



Isotopic composition of precipitation in Poland: a 44-year record

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Abstract

Isotopic composition of precipitation ($^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ isotope ratios, tritium content) is nowadays widely used in numerous applications of environmental isotopes—most notably in hydrology, climatology and biogeochemistry. Here we present a long record (44 years) of stable isotope composition and tritium content in monthly precipitation available for the Krakow station (southern Poland). Krakow is the only site in Poland for which long-term record of the isotopic composition of monthly precipitation is available. The tritium data are discussed here in the context of generally declining levels of bomb tritium in the global atmosphere and growing influence of technogenic emissions of this isotope. Two aspects of temporal variability of stable isotope composition of precipitation collected in Krakow are discussed here: (i) seasonality and (ii) interannual changes of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signal. Whereas the seasonality of stable isotope signal is generated mainly by seasonally varying the degree of rainout of air masses bringing moisture from the source regions (subtropical Atlantic Ocean) to the centre of the European continent, the North Atlantic Oscillation seems to govern interannual changes of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ on the decadal timescale. Progressing warming of the local atmosphere, in the order of 1.8 °C in the past four decades, leaves its imprint in stable isotope signal measured in Krakow precipitation; the slope of isotope–temperature relationship is in the order of 0.50‰/°C for $\delta^{18}\text{O}$ and 3.5‰/°C for $\delta^2\text{H}$.

Keywords Isotopes · Deuterium · Oxygen-18 · Precipitation · GNIP · NAO

Introduction

Isotopic composition of precipitation ($^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ isotope ratios, tritium content) is nowadays widely used in applications of environmental isotopes—most notably in hydrology, climatology and biogeochemistry. The Global Network of Isotopes in Precipitation (GNIP) jointly operated since 1961 by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) constitutes a basic source of information on present-day temporal and spatial variability of isotopic composition of monthly precipitation on the global scale (IAEA 1992; www.iaea.org/programs/ri/gnip/gnipmain). The GNIP database is supplemented by information gathered through national networks monitoring isotopic composition of monthly precipitation on a country scale (e.g. Schürch et al. 2003; Liu et al. 2014; Tadros et al. 2014; Stumpp et al. 2014).

The radioactive isotope of hydrogen, tritium (^3H), has a half-life of 4500 ± 8 days (Lucas and Unterweger 2000) and is present in water in very low concentrations. The concentration of tritium in water is often expressed in Tritium Units (T.U.). One Tritium Unit is defined as $^3\text{H}/^1\text{H}$ isotope ratio equal 10^{-18} and corresponds to specific activity of 0.118 Bq per kg of water. Natural tritium is produced mainly in the lower stratosphere as a result of nuclear reactions of nitrogen nuclei with neutrons generated by interactions of cosmic ray flux with constituents of Earth's atmosphere. Tritium atoms are oxidized to water molecules, such as $^3\text{H}^1\text{H}^{16}\text{O}$, which are then transported to the troposphere and are incorporated in the hydrological cycle. Transport of tritiated isotopologues of water occurs mainly through discontinuities of the tropopause and as a result of its seasonal ascent. This mechanism generates summer maxima of tritium content in precipitation visible mainly at mid- and high latitudes. The natural tritium content in precipitation varies within the range of 5 to 10 T.U., depending on the location (Różanski et al. 1991; Clark and Fritz 1997).

In the early 1960s, the concentrations of tritium in atmospheric moisture and precipitation raised dramatically

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as a result of atmospheric tests of nuclear bombs and reached several thousand T.U. at mid-latitudes of the northern hemisphere. Over time, the concentration of bomb tritium in precipitation gradually declined as a result of radioactive decay and isotope exchange with the ocean. Nowadays, the tritium content in precipitation is approaching in many parts of the world the level determined by its natural production, with the exception of areas where technogenic emissions of tritium dominate. Rapid changes of tritium content in precipitation in the second half of the twentieth century have been widely used in groundwater hydrology to quantify groundwater ages (e.g. Maloszewski and Zuber 1996; Kazemi et al. 2006; Newman et al. 2010).

Apart from tritium, also stable isotope composition of monthly precipitation ($^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ isotope ratios) is regularly measured in the framework of GNIP network operation. Deuterium and oxygen-18 are powerful tools to reconstruct past climatic and environmental changes (e.g. Leng 2006). They are also widely employed in hydrological studies to identify the origin of water (e.g. meteoric vs. non-meteoric, recent infiltration vs. infiltration under different climatic regimes), to determine residence time of water underground, to quantify mixing patterns of various water types as well as to quantify the elevation of recharge areas in mountainous regions, just to name few (e.g. Clark and Fritz 1997).

Systematic measurements of the isotopic composition of monthly precipitation began in Poland in 1975 (Dulinski et al. 2001). During the period 1975–1992, precipitation samples were collected on the premises of the Krakow branch of National Institute of Meteorology and Water Management (Krakow–Wola Justowska). Starting from 1993, precipitation samples are collected by the meteorological station located at the Krakow-Balice international airport, about 6 km west of the former sampling site. Isotope and meteorological data gathered by Krakow station are regularly reported to the GNIP database.

The major objective of this work was to evaluate long-term record (44 years) of tritium and stable isotope composition of monthly precipitation available for the Krakow station. The tritium data are discussed in the context of generally declining levels of bomb tritium in the global atmosphere and growing influence of technogenic emissions of this isotope. With respect to stable isotope composition of precipitation, the major issue discussed here is an apparent link between progressing warming of the local atmosphere and its imprint in stable isotope signal measured in Krakow precipitation. Krakow is the only site in Poland for which long-term record of the isotopic composition of monthly precipitation is available. It is important that potential users of this dataset in the country and abroad are well informed about all intricacies of the record.

Methods

Isotopic composition of monthly precipitation collected at Krakow station is analysed in the isotope laboratory of the Faculty of Physics and Applied Computer Science, AGH University of Science and Technology in Krakow. The tritium content is determined using electrolytic enrichment of water followed by liquid scintillation spectrometry (Florkowski and Grabczak 1975, 1977; Kuc and Grabczak 2005). Oxygen-18 content is measured using isotope ratio mass spectrometry (IRMS) combined with CO_2 –water equilibration method (Barański 1976; Rózanski et al. 1987), whereas deuterium content is analysed using water reduction on metallic zinc (Florkowski 1986) with subsequent analysis of $^2\text{H}/^1\text{H}$ ratios using IRMS technique. Since 2017, precipitation samples are also analysed using cavity ring-down laser spectrometry. Picarro L2140-*i* CRDS analyser is employed for this purpose (Pierchala et al. 2019).

Deuterium and oxygen-18 content in monthly precipitation is expressed in δ values defined as parts per thousand deviations relative to internationally accepted standard (VSMOW). As a part of quality assurance/quality control (QA/QC) strategy aimed at maintaining high quality of isotope analyses, the laboratory participates in dedicated interlaboratory comparisons organized regularly by the IAEA (Hillegonds et al. 2014; Wassenaar et al. 2018). The overall uncertainty of tritium analyses is ± 0.3 T.U. (one sigma level), whereas $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values determined using IRMS technique have overall uncertainties in the order of 1.0‰ and 0.1‰, respectively. The uncertainties of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ analyses using laser spectroscopy are substantially lower: approximately 0.18‰ and 0.037‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively (Pierchala et al. 2019).

