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

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Annotation

The isotopic composition of oxygen ($\delta^{18}O$) 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 is made with similar studies carried out by VSEGINGEO and IVP RAS 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 for 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 $\delta^2H = 6.09\times\delta^{18}O - 23.0$ ‰ ($R^2 = 0.87$), and is currently described by the relation $\delta^2H = 6.93\times\delta^{18}O - 11.3$ ‰ ($R^2 = 0.944$). There is also a decrease in depletion of the average values of δ^2H and $\delta^{18}O$, 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, taking 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.

Introduction

Contents of deuterium (^{2}H) and oxygen-18 (^{18}O) in precipitations 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).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 (http://isohis.iaea.org). 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 duration of 1–5 years were carried out on several hundred stations. The observations allowed estimating 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).

Validity of interpretations and correct using 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 is monitored from 1968, and in 2001-2003 a study of each case of rainfall was carried out (Hager and Foelsche, 2015). Significant difference in the statistical evaluation of the isotopic composition of precipitation was obtained for these observation methods that cause the necessity of the GNIP network density increase and interregional harmonization of sampling technique. 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 problemson the territory of Northern Eurasia especially as for the Russian area has no enough isotope information.

In the Soviet Union, the long-term average monthly rainfall monitoring was carried out on about 30 locations from 1969 till 1990. Maps of the isotopic composition of precipitation at the European territory of Russia have been created for the separate years (Brezgunov et al., 1987). After 1983, the amount of systematic observations has 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 assome research projects or as initiative of individual groups of scientists, so potential for linking of initial data in a single system are not available. The aim of the present study was to clarify the nature of the δ^2H and $\delta^{18}O$ 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 have been conducted.

1. Methods

Precipitation in Moscow region was regularly sampled during two campaigns. The first stage has been 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 the Zelyony village (Noginsk district, Moscow region, 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 ^2H – after the decomposition of water on the hot zinc. The laboratory reference samples bound to SMOW and SLAP, have been used as a standard. From 1970 to 1975, δ^2H have been measured in 59 and $\delta^{18}O$ – in 11 average monthly samples; and from 1975 to 1979, in 54 and 50 samples, respectively. Along the isotope sampling, the average monthly precipitations and temperatures were measured (WISER tool on the website of the IAEA (http://isohis.iaea.org)).

From 2005 to present, the authors take 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 till mid-2014 are presented in this paper). Along with isotope sampling, also the air and water temperatures were measured. Liquid precipitations were collected through a funnel into a thick-walled 9–20 ml plastic bottle. The snow was collected on a tray and melted in an airtight container at room temperature. In case of the long rain- or snowfalls, a series of samples were taken every 2 or 4 hours. At the end of the fallout, but not later than several hours, the obtained sample was 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 cool, dark place or in the fridge upside down. In some cases, evaporation (loss of the water volume in the vials) has been observed during the storage, such samples were rejected.

The analysis was carried out using infrared laser spectrometer Picarro L-2120i in Center of X-ray diffraction studies at the Research park of St. Petersburg State University. Standards of V-SMOW2, GISP and SLAP (IAEA), and also USGS-45 and USGS-46 (US Geological Survey) have been used as reference material. The measurement error was ±0.1 ‰ for $\delta^{18}O$ and ±1 ‰ for $\delta^{2}H$. The results are presented in per mille in relation to SMOW:

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

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

where subscript *SAMPLE* is ${}^{2}H/{}^{1}H$ or ${}^{18}O/{}^{16}O$ ratio, which were measured for analyzed material; and *SMOW* – the same ratios for Standard of Mean Ocean Water ${}^{2}H/{}^{1}H = (155.76 \pm 0.05)\times10^{-6}$ and ${}^{18}O/{}^{16}O = (2005.20 \pm 0.45)\times10^{-6}$.

2. Results

Only for 1975–1979 are both $\delta^{2}H$ and $\delta^{18}O$ data for whole year around in GNIP data base (see WISER on IAEA site), and for 1975–1979 the Local Meteoric Water Line (LMWL) for Moscow city was described by the next equation (Fig. 2):

