \delta^{18}O - 14.8 \ (R^2 = 0.963).$$

4. Discussion

The moderate continental climate of Moscow is formed under the predominant influence of the western transfer of air masses with periodic invasions of Arctic and southern anticyclones. Therefore, for every event of rain or snowfall, the individual isotope composition of moisture depends initially on its marine or continental origin, and the subsequent transformation of δ^2H and $\delta^{18}O$ parameters is a result of the synoptic situation and trajectories of movement of air masses. Besides that, the contents of deuterium and oxygen for each episode of rainfall in a particular point are impacted by the current conditions of nucleation, and the height distribution of temperature and humidity, which determine together the regime of condensation, evaporation and freezing. Therefore, it can be assumed in advance that the range of variations in δ^2H and $\delta^{18}O$ parameters when sampling individual events will be higher than when taking monthly average samples.

The data array of 1970–2014 shows the well-known quasi-sinusoidal distribution of oxygen-18 and deuterium concentrations, when the isotopic composition of precipitation in the warm season is relatively heavier than in the cold season (Fig. 4).

The observations of the single rainfalls in 2005–2014 give a much greater range of variations in $\delta^{18}O$ and δ^2H compared to the monthly average samples of 1970–1979
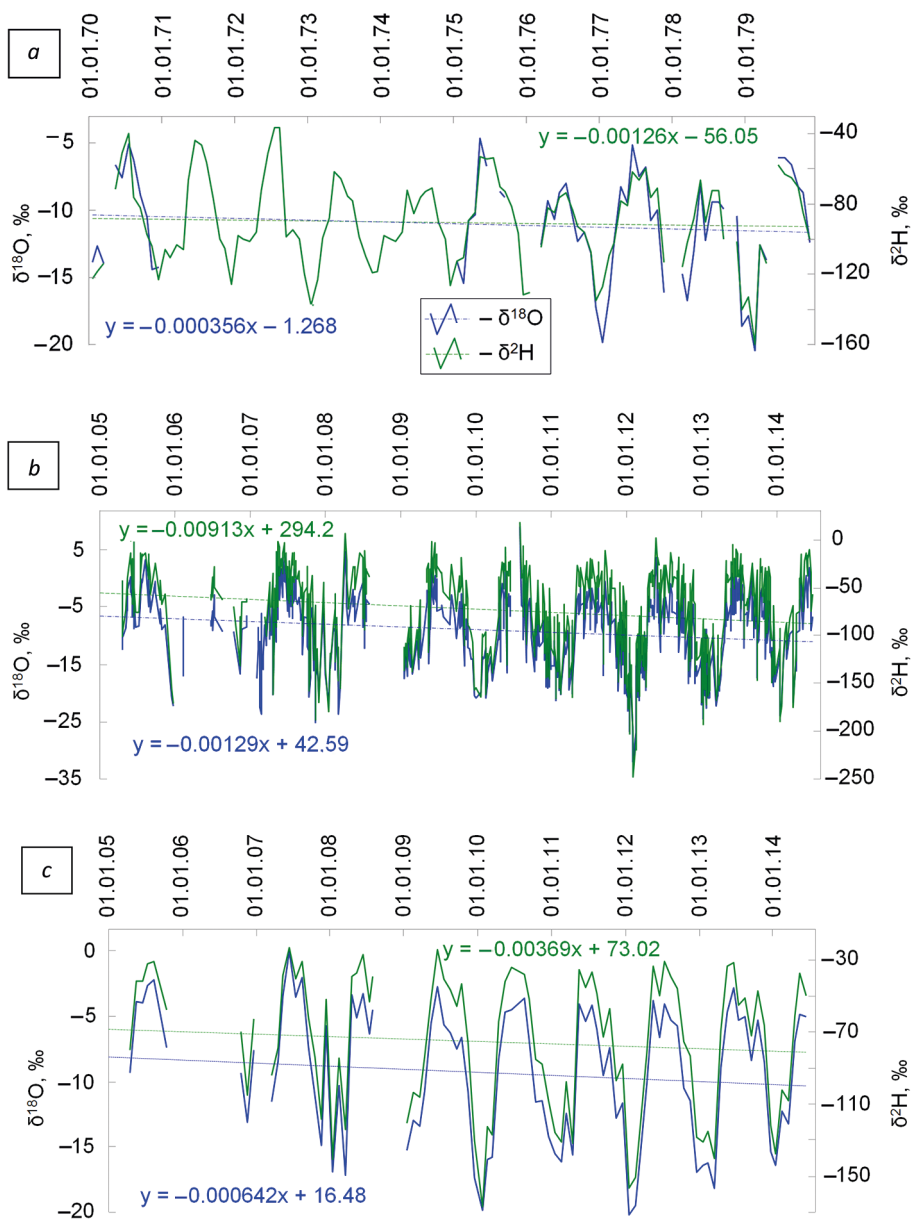
Fig. 4. The chronological graph of deuterium and oxygen-18 contents in precipitation in Moscow