Results and discussion

Tritium content in monthly precipitation

Temporal changes of tritium content in monthly precipitation in Krakow are presented in Fig. 1. The record has two parts: (i) the period from January 1975 to December 2018 for which the tritium content in monthly precipitation was measured in Krakow and (ii) the period from January 1961 to January 1975 for which reconstructed values of tritium content in Krakow precipitation are presented (see below).

Despite substantial spatial variability of tritium content in precipitation on a global scale (Rózanski et al. 1991), there is in general good correlation of temporal changes in tritium concentrations among different locations. This

Fig. 1 Tritium concentration in monthly precipitation in Krakow. Shown are tritium concentrations measured in monthly cumulative precipitation samples collected in Krakow during the period 1975–2018 and the reconstructed tritium concentrations for the period 1961–1974 (dotted line—see text for details). The insert shows seasonal variations in tritium concentrations in Krakow, averaged for two decadal periods (1987–1996 and 2007–2016). Uncertainties shown are standard uncertainties of individual monthly values contributing to the mean value for the given month

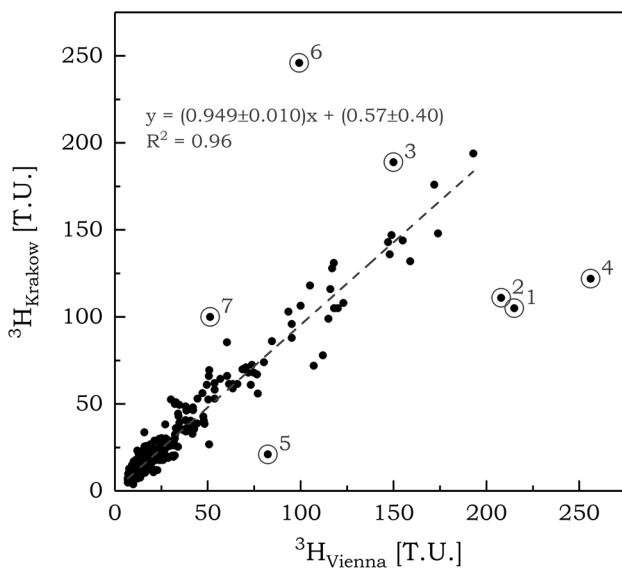
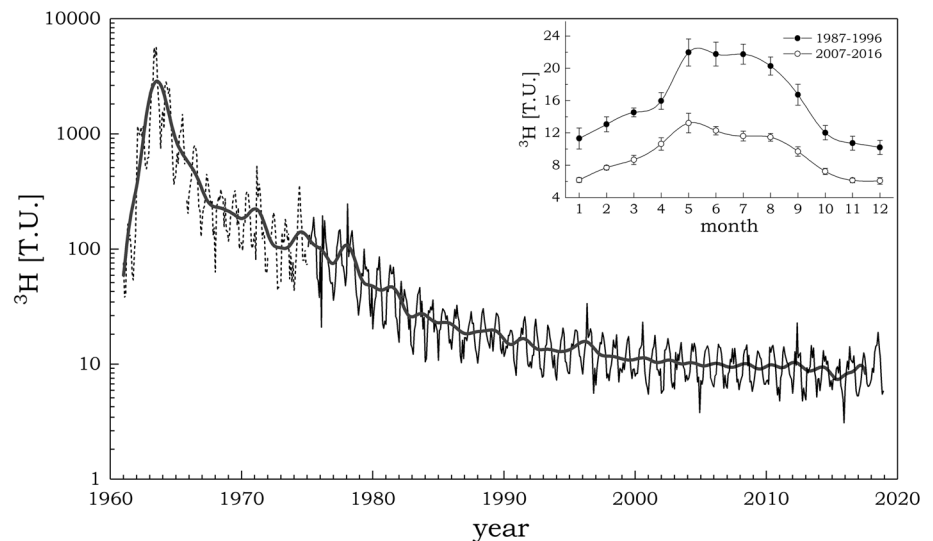


Fig. 2 Scatter plot of tritium concentration in monthly precipitation collected in Krakow and in Vienna during the period 1975–2018

allows a reconstruction of tritium content in precipitation for areas for which direct measurements are not available (Doney et al. 1992). Figure 2 shows scatter plot of measured tritium concentrations in monthly precipitation in Krakow and in Vienna, a station located ca. 450 km southwest of Krakow, for the period of common operation of both stations (January 1975–December 2018). After rejection of 7 outliers marked by circles in Fig. 2 (cf. discussion below), the best-fit line of the data points yields the following correlation equation:

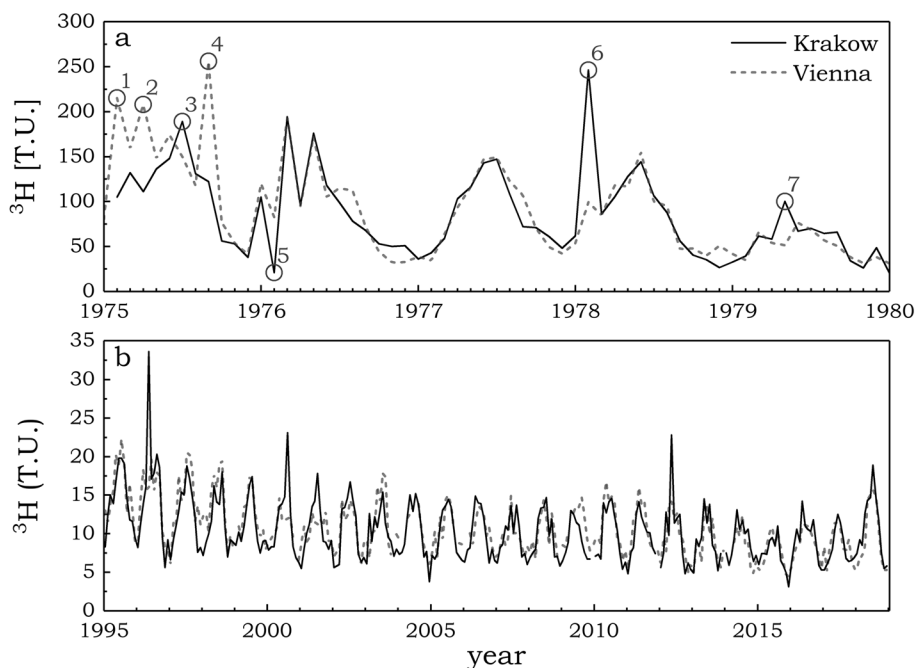
$${}^3\text{H}(\text{Krakow}) = (0.949 \pm 0.010) \times {}^3\text{H}(\text{Vienna}) + (0.57 \pm 0.40), R^2 = 0.96$$

This correlation equation was applied to extrapolate Krakow data back in time from 1974 to 1961. This extrapolation is needed for defining input function of bomb tritium to groundwater systems in applications of this isotope as dating tool in groundwater hydrology (e.g. Maloszewski and Zuber 1996).

