GEOLOGIJA *51/2*, 169-180, Ljubljana 2008
https://doi.org/10.5474/geologija.2008.018

Isotopic composition of precipitation in Ljubljana (Slovenia)

Izotopska sestava padavin v Ljubljani

Polona VREČA[1], Ines KRAJCAR BRONIĆ[2], Albrecht LEIS[3] & Mihael BRENČIČ[4]

[1] Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
[2] Rudjer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia
[3] Institute of Water Resources Management, JOANNEUM RESEARCH, Elisabethstrasse 16/II, 8010 Graz, Austria
[4] University of Ljubljana, NTF, Department of Geology, Aškerčeva cesta 12, 1000 Ljubljana, Slovenia

Key words: precipitation, isotopes, oxygen, hydrogen, tritium, Slovenia
Ključne besede: padavine, izotopi, kisik, vodik, tricij, Slovenija

Abstract

The stable isotopic composition of hydrogen and oxygen (δ^2H and $\delta^{18}O$) and tritium activity (^3H) are monitored in monthly precipitation at Ljubljana since 1981. Here we present complete set of numerical data and the statistical analysis for period 1981–2006. Seasonal variations of δ^2H and $\delta^{18}O$ are observed and are typical for continental stations of the Northern Hemisphere. The weighted mean δ^2H and $\delta^{18}O$ values are –59 ‰ and –8.6 ‰, respectively. The orthogonal Local Meteoric Water Line is $\delta^2H = (8.06 \pm 0.08)\delta^{18}O + (9.84 \pm 0.71)$, and the temperature coefficient of $\delta^{18}O$ is 0.29 ‰/°C. Deuterium excess weighted mean value is 9.5 ‰ and indicates the prevailing influence of the Atlantic air masses. Tritium activity in monthly precipitation shows also seasonal variations which are superposed to the decreasing trend of mean annual activity.

Izvleček

Spremljanje izotopske sestave kisika in vodika (δ^2H in $\delta^{18}O$) ter aktivnosti tricija (^3H) v mesečnih vzorcih padavin poteka v Ljubljani od leta 1981. V prispevku predstavljamo celoten niz pridobljenih podatkov in osnovne statistične obdelave za obdobje 1981–2006. Opažene sezonske spremembe δ^2H in $\delta^{18}O$ so značilne za kontinentalne postaje severne poloble. Srednje tehtane δ^2H in $\delta^{18}O$ vrednosti znašajo –59 ‰ oziroma –8.6 ‰. Ortogonalno lokalno padavinsko premico (LMWL) lahko zapišemo kot $\delta^2H = (8.06 \pm 0.08)\delta^{18}O + (9.84 \pm 0.71)$, temperaturni koeficient za $\delta^{18}O$ pa znaša 0.29 ‰/°C. Srednja tehtana vrednost devterijevega presežka (deuterium excess) znaša 9.5 ‰ in nakazuje prevladujoči vpliv zračnih mas iz Atlantika. Tudi podatki o aktivnost tricija v mesečnih padavinah kažejo sezonske spremembe, ki nakazujejo hkrati padajoči trend srednje letne aktivnosti.

Introduction

The stable isotope ratios of oxygen ($^{18}O/^{16}O$) and hydrogen ($^2H/^1H$) and the radioactive isotope tritium (^3H) offer a broad range of possibilities for studying processes within the water cycle and thus became an important tool not only in isotope hydrology, routinely applied in studies of the origin and dynamics of surface and groundwaters, but also in studies related to atmospheric circulation and paleoclimatic investigations (Araguas-Araguas et al., 2000). Understanding the formation of precipitation and its isotopic composition ($\delta^{18}O$, δ^2H and ^3H activity), as well as a knowledge of temporal and spatial variations in the amount and mode of precipitation and in its isotopic composition, are important for basin-wide balance studies (e.g. Gat, 1996).

Most European countries have established networks of stations where isotopic composition of precipitation is regularly determined on monthly basis. In Slovenia, the precipitation monitoring programme is performed in the framework of the regular activities of the Environmental Agency of the Republic of Slovenia. However, monitoring of isotopic composition of precipitation is not included into the regular national programme but has been performed at Ljubljana by the Jožef Stefan Institute since 1981. The data obtained are part of the worldwide monitoring of isotopes in precipitation and are included into Global Network of Isotopes in Precipitation (GNIP) organised jointly by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) (IAEA 1986, 1990, 1994; Pezdič, 2003). The GNIP database contains data on isotopic composition of hydrogen and oxygen, and relevant meteorological data on a monthly basis, and is thus extremely valuable for modelling climatic changes, as well as in hydrological and hydrogeological investigations (IAEA/WMO, 2008). However, GNIP data are collected and published slowly. Therefore, the main purposes of this paper are to 1) report on history of monitoring of isotopic composition of precipitation at Ljubljana, 2) to present the long-term monthly record, and 3) to present basic statistical evaluation of available data for period 1981–2006.