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

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

$$\delta^{2}H = 6.93\cdot\delta^{18}O - 11.3\ ‰\ (R^{2} = 0.944),$$

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

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

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

3. Discussion

Moderate continental climate of Moscow is formed under the predominant influence of the western transfer of air masses with periodic invasions of the Arctic and southern anticyclones. Therefore, every event of rain or snowfall has initially the individual isotope composition of moisture depends on its marine or continental origin and subsequent transformation of $\delta^{2}H$ and $\delta^{18}O$ parameters is result of the synoptic situation and trajectories of movement of air masses. Besides it, 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. 3, 4 a and 4 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 scatter of variations is still much wider than in 1970–1979 (Fig. 4 a and 4 c). In Chizhova et al. (2017) the results of the ^{18}O independent observations of individual precipitation of 2014 in Moscow, are presented. Variation limits of oxygen isotope composition ($\delta^{18}O$ = -0.09..-26.29 ‰) as well as the moments of the extremum occurrence are consistent with the data obtained by the authors of the present paper. Therefore, the changes in the annual and seasonal variations of the isotopic composition of precipitation from 1970–1979 to 2005–2014, apparently, take place.

The deuterium excess varies significantly from season to season, due to the influence of the 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 the increase of annual average deuterium excess has been observed (Fig. 5 b). In the summer months, the deuterium excess takes 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 iscaused by breakouts of Arctic air and the enriched ones should be associated with the Mediterranean air flow or local sources of moisture. The source of the moisture in the isotopically unusual precipitation could be identifiedby the recovery of backward trajectories using the HYSPLIT tool from the NOAA website (Rolph, 2016; Stein et al., 2015). 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 $\delta^{2}H$ = 45 ‰), when the humidity of the almost entire 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 $\delta^{2}H$ = 19 ‰, Fig. 6 b).

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

Comparison of 1970–1979 and 2005–2014 data detects significant multiannual trends in $\delta^{2}H$ and $\delta^{18}O$ along with seasonal variations (Fig. 4). In 2005–2014, the oxygen isotope composition got on 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) it is some depletion of the isotope composition of precipitation 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), that makes dubious (or impossible) the opportunity a 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 equations (Ferronsky and Polyakov 2009):

$$\delta^{18}O = (0.34\pm0.03)\cdot t_m - (12.6\pm0.3)\ ‰\ (R^2 = 0.82)$$

$$\delta^{2}H = (2.4\pm0.2)\cdot t_m - (101\pm2)\ ‰\ (R^2 = 0.89).$$

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

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

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

and the relationship for weighted monthly values is:

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

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

In Chizhova et al. (2017), the next ratios for Moscow precipitations in 2014 have been obtained:

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

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

i.e. for 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.

Conclusion

In 2005–2014, the monitoring of isotopic composition of individual events of precipitation in Moscow has been 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:

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

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

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

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 on 1.8 ‰ for oxygen-18 and 16 ‰ for deuterium, compared to the period of 1970–1979, took place. These enrichments are corresponded to an increase of the mean annual temperature by 2.1 °C. In contrast, the little depletion of isotopic composition has been observed within each period.

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

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

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

The last 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. It should be taken into

account, when constructing mathematical models, which use these parameters from the IAEA database.

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

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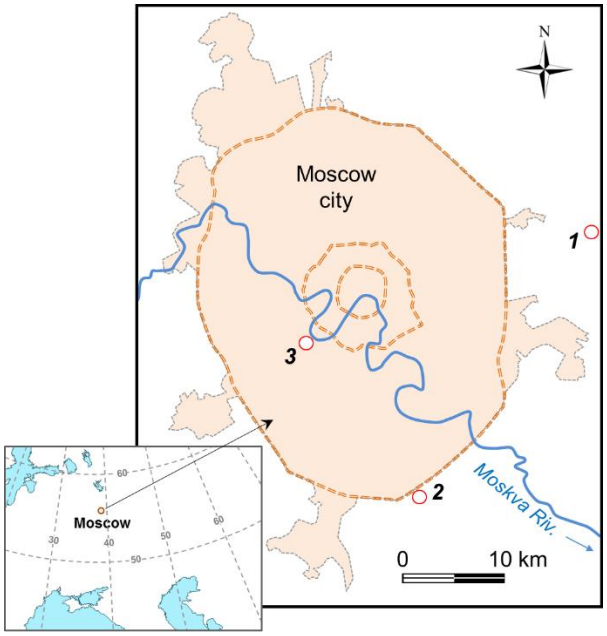


Fig. 1. Location of sampling points: 1 – IAEA monitoring site in 1970–1979; 2 – the point used in this work 2005–2014; 3 – point of observation only $\delta^{18}O$ in 2014 (Chizhova et al., 2017).