The data record presented in Fig. 1 reveals the expected seasonality of the tritium content in monthly precipitation. Temporal evolution of this seasonality is shown in the insert in Fig. 1 where seasonal cycle of tritium content in precipitation measured in Krakow and averaged for two selected decadal periods (1987–1996 and 2007–2016) is compared. Seasonal variations in tritium content during these two periods are very similar, despite significantly lower tritium levels recorded during 2007–2016 period. Almost linear increase in tritium content in precipitation is observed during the first 4 months of a year (January–April), reflecting gradual ascent of the tropopause level incorporating parts of the lower stratosphere with elevated tritium levels into the troposphere. The maximum of tritium content is reached in May and stays high for three subsequent months with only minor fluctuations. Starting from September, the tritium content declines gradually, reaching minimum in December. This seasonal evolution of tritium content reflects mainly seasonal changes in the dynamics of tritium transport from the stratospheric reservoir down to the troposphere where hydrological cycle is operating.

Comparison of tritium concentrations in monthly precipitation collected in Krakow and in Vienna is shown in Fig. 3 for two selected periods: (i) the 5-year period between 1975 and 1980, and (ii) the last 23 years (1995–2018). Average concentrations of tritium for those two periods differ for Krakow data by almost one order

Fig. 3 Tritium concentrations in monthly precipitation collected in Krakow and in Vienna for two selected periods: **a** 1975–1980 and **b** 1995–2018. Values marked with circles in (a) are identical with those marked with circles in Fig. 2



of magnitude (ca. 78 T.U. vs. 10 T.U.). Figure 3a shows that relatively high tritium concentrations were observed in January, March and August 1975 in Vienna but not in Krakow, and in January 1978 and April 1979 in Krakow only. In the more recent period (Fig. 3b), anomalously high tritium concentrations have been recorded in Krakow in May 1996, August 2000, May 2012 and in July 2018. These anomalously high concentrations are most probably linked to episodic emissions of technogenic tritium on the European continent (Hebert 1990). Possible sources are nuclear power reactors and applications of artificial tritium in medicine and in watch industry.

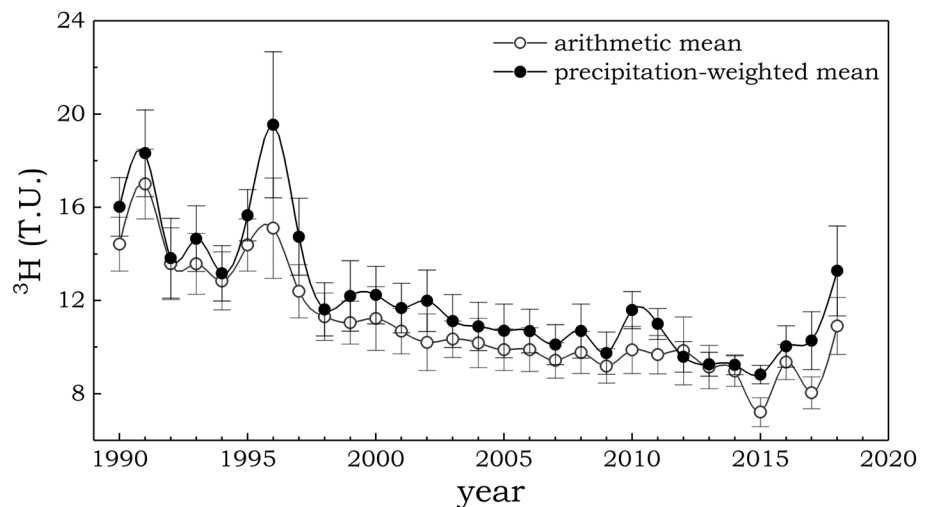
Figure 3b shows that very low concentrations of tritium, at the level of 5 T.U. or lower, are recorded from time to time in monthly precipitation at both locations. In Krakow, such anomalously low tritium contents were recorded in November 1996 (5.6 T.U.), December 2004 (3.8 T.U.) and December 2015 (3.1 T.U.). In Vienna, the tritium concentrations lower than 5 T.U. were recorded in November 2014 and in November and December 2015. These low tritium levels most probably reflect episodes of specific circulation patterns over Europe, when fast transport of oceanic water vapour from the Atlantic Ocean to central Europe occurs without significant rainout and moisture exchange with the surface of the continent. It is worth noting that those episodes occur only during winter, when stratospheric reservoir of tritium is cut off and backward flux of moisture from the continental biosphere (transpiration process) is largely absent.

The annual arithmetic and precipitation-weighted averages of tritium concentration recorded in Krakow during the period 1990–2018 are presented in Fig. 4 (see also Table 1). Whereas arithmetic averages reflect average conditions in the atmosphere during a given year, the precipitation-weighted averages are better suited for applications of tritium in hydrology. General declining trend for both types of averages is apparent in the data. However, substantial departures from this trend are also apparent. The most prominent one occurred in 1996, when high values of both types of averages were recorded. They were caused by exceptionally high tritium content in May 1996 (33.6 T.U.), combined with very high precipitation amount during that month (147 mm). Also the last year in the record shown in Fig. 4 (2018) is characterized by relatively high values of annual averages. In this case, higher than average tritium contents were recorded during summer 2018, with the maximum of 18 T.U. measured for July 2018, which was also the month with high precipitation amount.

Stable isotope composition of monthly precipitation

Processes controlling stable isotope composition of precipitation on different temporal and spatial scales are relatively well understood (e.g. Dansgaard 1964; Rozanski et al. 1993). Deuterium and oxygen-18 isotope composition of precipitation collected at a given location on Earth's surface is a function of several environmental parameters, called 'effects' (temperature effect, continental effect,

Fig. 4 Annual averages (arithmetic and precipitation-weighted) of tritium content recorded in Krakow precipitation during the period 1990–2018. Shown are also standard uncertainties of the mean values



latitude and altitude effects, and amount effect). Modelling of physical processes responsible for the observed spatial and temporal variability of stable isotope composition of precipitation revealed that, in the context of the European continent, this variability is controlled in the first instance by the conditions in the source regions of atmospheric moisture generating precipitating over the continent (sub-tropical Atlantic Ocean) such as temperature of surface ocean, wind speed and relative humidity, as well as by difference in surface air temperature of moisture source regions and the precipitation site (e.g. Rozanski et al. 1982; Sonntag et al. 1983).

Stable isotope composition of precipitation over the European continent reveals strong seasonality, with maximum $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values recorded during summer and minimum values during winter season. Figure 5 shows records of $\delta^{18}\text{O}$ in monthly precipitation, surface air temperature and monthly precipitation amount recorded in Krakow station during the period 1975–2018. All three variables shown in Fig. 5 reveal distinct seasonality, superimposed on their long-term trends. Since both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are linearly correlated (cf. discussion below), the seasonality of $\delta^2\text{H}$ is similar to that presented for $\delta^{18}\text{O}$ in Fig. 5a.