a — 1970–1979 (average monthly samples); *b* — 2005–2014 (every event samples); *c* — recalculation in monthly weighted averaging for 2005–2014 (the diagrams show linear trends: the top equation — of δ^2H, the bottom equation — of $\delta^{18}O$).
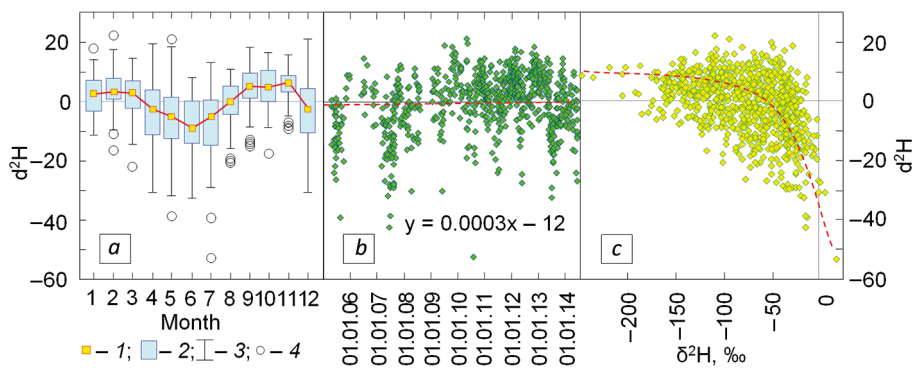
Fig. 5. Deuterium excess for the precipitation in Moscow in 2005–2014

a — median (*1*); 25–75 % (*2*); sample span (*3*); outliers (*4*); *b* — chronological graph (the trend equation is presented on the diagram); *c* — relation to the isotopic composition of hydrogen.

(Fig. 3, 4, *a* and *b*). The conversion of individual precipitation data for 2005–2014 to the monthly weighted values reduces the scale of $\delta^{18}O$ and δ^2H variation. However, in 2005–2014 the scatter of variations is still much wider than in 1970–1979 (Fig. 4, *a* and *c*). Chizhova et al. (2017) presented the results of the ^{18}O independent observations of individual precipitation of 2014 in Moscow. Variation limits of oxygen isotope composition ($\delta^{18}O = -0.09..-26.29\,‰$), as well as the moments of extremum occurrence, are consistent with the data obtained by the authors of the present paper. Therefore, changes in the annual and seasonal variations of the isotopic composition of precipitation from 1970–1979 to 2005–2014 have apparently taken place.

The deuterium excess varies significantly from season to season, due to the influence of secondary non-equilibrium fractionation (Fig. 5). The intra-annual amplitude of deuterium excess in 1970–1979 coincides with the observations of 2005–2014, although for the first period of observations, the magnitude of the variations is somewhat less. In April — May and December, there are the greatest variations of deuterium excess as a result of the influence of summer and winter anticyclones on the type of atmospheric circulation (Fig. 5, *a*). In 2005–2014, the trend towards an increase of annual average deuterium excess was observed (Fig. 5, *b*). In the summer months, the deuterium excess takes a negative value, which should be linked to the influence of evaporation (Fig. 5, *a*, *c*).