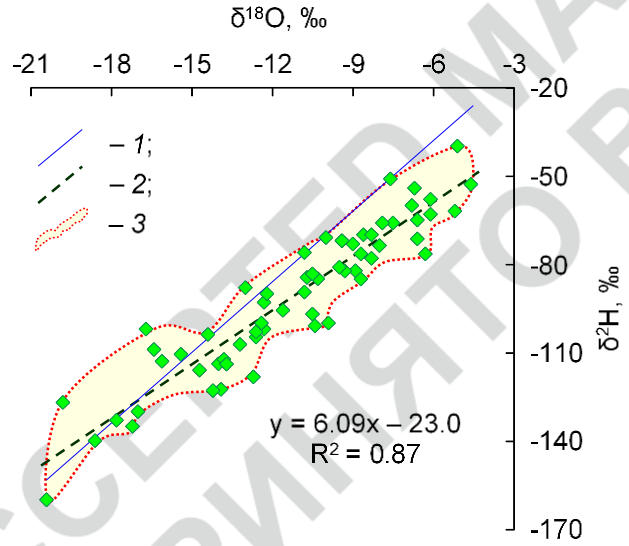


Fig. 2. The relationship between deuterium and oxygen-18 abundance in precipitation for Moscow city (the 1970–1979 average monthly samples (http://isohis.iaea.org)): 1 – the Global Meteoric Water Line (GMWL); 2 – the Local Meteoric Water Line (LMWL) (its equation is shown in the diagram); 3 – distribution of isotopic composition of precipitation (to be used in the following figure).

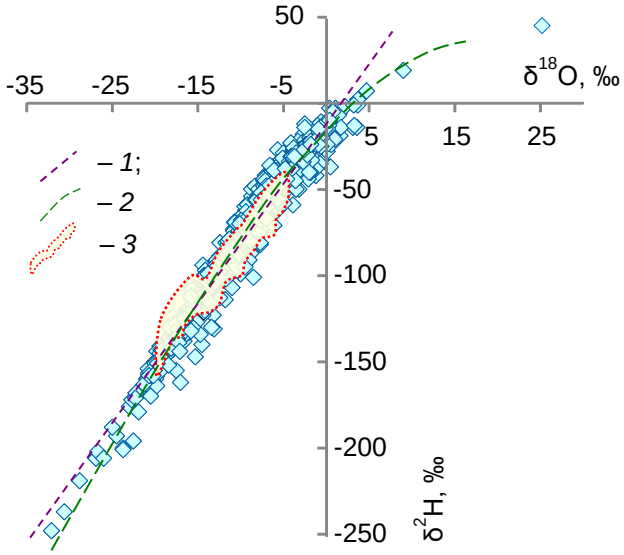
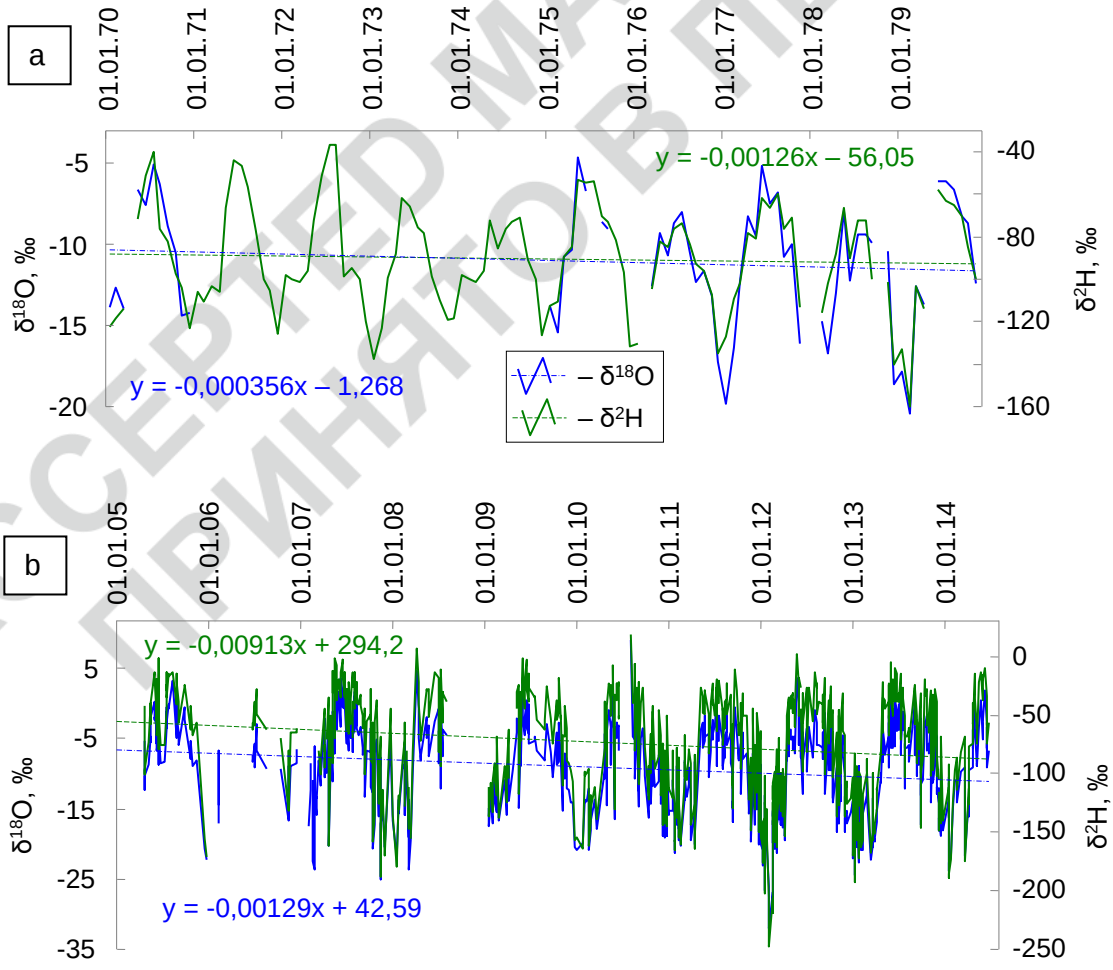