Intra-annual variability of the parameters presented in Fig. 5 is summarized in Fig. 6 in the form of long-term monthly means of $\delta^{18}\text{O}$, surface air temperature and precipitation amount. Also, the seasonality of secondary parameter, the so-called deuterium excess (d-excess) defined as $d = \delta^2\text{H} - 8 \times \delta^{18}\text{O}$, is shown in this figure. Peak-to-peak amplitude of seasonal $\delta^{18}\text{O}$ variations shown in Fig. 6 amounts to approximately 7‰, whereas for surface air temperature it reaches ca. 21 °C. Seasonality of monthly precipitation amount is also well visible; it varies from ca. 30 mm during winter to approximately 80 mm during summer. The d-excess parameter decreases from approximately 8‰ in January to 7‰ in June, then rises to the maximum value of

ca. 10‰ in September/October and decreases to 9.5‰ in November/December (see also Fig. 8b).

A characteristic feature of heavy stable isotope composition of precipitation is a strong linear relationship between their ^2H and ^{18}O content. On the global scale, precipitation samples cluster in the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ space along a straight line called Global Meteoric Water Line (GMWL): $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$ (Craig 1961). On the local scale, significant deviations from the global relationship can be observed, with respect to both the slope and the intercept (e.g. Rozanski et al. 1993). Local Meteoric Water Line (LMWL) defined by the Krakow data is shown in Fig. 7. LMWL for Krakow has slightly lower slope and intercept (7.82 ± 0.04 and 6.6 ± 0.4 , respectively) when compared to the global relationship.

Relation between isotopic composition of precipitation and surface air temperature

Relationship between isotopic composition of precipitation and surface air temperature is of primary importance for numerous applications of heavy stable isotopes of water in palaeoclimatology. Three types of isotope–temperature relationship for the present-day climate can be considered (e.g. Rozanski et al. 1993): (i) spatial relation between long-term (annual) averages of $\delta^{18}\text{O}$ ($\delta^2\text{H}$) of precipitation and surface air temperature for different locations, (ii) temporal relation between short-term (seasonal) changes of $\delta^{18}\text{O}$ ($\delta^2\text{H}$) and temperature for a given site and (iii) temporal relation between long-term (interannual) changes of $\delta^{18}\text{O}$ ($\delta^2\text{H}$) and temperature at a given location. Relationship (iii) is most relevant as far as palaeoclimatic applications of heavy stable isotopes of water are concerned. In the following, we will discuss relationships (ii) and (iii) for Krakow dataset.

Figure 8a shows apparent link between long-term monthly means of $\delta^{18}\text{O}$ and surface air temperature for

Table 1 Summary statistics of isotope and meteorological data available for Krakow station

Year	P [mm]	Tritium Units [T.U.]		$\delta^{18}\text{O}$ [‰]		$\delta^2\text{H}$ [‰]		d-excess		T [°C]	Vapour pressure [hPa]
		Weighted average	Average	Weighted average	Average	Weighted average	Average	Weighted average	Average		
1975	627	125.1	107.9	-8.30	-10.01	-56.7	-70.2	9.7	9.9	8.6	10.1
1976	607	97.4	92.4	-9.32	-10.39	-66.5	-74.8	8.1	8.3	7.1	8.8
1977	678	88.8	83.9	-9.14	-9.20	-64.2	-64.7	8.9	8.9	8.1	9.5
1978	667	93.9	93.7	-9.30	-10.62	-66.8	-77.4	7.6	7.6	7.1	8.9
1979	648	59.3	55.7	-10.57	-10.58	-77.0	-77.2	7.6	7.4	7.5	9.3
1980	575	47.8	41.9	-10.45	-10.88	-74.8	-78.4	8.8	8.6	6.8	8.9
1981	671	49.1	46.3	-10.65	-11.44	-75.8	-82.2	9.4	9.3	8.0	9.5
1982	458	30.6	32.1	-9.13	-10.08	-64.0	-71.8	9.0	8.8	8.2	9.7
1983	463	29.1	27.8	-9.10	-9.10	-65.4	-65.2	7.4	7.7	9.1	9.4
1984	508	24.8	23.3	-9.45	-10.61	-68.1	-77.4	7.5	7.4	7.8	9.4
1985	790	24.4	22.4	-8.78	-9.48	-61.8	-66.9	8.5	9.0	7.0	9.4
1986	679	23.0	20.1	-8.23	-9.03	-58.8	-64.6	7.0	7.7	7.6	9.4
1987	675	20.8	19.4	-9.35	-9.96	-66.5	-72.0	8.2	7.6	7.1	9.0
1988	551	20.6	19.1	-8.51	-9.13	-60.3	-64.6	7.8	8.4	8.6	9.6
1989	638	22.3	19.3	-7.36	-7.86	-48.5	-53.2	10.4	9.7	9.3	10.4
1990	666	16.0	14.4	-8.69	-9.46	-59.7	-65.4	9.8	10.2	9.1	9.1
1991	604	18.3	17.0	-8.50	-9.25	-58.2	-64.7	9.8	9.3	7.9	9.7
1992	593	13.8	13.6	-10.51	-10.16	-75.2	-72.6	8.9	8.7	8.8	9.4
1993	471	14.7	13.6	-9.25	-10.00	-68.0	-73.5	6.0	6.6	8.1	9.1
1994	716	13.2	12.8	-8.70	-9.11	-63.6	-66.6	6.0	6.3	9.3	9.8
1995	660	15.7	14.4	-10.16	-10.87	-73.2	-78.6	8.1	8.4	8.2	9.5
1996	748	19.5	15.1	-9.75	-11.42	-68.6	-81.8	9.5	9.5	6.6	8.9
1997	824	14.7	12.4	-10.04	-10.54	-69.8	-74.0	10.6	10.3	7.8	9.3
1998	709	11.6	11.3	-9.09	-9.66	-64.0	-68.0	8.8	9.2	8.6	9.7
1999	703	12.2	11.1	-8.63	-9.68	-58.4	-67.8	10.7	9.7	9.0	10.0
2000	722	12.2	11.2	-9.23	-9.11	-66.4	-65.0	7.5	7.9	9.8	10.1
2001	823	11.7	10.7	-9.03	-9.78	-62.6	-69.1	9.6	9.1	8.5	9.8
2002	744	12.0	10.2	-8.41	-9.39	-58.0	-66.0	9.3	9.1	9.3	10.0
2003	565	11.1	10.3	-9.03	-10.10	-64.2	-72.8	8.1	8.0	8.6	9.3
2004	488	10.9	10.2	-9.59	-9.74	-68.1	-69.3	8.6	8.7	8.8	9.4
2005	604	2.3	8.1	-2.58	-9.00	-18.4	-63.9	2.3	8.2	8.3	9.3
2006	524	9.1	10.7	-5.94	-7.38	-44.0	-54.6	3.5	4.5	8.4	9.6
2007	889	10.1	9.4	-8.75	-9.15	-60.3	-64.8	9.8	8.4	9.7	9.9
2008	618	10.7	9.8	-8.95	-9.55	-63.1	-68.3	8.5	8.1	9.5	9.7
2009	674	9.7	9.2	-9.94	-10.45	-70.1	-74.3	9.4	9.3	8.7	9.9