On the background of regular seasonal variations of the isotopic composition of precipitation and deuterium excess, some exotic rainfalls can be noticed. It is considered that isotopically depleted precipitation in Eastern Europe is caused by breakouts of Arctic air, and enriched precipitation events should be associated with Mediterranean air flow or local sources of moisture. The source of moisture in isotopically unusual precipitation could be identified by the recovery of backward trajectories using the HYSPLIT tool from the NOAA website (Stein et al., 2015; Rolph, 2016). Observations over the isotopically enriched precipitation in Moscow confirm the above-mentioned proposition. For example, the least isotopically depleted precipitation was observed on 17.06.2006 ($\delta^{18}O = 25.2\,‰$ and $\delta^2H = 45\,‰$), when the humidity of almost all the air over Moscow had been generated by local or southern sources (Fig. 6, *a*). A similar phenomenon was observed on 03.08.2010 ($\delta^{18}O = 9.0\,‰$ and $\delta^2H = 19\,‰$, Fig. 6, *b*).
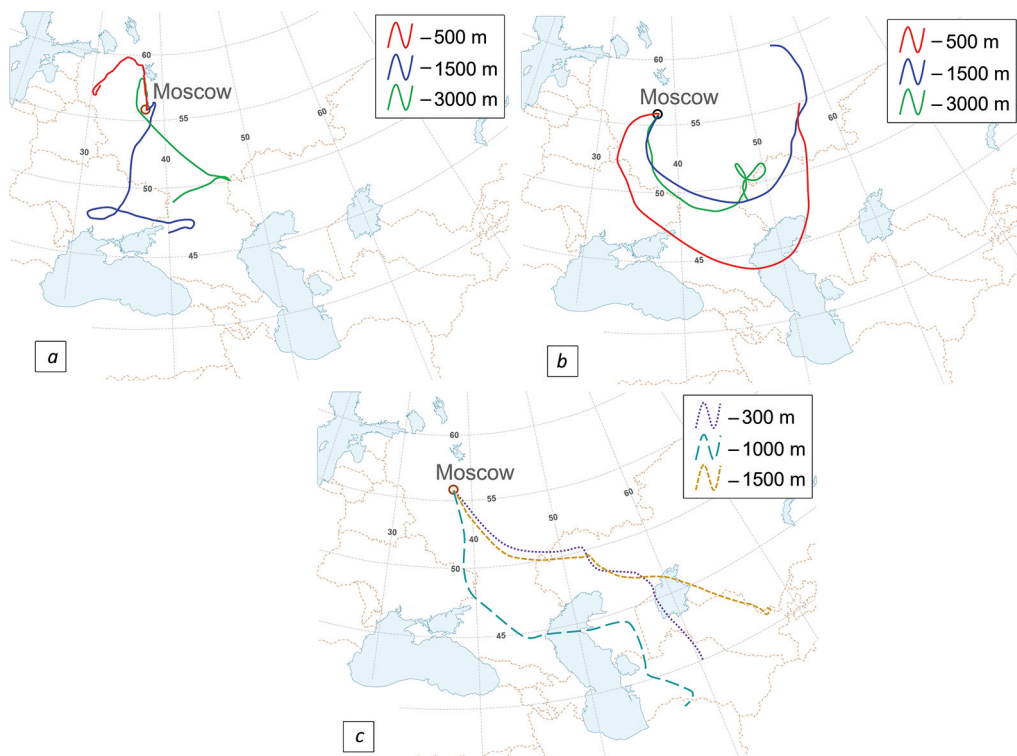
Fig. 6. Recovery of the backward trajectories of air masses for 120 hours using HYSPLIT tool (NOAA website)

a — event of 17.06.2006: $\delta^{18}O = 25.2‰$ and $\delta^2H = 45‰$; *b* — event of 03.08.2010: $\delta^{18}O = 9.0‰$ and $\delta^2H = 19‰$; *c* — event of 02.02.2012: $\delta^{18}O = -30.6‰$ and $\delta^2H = -237‰$, and 4 hours later: $\delta^{18}O = -32.1‰$ and $\delta^2H = -248‰$. For summer precipitation, the trajectories at the altitudes of 500, 1500 and 3000 m are shown; for the winter precipitation — ones at the altitudes of 300, 500 and 1000 m, are shown.

It is interesting that on 02.02.2012, when the most isotopically depleted precipitation occurred ($\delta^{18}O = -30.6‰$ and $\delta^2H = -237‰$), and 4 hrs after the start of snowfall the depletion reached $\delta^{18}O = -32.1‰$ and $\delta^2H = -248‰$, the source of moisture was not from the Arctic regions, but from the central regions of Eurasia (Fig. 6, *c*). Our direct observations of rain and snowfall in East Kazakhstan in 2014 and 2015 revealed very isotopically depleted monthly average precipitation in January — February, $\delta^{18}O = -30.9‰$ and $\delta^2H = -233‰$. For this event, depletion of the snow as it is falling can be noticed, and it is consistent with previously published observations for long snowfalls (Vasilchuk, 2014).