Fig 3. The relationship between deuterium and oxygen-18 abundance in precipitation for Moscow city (sampling the individual events in 2005–2014): 1 – linear approximation, 2 – polynomial approximation (equations are presented in the text); 3 – area of the monthly isotopic composition of precipitation in 1970–1979.



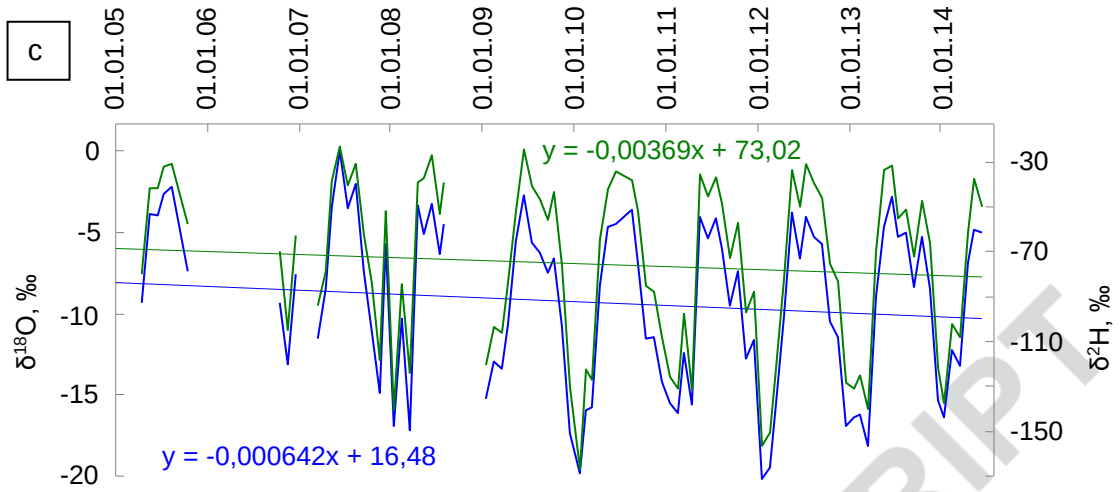


Fig. 4. The chronological graph of deuterium and oxygen-18 contents in precipitation in Moscow: a) 1970–1979 (average monthly samples); b) 2005–2014 (every event samples); c) recalculation in monthly weighted averaging for 2005–2014 (the diagrams show linear trends: the top equation – of δ^2H, the bottom equation – of $\delta^{18}O$).