Table 1 (continued)

Year	P [mm]	Tritium Units [T.U.]		$\delta^{18}\text{O}$ [‰]		$\delta^2\text{H}$ [‰]		d-excess		T [°C]	Vapour pressure [hPa]
		Weighted average	Average	Weighted average	Average	Weighted average	Average	Weighted average	Average		
2010	963	11.6	9.9	-10.00	-11.35	-70.9	-82.0	9.1	8.9	7.6	9.7
2011	556	11.0	9.7	-6.92	-8.70	-49.6	-62.0	5.8	7.6	8.8	9.8
2012	555	9.4	9.8	-9.02	-9.11	-65.7	-66.6	6.5	6.2	8.6	9.7
2013	558	9.0	9.1	-9.89	-10.21	-69.8	-73.3	9.3	8.4	8.6	9.9
2014	679	10.0	9.0	-8.15	-8.88	-56.3	-62.2	8.9	8.8	9.8	10.5
2015	582	7.8	7.2	-7.88	-8.78	-56.0	-63.3	7.0	7.0	10.0	9.8
2016	689	9.6	9.4	-9.33	-9.53	-64.7	-66.9	9.9	9.3	9.4	10.0
2017	742	8.0	8.0	-9.59	-10.11	-66.6	-71.9	10.1	9.0	9.1	9.8
2018	556	13.3	10.9	-8.13	-8.61	-57.4	-61.6	7.6	7.2	10.0	10.4
Average	647			-8.89	-9.71	-62.9	-69.4	8.3	8.4	8.5	9.6
1 σ	110			1.35	0.88	9.8	6.7	1.7	1.2	0.9	0.4

The data cover the period 1975–2018

Krakow station (cf. also Table 2). Seasonality in the isotopic composition of European precipitation is generated mainly by seasonally varying the degree of rainout of moist air masses arriving in Europe from the Atlantic Ocean, which in turn is controlled by the difference in temperature of moisture source regions and precipitation site (Rozanski et al. 1982; Sonntag et al. 1983).

Worth commenting is also trajectory of seasonal changes of the d-excess as a function of surface air temperature, shown in Fig. 8b. Apparent ‘hysteresis loop’ with generally low d-excess values during the first half of a year and high d-excess values during the second half stems most likely from asymmetry in the seasonal evolution of surface air and sea surface temperatures in the main source regions of moisture generating precipitation over the European continent (subtropical Atlantic, 30–40°N). Due to high thermal capacity of water, surface ocean in the moisture source regions stays warm also in September and October when surface air temperatures already decline (www.ospo.noaa.gov/data/sst/mean_mon). Since the d-excess value of net evaporation flux is controlled mainly by relative humidity normalized to the temperature of the surface ocean (e.g. Horita et al. 2008), the above-indicated asymmetry leads to a marked reduction in the relative humidity and results in higher d-excess values of oceanic water vapour generated in the source regions in early autumn, when thermal contrast between surface ocean and surface air is at its maximum. Low d-excess values recorded in June–July are most probably linked to enhanced role of partial evaporation of raindrops on their way from the cloud base level to the ground during warm season.

Temporal evolution of annual averages of $\delta^{18}\text{O}$ measured in monthly precipitation collected in Krakow is shown in Fig. 9a. Two types of annual means are shown: arithmetic and precipitation-weighted. Because precipitation amount is biased towards summer season (cf. Fig 6), precipitation-weighted mean $\delta^{18}\text{O}$ values are generally higher than arithmetic means (see also Table 1). Interannual variability of $\delta^{18}\text{O}$ is substantial. The range of annual mean $\delta^{18}\text{O}$ values shown in Fig. 9a and reported in Table 1 is in the order of 3‰, comparable with the shift of $\delta^{18}\text{O}$ in precipitation which occurred in Poland at the transition from late Glacial to Holocene (Róžański and Zuber 2000). Worth noting is also quasi-periodic character of the interannual $\delta^{18}\text{O}$ variations, particularly well visible for annual arithmetic means of $\delta^{18}\text{O}$. Distinct minima of annual mean $\delta^{18}\text{O}$ values were recorded in 1981, 1995 and 2010. The last two minima coincide very well with distinct minima in North Atlantic Oscillation (NAO) index (Comas-Bru et al. 2016). North Atlantic Oscillation is a weather phenomenon in the North Atlantic described by the difference of atmospheric pressure at sea level between Icelandic Low and Azores High. This pressure difference controls the direction and strength of westerly winds and location of