Basic definitions

There are three naturally occurring isotopes of hydrogen (^{1}H – protium, ^{2}H – deuterium and ^{3}H – tritium) and three isotopes of oxygen (^{16}O, ^{17}O and ^{18}O) that are also constituents of the water molecule. Among water isotopes only ^{3}H is radioactive and decays spontaneously over time while the other water isotopes are stable.

Stable isotopes of hydrogen and oxygen

Stable isotopic compositions of hydrogen and oxygen are normally reported as δ values in units of parts per thousand (‰) relative to a standard V-SMOW (Vienna-SMOW). δ values are calculated by:

$$\delta^Y Z = (R_x / R_s - 1) \cdot 1000 \qquad (1)$$

where ^{Y}Z is ^{18}O or ^{2}H, R denotes the ratio of the heavy (less abundant) to light (more abundant) isotope (e.g., ^{2}H/^{1}H, ^{18}O/^{16}O), and R_x and R_s are the ratios in the sample (x) and standard (s), respectively. A positive δ value means that the isotopic ratio R of the sample is higher than that of the standard, and the sample is "heavier" or enriched relative to the standard; a negative δ value means that the isotopic ratio of the sample is lower than that of the standard; the sample is "lighter" or depleted.

The observed variations of stable isotopic composition of hydrogen and oxygen in natural waters are closely related to isotopic fractionation occurring during the evaporation and condensation of water, when the heavy water molecules preferentially remain in or pass into the liquid (solid) phase, respectively (Araguas-Araguas et al., 2000). When water evaporates from the surface of the ocean the water vapour is enriched in ^{1}H and ^{16}O because $^1H_2{}^{16}O$ has a higher vapour pressure than a water molecule containing deuterium or ^{18}O. Water vapour living the surface of the ocean cools as it rises and precipitation forms when the dew point is reached. Consequently, during removal of precipitation from a moist air mass, the residual vapour is continuously depleted in the heavy isotopes, because the water leaving the system is enriched in deuterium and ^{18}O (Craig & Gordon, 1965, Schotterer et al., 1996). The theoretical approach to explain isotope variations in meteoric waters evolved from the models that are based on Rayleigh condensation, with immediate removal of precipitation or with a part of the condensate being kept in the cloud during the precipitation process (Dansgaard, 1964; Rozanski et al., 1993).

In all processes concerning evaporation and condensation, hydrogen isotopes are fractionated in proportion to oxygen isotopes. Therefore, hydrogen and oxygen isotope distributions are correlated in meteoric waters. Craig (1961) first defined the relation generally known as the "Global Meteoric Water Line" (GMWL):

$$\delta^2H = 8\ \delta^{18}O + 10 \qquad (2)$$

Craig's GMWL is only global in application, and is actually an average of many local or regional meteoric water lines that differ from the global line due to varying climatic and geographic parameters. A key observation made by Craig was that isotopically depleted waters are associated with cold regions and enriched waters are found in warm regions. This partitioning was soon recognized as a tool for characterizing groundwater recharge, and is now the basis of groundwater provenance studies (Clark & Fritz, 1997).

Craig's GMWL was later refined from a worldwide monitoring of the stable isotopic composition of precipitation (Rozanski et al., 1993, Gourcy et al., 2005). The regression line for the long-term averages (1961–2000) of δ^{18}O and δ^{2}H in precipitation from nearly 410 stations in the IAEA/WMO network added some precision to Craig's GMWL (Gourcy et al., 2005):

$$\delta^2H = (8.07 \pm 0.02)\ \delta^{18}O + (9.9 \pm 0.01) \qquad (3)$$

Furthermore, Dansgaard (1964) proposed the use of the value, d – deuterium excess, to characterize the deviation of isotopic composition of precipitation from GMWL. The value d is defined for a slope of 8, and is calculated for any precipitation sample as:

$$d = \delta^2H - 8\ \delta^{18}O \qquad (4)$$

Neither the numerical coefficient, 8 (Eq. 2), nor the d value (Eq. 4), are really constant, but depend on local climate.

The first detailed evaluation of the equilibrium and nonequilibrium factors that determine the isotopic composition of precipitation was published by Dansgaard (1964). He demonstrated that the observed geographic distribution in isotopic composition of precipitation is related to many environmental parameters, such as latitude (latitude effect), altitude (altitude effect), distance from the coast (continental effect), amount of precipitation (amount effect), and surface air temperature.

The two main factors that control the isotopic character of precipitation at a given location are the temperature of condensation of the precipitation and the degree of rainout of the air mass (the ratio of water vapour that has already condensed into precipitation to the initial amount of water vapour in the air mass). Most water vapour in the atmosphere is derived from evaporation of low-latitude oceans. Precipitation derived from this vapour is always enriched in deuterium and ^{18}O relative to the vapour, with the fractionation between the rain and vapour as a function of condensation temperature. Therefore, progressive rain out as clouds move across the continent causes successive rainstorms to become increasingly lighter. For example, non-equilibrium evaporation from the ocean with a $\delta^{18}O = 0$ ‰ produces vapour of –12 ‰. Later equilibrium condensation of precipitation from this vapour results in water with a $\delta^{18}O = -3$ ‰ and residual vapour with a $\delta^{18}O = -21$ ‰ (INGRAHAM, 1998).