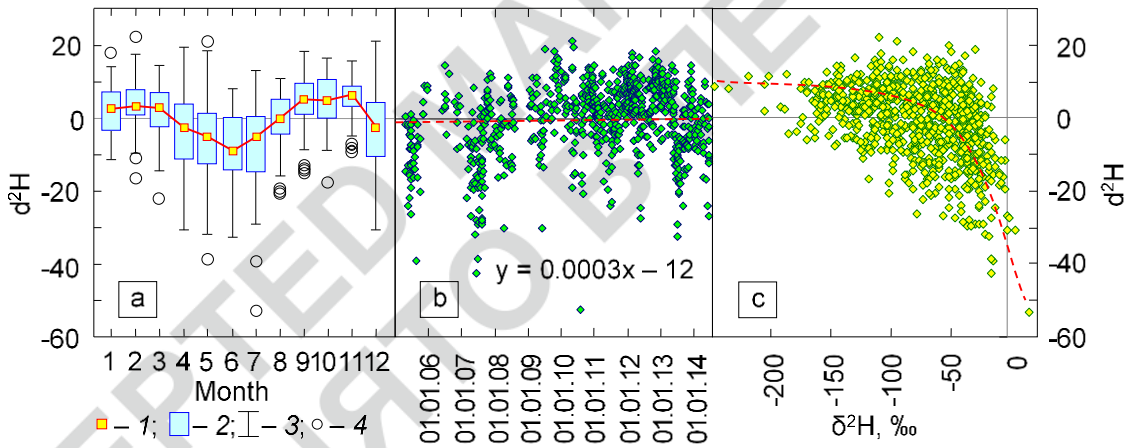


Fig. 5. Deuterium excess for the precipitation in Moscow in 2005–2014: (a): 1 – median; 2 – 25–75 %; 3 – sample span; 4 – outliers; (b) – chronological graph (the trend equation is presented on the diagram); (c) – relation to the isotopic composition of hydrogen.

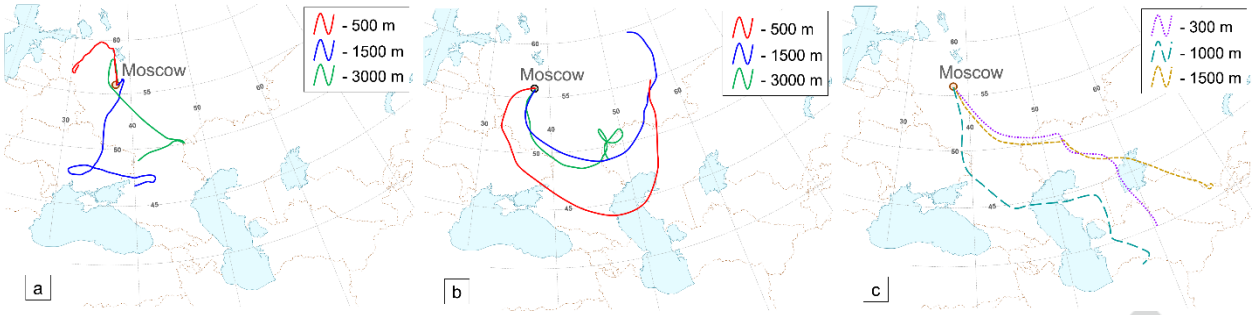


Fig. 6. Recovery of the backward trajectories of air masses for 120 hours using HYSPLIT tool (NOAA website): (a) event of 17.06.2006: $\delta^{18}O$ = 25.2 ‰ and $\delta^{2}H$ = 45 ‰; (b) event of 03.08.2010: $\delta^{18}O$ = 9.0 ‰ and $\delta^{2}H$ = 19 ‰; (c) event of 02.02.2012: $\delta^{18}O$ = -30.6 ‰ and $\delta^{2}H$ = -237 ‰, and 4 hours later: $\delta^{18}O$ = -32.1 ‰ and $\delta^{2}H$ = 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

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

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Аннотация

Изучен изотопный состав кислорода (δ18O) и водорода (δ2H) атмосферных осадков в г. Москве в 2005–2014 г. методом опробования единичных выпадений (всего 842 измерения после отбраковки недостоверных проб). Проведено сравнение с аналогичными исследованиями, выполненными ВСЕГИНГЕО и ИВП РАН для сети GNIP МАГАТЭ-ВМО в 1969–1979 г., когда отбирались среднемесячные пробы методом накопления (61 парное определение дейтерия и кислорода-18, в основном, в 1975–1979 г.). Ряд 2005–2015 г. приведен к аналогичному виду для ряда 1969–1979 г. 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 δ2H = 6.09·δ18O – 23.0 ‰ (R2 = 0.87), а в настоящее время описывается соотношением δ2H = 6.93·δ18O – 11.3 ‰ (R2 = 0.944). Имеет место также утяжеление средних значений δ2H и δ18O, 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 г. 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.