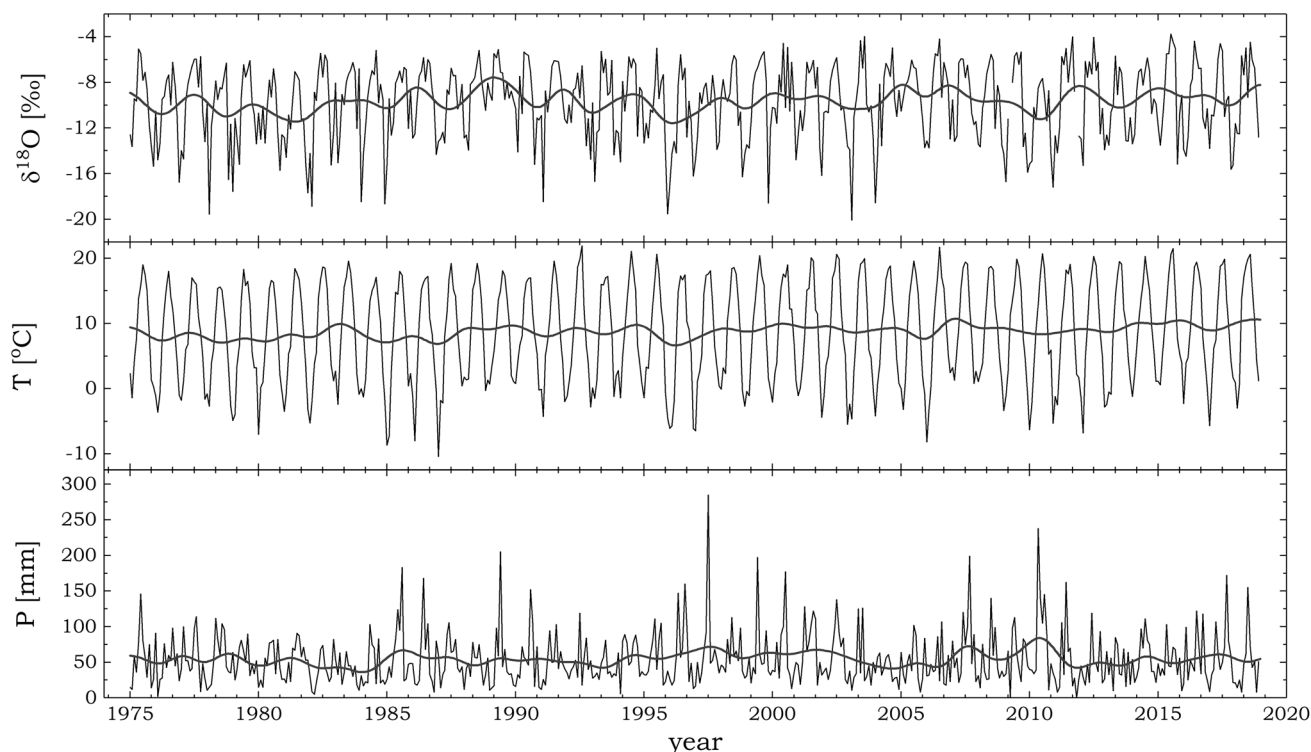


Fig. 5 Temporal changes of $\delta^{18}\text{O}$ values in monthly precipitation, monthly surface air temperature and monthly precipitation amount, recorded in Krakow during the period 1975–2018. Long-term trends

of the parameters shown were calculated with the aid of CCGvu 4.40 routine (Thoning et al. 1989)

storm tracks across North Atlantic (Hurrell 2003). Negative values of NAO index signify shift of storm tracks to the south resulting in cold and dry winters in western and central Europe. Colder-than-normal winters mean generally lower $\delta^{18}\text{O}$ values of winter precipitation (cf. Fig 8a).

A deeper insight into interannual variability of heavy isotope composition of precipitation can be gained by considering separately summer and winter portion of this variability. Figure 9b shows interannual changes of the arithmetic mean $\delta^{18}\text{O}$ values for summer (June–August) and winter (December–February) precipitation in Krakow. Interannual changes of average surface air temperatures for those two periods are presented in Fig. 9c. Figure 9b shows that interannual variability of the isotopic composition of precipitation is significantly higher during cold season (the range of $\delta^{18}\text{O}$ values exceeding 8‰, to be compared with approximately 5‰ during summer period). This smaller interannual variability of summer $\delta^{18}\text{O}$ values stems from the fact that continental recycling of moisture plays an important role in atmospheric water balance over the European continent during this season (e.g. Rozanski et al. 1982). The isotopic composition of moisture flux which is returned regional atmosphere by plants in the transpiration process resembles annual mean δ value of

local precipitation, thus strongly buffering variations in the isotopic composition of moisture of oceanic origin.

Linear fits of isotope and temperature records shown in Fig. 9b, c reveal that statistically significant increase in the mean $\delta^{18}\text{O}$ and surface air temperature with time is restricted to summer months. The slopes of best-fit lines approximating summer data points are equal $0.28 \pm 0.11\text{‰}$ and $0.66 \pm 0.09\text{ °C}$ per decade, for $\delta^{18}\text{O}$ and temperature, respectively (Table 2). Linear fit of winter values yields slopes which are indistinguishable from zero.

Figure 10 illustrates the link between annual averages of ^{18}O content (arithmetic— $\delta^{18}\text{O}_{\text{PA}}$ and precipitation-weighted— $\delta^{18}\text{O}_{\text{PW}}$) and mean annual temperatures (MAT), recorded in Krakow during the period 1975–2018. Linear fit was applied to both types of data. The slopes of $\delta^{18}\text{O}$ -temperature relationship are equal $0.57 \pm 0.12\text{‰/°C}$ and $0.42 \pm 0.13\text{‰/°C}$, for arithmetic and precipitation-weighted annual averages of $\delta^{18}\text{O}$, respectively (cf. Table 2). They are in the range of the slopes reported for other locations on the European continent (e.g. Rozanski et al. 1993). In the context of palaeoclimatic reconstructions based on isotopic composition of precipitation preserved in various environmental archives such as ice cores, lake sediments and speleothems, the choice of proper slope should be guided by the

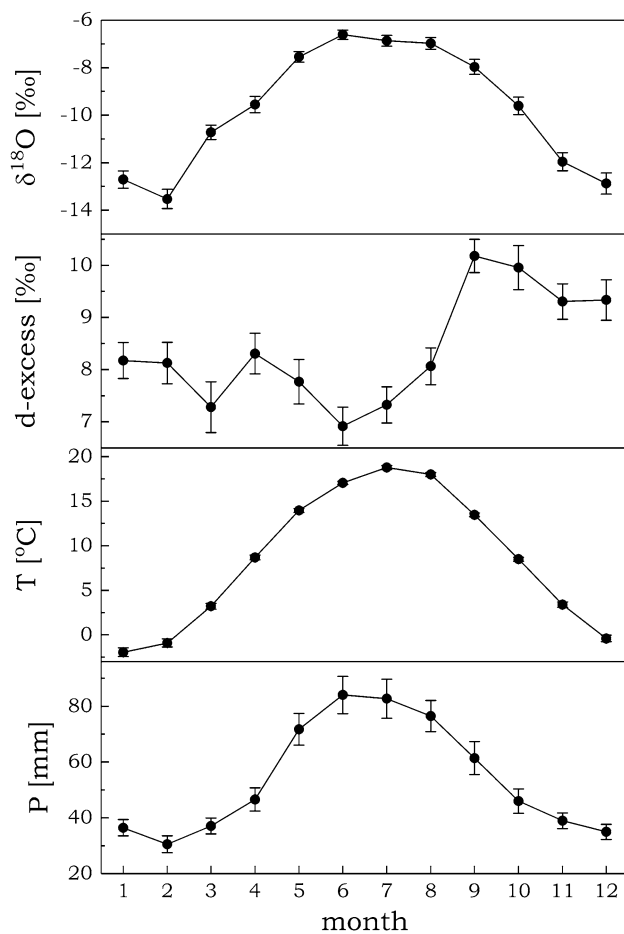


Fig. 6 Seasonal variability of long-term monthly means of $\delta^{18}\text{O}$, d-excess, surface air temperature and precipitation amount recorded in Krakow station during the period 1975–2018. Shown are standard uncertainties of the mean values

way in which the isotope signal of precipitation is preserved in the given archive, taking into account for instance possible seasonal bias.

The ^{18}O -temperature relationship calculated for inter-annual variations in summer (June–August) and winter (December–February) mean values of $\delta^{18}\text{O}$ and surface air temperature (Fig. 9b, c) reveals the slopes equal $0.36 \pm 0.12\text{‰}/^\circ\text{C}$ and $0.43 \pm 0.12\text{‰}/^\circ\text{C}$, respectively. Significantly lower slope for summer season is linked to the impact of transpiration flux on the water balance of the regional atmosphere (cf. discussion above).