Comparison of 1970–1979 and 2005–2014 data detects significant multiannual trends in δ^2H and $\delta^{18}O$ along with seasonal variations (Fig. 4). In 2005–2014, the oxygen isotope composition was 1.8‰ and hydrogen composition — up to 16‰ heavier in average than in 1970–1979. The average temperature at the moments of sampling increased from +5.7 °C in 1970–1979 to +7.8 °C in 2005–2014. In contrast, the trends of the isotopic composition of precipitation, separately for 1970–1979 and 2005–2014, have negative angle coefficients (Fig. 4). That is, during the individual time interval (1970–1979 and 2005–2014) some depletion of the isotope composition of precipitation was observed, in comparison to both monitoring times together. The latter should be associated with the

non-linear nature of changes in climatic parameters in time (West et al., 2010), which makes dubious (or impossible) the opportunity for linear extrapolation of isotope data outside of the observation periods.

For the period of 1970–1979, the dependence of the isotopic composition of oxygen and hydrogen in atmospheric precipitation from the mean monthly temperature (t_m) was described by the equations (Ferronsky and Polyakov, 2012):

$$\delta^{18}O = (0.34 \pm 0.03) \cdot t_m - (12.6 \pm 0.3)\ ‰\ (R^2 = 0.82),$$

$$\delta^2H = (2.4 \pm 0.2) \cdot t_m - (101 \pm 2)\ ‰\ (R^2 = 0.89).$$

In 2005–2014, the dependence of the isotopic composition of individual precipitation samples on the air temperature (t) at the time of sampling is:

$$\delta^{18}O = 0.455 \cdot t - 12.9\ (R^2 = 0.68),$$

$$\delta^2H = 3.24 \cdot t - 101\ (R^2 = 0.67),$$

and the relationship for weighted monthly values is:

$$\delta^{18}O = 0.437 \cdot t_m - 12.7\ (R^2 = 0.81),$$

$$\delta^2H = 3.21 \cdot t_m - 100\ (R^2 = 0.81).$$

Chizhova et al. (2017) obtained the following ratios for Moscow precipitation in 2014:

$$\delta^{18}O = 0.47 \cdot t - 14.38\ (R^2 = 0.62)\ \text{— for individual samples,}$$

$$\delta^{18}O = 0.33 \cdot t_m - 12.83\ (R^2 = 0.72)\ \text{— for mean monthly values,}$$

i. e., for an individual event the relationship between $\delta^{18}O$ of precipitations and air temperature is close to the one found by the authors of the present paper.

5. Conclusion

In 2005–2014, the monitoring of isotopic composition of individual events of precipitation in Moscow was carried out; the results were compared with the data on the mean monthly composition of precipitation in 1970–1979 (IAEA database). The equation of the Local Meteoric Water Line (LMWL) for 2005–2014 is:

$$\delta^2H = 6.93 \cdot \delta^{18}O - 11.3\ ‰,$$

which is slightly different from the equation for 1970–1979:

$$\delta^2H = 6.09 \cdot \delta^{18}O - 23.0\ ‰.$$

The dependence of the isotopic composition of precipitation on the initial source of moisture and the air mass trajectory, as well as a significant effect of evaporation in summer, have been revealed.

In 2005–2014, an enrichment of the isotopic composition of precipitation of 1.8 ‰ for oxygen-18 and 16 ‰ for deuterium, compared to the period of 1970–1979, took place. These enrichments corresponded to an increase of the mean annual temperature by 2.1 °C. In contrast, slight depletion of isotopic composition was observed within each period.

Between the periods of observations, there were some changes in the relationship between isotopic composition of precipitation and air temperature. For the mean monthly values, it is:

$$1970-1979: \delta^{18}O = (0.34 \pm 0.03) \cdot t_m - (12.6 \pm 0.3); \delta^2H = (2.4 \pm 0.2) \cdot t_m - (101 \pm 2),$$

$$2005-2014: \delta^{18}O = 0.437 \cdot t_m - 12.7; \delta^2H = 3.21 \cdot t_m - 100.$$

The latter indicates the nonlinear nature of the process of warming and the impossibility of the extrapolation of the isotope data outside the observation period. This also means that the restoration of the isotopic composition of precipitation in the past through the air temperature in case of the absence of direct observations is highly problematic.

The analysis described above shows that the evaluation of seasonal variations and long-term trends in the isotopic composition of precipitation depends, to some extent, on the method of observations and means of mathematical processing of the data. This should be taken into account when constructing mathematical models that use these parameters from the IAEA database.

Dedication. This article is to the memory of Vladimir Andreevich Polyakov — an outstanding scientist and fine person.