Concluding remarks

A 44-year record of tritium and stable isotope composition of monthly precipitation collected in Krakow station during the period 1975–2018 and discussed here allows to quantify short- and long-term variability of this composition. The

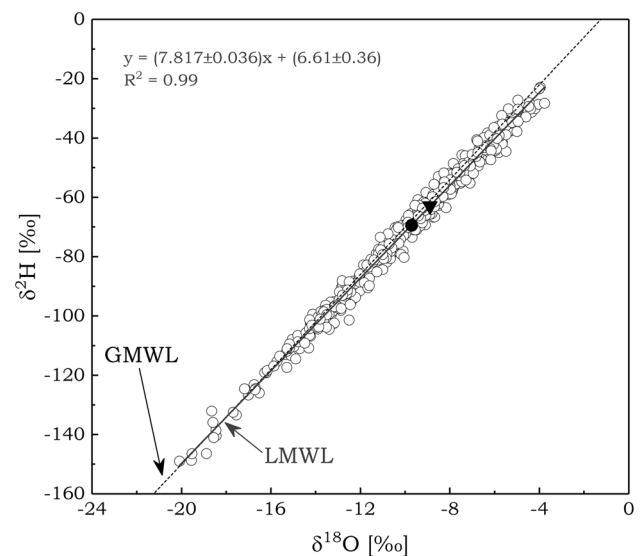


Fig. 7 Relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of monthly precipitation samples collected in Krakow during the period 1975–2018. Dashed line—Global Meteoric Water Line (GMWL), heavy line—best linear fit of monthly data (Local Meteoric Water Line). Full circle—arithmetic mean of monthly data, full triangle—precipitation-weighted mean of monthly data

major findings of this analysis are summarized below. They are representative for Central–Eastern Europe.

The presented tritium data demonstrate declining role of bomb tritium and growing influence of technogenic emissions of this isotope on its concentrations observed in the regional atmosphere. The concentrations of tritium in Central–Eastern European precipitation are still decreasing (cf. Fig. 4). From the perspective of hydrological applications of tritium, this implies that the ‘constant input’ scenario for interpretation of tritium data in hydrology (Michel et al. 2015) should be carefully evaluated on case-by-case basis before it is employed in hydrological practice.

Deuterium and oxygen-18 isotope composition of monthly precipitation available for Krakow station reveal several interesting features related to their temporal variability. The location of the station in the centre of the European continent results in substantial seasonal changes in the thermal gradient between the main moisture source region (subtropical Atlantic Ocean) and the site where precipitation is collected. This in turn generates seasonal variations in the degree of rainout of moist air masses transported eastward over the continent and the resulting seasonal variations in the isotopic composition of precipitation. The peak-to-peak amplitude of these seasonal variations is large and exceeds 7‰ for $\delta^{18}\text{O}$ and 56‰ for $\delta^2\text{H}$. An interesting aspect of the observed intra-annual changes of ^{18}O and ^2H content is that their product, the so-called deuterium excess ($d = \delta^2\text{H} - 8 \times \delta^{18}\text{O}$), apparently preserves information on changing conditions at moisture source regions. This

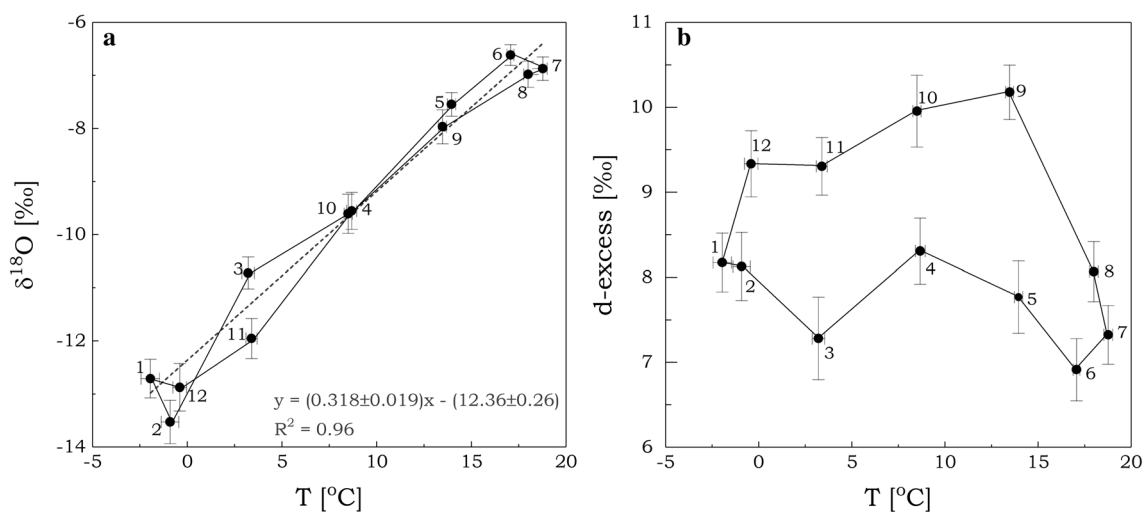


Fig. 8 Relationship between **a** long-term monthly means of $\delta^{18}\text{O}$ and **b** d-excess parameter and the monthly mean surface air temperature recorded in Krakow station between 1975 and 2018. Numbers accompanying data points (from 1 to 12) indicate subsequent months

Table 2 Statistical relations between stable isotope composition of precipitation and surface air temperature for Krakow station

Type of correlation	Correlation equation
Monthly $\delta^{18}\text{O}$ ($\delta^2\text{H}$) versus mean monthly surface air temperature	$\delta^{18}\text{O} = (0.32 \pm 0.02) \cdot T - (12.4 \pm 0.3)$ $R^2 = 0.96, N = 12$ $\delta^2\text{H} = (2.25 \pm 0.15) \cdot T - (90.3 \pm 2.1)$ $R^2 = 0.96, N = 12$
Summer (June–August) mean $\delta^{18}\text{O}$ ($\delta^2\text{H}$) versus summer mean surface air temperature	$\delta^{18}\text{O} = (0.36 \pm 0.12) \cdot T - (13.2 \pm 2.1)$ $R^2 = 0.17, N = 44$ $\delta^2\text{H} = (2.73 \pm 0.90) \cdot T - (96 \pm 16)$ $R^2 = 0.17, N = 44$
Winter (December–February) mean $\delta^{18}\text{O}$ ($\delta^2\text{H}$) versus winter mean surface air temperature	$\delta^{18}\text{O} = (0.43 \pm 0.13) \cdot T - (12.57 \pm 0.27)$ $R^2 = 0.21, N = 44$ $\delta^2\text{H} = (3.37 \pm 0.96) \cdot T - (92.1 \pm 2.1)$ $R^2 = 0.21, N = 44$
Annual (arithmetic) mean $\delta^{18}\text{O}$ ($\delta^2\text{H}$) versus mean annual temperature	$\delta^{18}\text{O} = (0.57 \pm 0.12) \cdot T - (14.58 \pm 0.95)$ $R^2 = 0.37, N = 44$ $\delta^2\text{H} = (4.48 \pm 0.86) \cdot T - (107.5 \pm 7.3)$ $R^2 = 0.38, N = 44$
Annual (precipitation-weighted) mean $\delta^{18}\text{O}$ ($\delta^2\text{H}$) versus mean annual temperature	$\delta^{18}\text{O} = (0.42 \pm 0.13) \cdot T - (12.6 \pm 1.1)$ $R^2 = 0.19, N = 44$ $\delta^2\text{H} = (3.35 \pm 0.98) \cdot T - (92.7 \pm 8.3)$ $R^2 = 0.20, N = 44$

concerns mainly relative humidity of marine atmosphere normalized to the temperature of the surface ocean, which largely determines d-excess value of the moisture flux generated by evaporation of the ocean.

Mean annual surface air temperatures recorded at Krakow station have increased since 1975 by 1.8 °C. This is approximately two times higher value than the reported global increase in surface air temperature by the end of 2018 (<https://data.giss.nasa.gov/gistemp/>). This higher temperature rise is linked to the location of the station within the Krakow agglomeration (urban heat island effect). Interestingly, the

observed increase in surface air temperature is restricted to summer season. The analysis of an apparent link between progressing warming of the local atmosphere and its imprint in stable isotope signal measured in Krakow precipitation generates the slopes of the isotope–temperature relationships which are similar to the previously reported values.

Interannual variability of stable isotope composition of Krakow precipitation is substantial. The observed variability of annual mean $\delta^{18}\text{O}$ values is in the order of 3‰, comparable with the shift of $\delta^{18}\text{O}$ in precipitation which occurred in Poland at the transition from late Glacial to

Fig. 9 **a** Interannual variations in $\delta^{18}\text{O}$ values of monthly precipitation collected in Krakow during the period 1975–2018. Shown are annual means (arithmetic and precipitation-weighted), **b** interannual variations in average $\delta^{18}\text{O}$ values representing summer (June–August, full circles) and winter (December–February, empty circles) seasons. **c** Interannual variations in average surface air temperature representing summer (June–August, full circles) and winter (December–February, empty circles) seasons

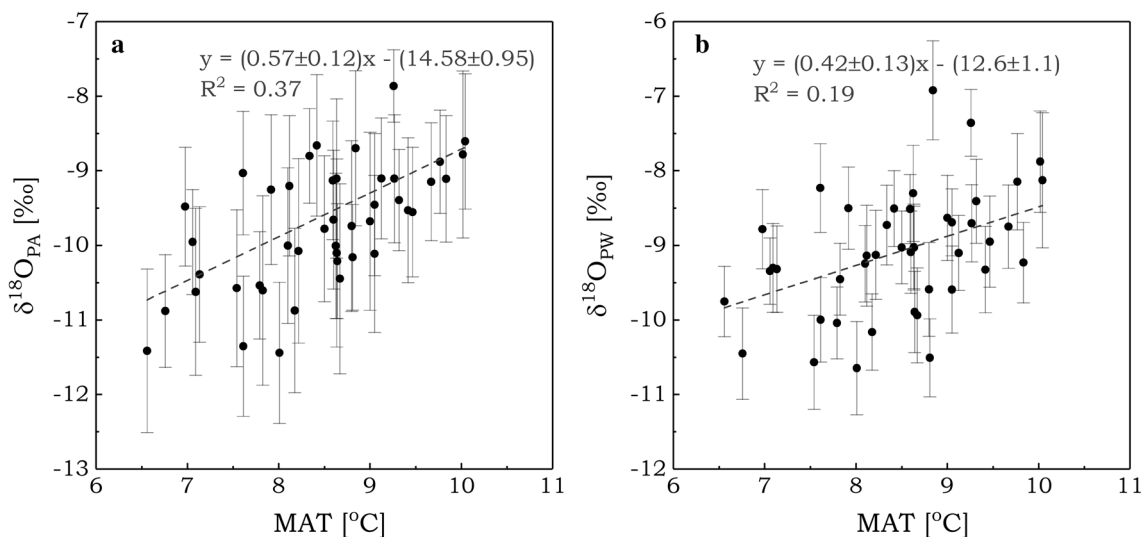
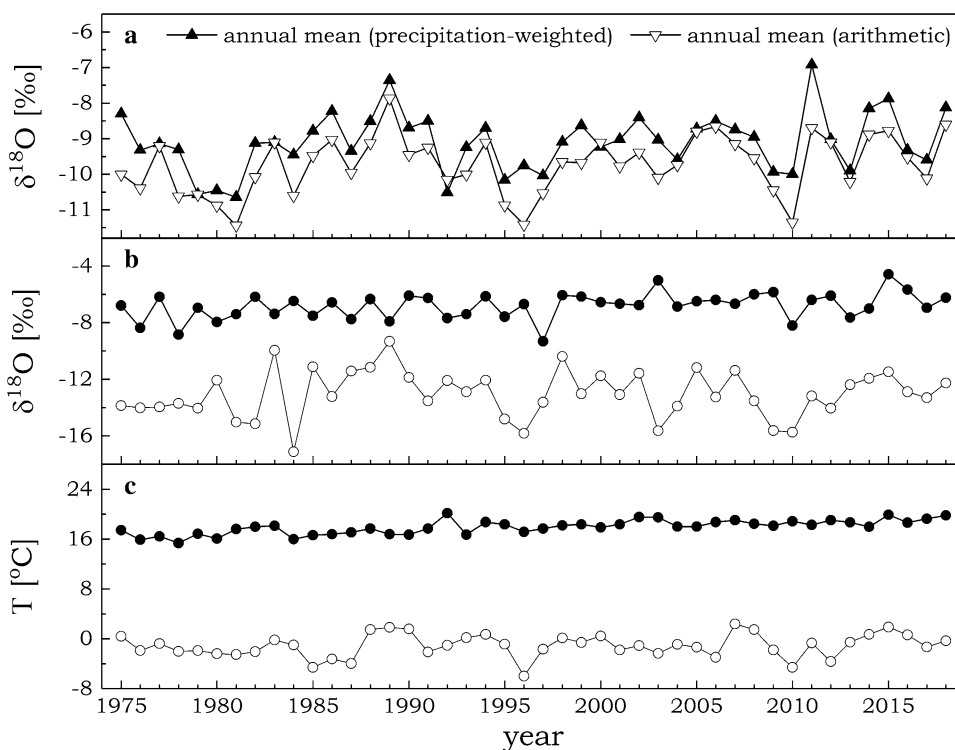


Fig. 10 Relationship between annual arithmetic (a) and precipitation-weighted (b) mean values of ^{18}O content in precipitation and mean annual surface temperatures (MAT) recorded in Krakow station during the period 1975–2018. Shown are also standard uncertainties of the mean $\delta^{18}\text{O}$ values

ing the period 19975–2018. Shown are also standard uncertainties of the mean $\delta^{18}\text{O}$ values

Holocene. An interesting aspect of this variability is its link to North Atlantic Oscillation (NAO) which apparently governs interannual changes of stable isotope composition of precipitation in Krakow on the decadal timescale.

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Compliance with ethical standards

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Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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