References

Brezgunov, V. S., Esikov, A. D. and Yakimova, T. V. (1987). Distribution of the mean annual concentrations of oxygen-18 in precipitation of the European part of the USSR. *Materials of meteorological investigations*, 12, 54–58. (In Russian)

Chizhova, Yu. N., Eremina, I. D., Budantseva, N. A., Surkova, G. V. and Vasil'chuk, Yu. K. (2017). Concentration of ^{18}O in Precipitation over Moscow in 2014. *Russian Meteorology and Hydrology*, 42 (1), 54–63.

Dansgaard, W. (1964). Stable isotopes in precipitation. *Tellus*, 19, 435–463.

Ferronsky, V. I. and Polyakov, V. A. (2012). *Isotopes of the Earth's Hydrosphere*. Dordrecht: Springer.

Hager, B. and Foelsche, U. (2015). Stable isotope composition of precipitation in Austria. *Austrian Journal of Earth Sciences*, 108 (2), 2–13. https://doi.org/10.17738/ajes.2015.0012

iaea.org. (n. d.). *Official Web Site of the IAEA*. [online] Available at: http://iaea.org [Accessed 28 Dec. 2021].

Mook, W. G. (2001). *Environmental isotopes in the hydrological cycle. Principles and applications*. Paris: UNESCO, I.

Rolph, G. D. (2016). *Real-time environmental applications and display system (ready).* [online] Available at: http://www.ready.noaa.gov [Accessed 30 Jan. 2021].

Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., Cohen, M. D. and Ngan, F. (2015). NOAA's HYSPLIT atmospheric transport and dispersion modeling system. *Bull. Amer. Meteor. Soc.*, 96, 2059–2077. http://dx.doi.org/10.1175/bams-d-14-00110.1

Vasilchuk, Yu. K. (2014). New Data on the Tendency and Causes of Deuterium Excess Variations during One Snowfall. *Doklady Earth Sciences*, 459 (1), 1400–1402. https://doi.org/10.1134/S1028334X14110105

West, J. B., Bowen, G. J., Dawson, T. E. and Tu, K. P. (eds) (2010). *ISOSCAPES. Understanding movement, pattern, and process on earth through isotope mapping*. Dordrecht, Heidelberg, London, New York: Springer. https://doi.org/10.1007/978-90-481-3354-3

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Мониторинг стабильных изотопов (δ^2H, δ^{18}O) в осадках Москвы (Россия): сравнение периодов 2005–2014 и 1970–1979 гг.

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Изучен изотопный состав кислорода (δ^{18}O) и водорода (δ^2H) атмосферных осадков в Москве в 2005–2014 гг. методом опробования единичных выпадений (всего 842 измерения после отбраковки недостоверных проб). Проведено сравнение с аналогичными исследованиями, выполненными Всероссийским научно-исследовательским институтом гидрогеологии и инженерной геологии и Институтом водных проблем Российской академии наук для сети GNIP МАГАТЭ-ВМО в 1969–1979 гг., когда отбирались среднемесячные пробы методом накопления (61 парное определение дейтерия и кислорода-18, в основном в 1975–1979 гг.). Ряд 2005–2015 гг. приведен к аналогичному виду для ряда 1969–1979 гг. пересчетом через данные по объему осадков на ближайшей метеостанции. Установлено, что в последнее десятилетие имеет место существенное изменение уравнения локальной линии метеорных вод, которая для первого периода имела вид δ^2H = 6.09·δ^{18}O – 23.0 ‰ (R^2 = 0.87), а в настоящее время описывается соотношением δ^2H = 6.93·δ^{18}O – 11.3 ‰ (R^2 = 0.944). Имеет место также утяжеление средних значений δ^2H и δ^{18}O, по сравнению с первым периодом наблюдений, что отражает, по-видимому, ход климатических изменений. При этом внутри каждого из периодов отмечается хотя и относительно небольшой, но отрицательный угловой коэффициент линии аппроксимации хронологических данных. Дейтериевый эксцесс закономерно изменяется по сезонам, принимая отрицательные значения летом, в первую очередь за счет неравновесного фракционирования при испарении. В 2005–2014 гг. существенно изменилась зависимость изотопного состава осадков от температуры, что не позволяет реконструировать состав осадков в прошлом по метеонаблюдениям.

Ключевые слова: атмосферные осадки, изотопный состав кислорода и водорода, климат.

К о н т а к т н а я   и н ф о р м а ц и я :

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