The correlation between local surface air temperature and the isotopic composition of precipitation is of special interest mainly because of the potential importance of stable isotopes as paleoclimatic indicators. However, this correlation is typical for mid and high latitudes where seasonally changing temperatures lead to variations in the total precipitable water, due to the varying degrees of rain out from air masses as they are transported polewards. Contrary, low latitudes show different response. Isotopic content is modulated by the seasonal variations in the amount of precipitation (SCHOTTERER et al., 1996).

At a given location, the seasonal variations in $\delta^{18}O$ and $\delta^{2}H$ values of precipitation and the weighted average annual $\delta^{18}O$ and $\delta^{2}H$ values of precipitation remain fairly constant from year to year. This happens because the annual range and sequence of climatic conditions (temperatures, vapour source, direction of air mass movement, etc.) do not change significantly from year to year. In general, precipitation in the summer is isotopically heavier than precipitation in the winter. This change in average isotopic composition is principally caused by seasonal temperature differences but is also affected by seasonal changes in moisture sources and storm tracks. In the case of snow, various post-depositional processes, such as melting and subsequent infiltration of surface layers and evaporation, may alter the isotopic content of the snow pack, often leading to melt water δ values that become progressively enriched (INGRAHAM, 1998).

Tritium

Tritium is the radioactive isotope of hydrogen, ^{3}H, which is naturally produced in the upper atmospheric strata by the reaction of cosmic radiation (thermal neutrons) with nitrogen atoms:

$$^{14}N + n \rightarrow {}^{15}N \rightarrow {}^{12}C + {}^{3}H \qquad (5)$$

Tritium combines/reacts in the atmosphere with oxygen to form water and may precipitate on earth as rain and thus reach the groundwater. Tritium is usually symbolised as T. Its concentration in water is commonly expressed in Tritium Units (TU): 1 TU corresponds to 1 atom ^{3}H per 10^{18} atoms ^{1}H. Tritium may also be reported in terms of activity concentration in BqL^{-1}, which is related to the commonly used TU as 1 TU = 0.118 BqL^{-1} (INGRAHAM, 1998; GAT et al., 2001).

Tritium decays by β-decay with a half-life of 12.32 years (LUCAS & UNTERWEGER, 2000). The atmospheric concentration of tritium prior to 1953 was about 3–5 TU. Due to nuclear weapon tests the concentrations in precipitation up to 1963 reached several thousand TU (INGRAHAM, 1998). Part of the tritium was flushed out rapidly from the troposphere, but most reached the stratosphere where its residence time is of the order of years. Since the early 1960s, the concentration of tritium in precipitation and meteoric waters has significantly dropped. This reduction in concentration is due in part to radioactive decay; however, a large factor is that the tritium is being lost to the oceans that are naturally tritium-free due to the mass of the oceans and long residence time of water in the oceans (INGRAHAM, 1998; GAT et al., 2001).

The seasonality of the stratosphere-to-troposphere transport results in the marked seasonal cycle of the tritium content in precipitation, opposite in phase between the Northern and Southern Hemisphere (GAT et al., 2001). Maximal concentrations are observed in early summer, and the minimal winter concentrations already approach the pre-bomb levels.

Basic climatic characteristics

The characteristic geographic diversity influences the climate in Slovenia considerably (PUČNIK, 1980). Consequently, there is a mixture of (1) a continental climate that influences the major part of Slovenia, (2) an Alpine climate that influences the NW part of Slovenia, and (3) along the N Adriatic coast the sub-Mediterranean climate prevails. Furthermore, there are four major air masses influencing the weather in Slovenia: (1) maritime polar air masses, which originate in the Northern Atlantic and North Sea; (2) maritime tropical air masses, which originate predominantly in the Azores; (3) continental tropical air masses, originating from northern Africa and Asia Minor; (4) continental polar air masses, which originate in Scandinavia, Finland, Russia, and the Pannonian Plain. Both maritime air masses are generally moist, containing considerable amounts of water vapour, while continental air masses are usually drier. Ljubljana is located in central Slovenia and is consequently under the influence of different climate regimes described above.

History of sampling

Monitoring of isotopes in precipitation started in Ljubljana in 1981 (PEZDIČ, 1999). Samples were collected at meteorological station Ljubljana – Bežigrad at former Hydrometeorological Survey of Slovenia (today Environmental Agency of the Republic of Slovenia; 46°03’N, 14°31’E; 299 m a.s.l.). In 1993 collection of precipitation was moved to the Jožef Stefan Institute (46°03’N, 14°29’E; 292 m a.s.l.). Finally, the station was moved to the Reactor Centre of the Jožef Stefan Institute (46°06’N,

Figure 1. Location map. Stations: 1 – Ljubljana – Bežigrad, 2 – Jožef Stefan Institute, 3 – Reactor Centre of the Jožef Stefan Institute.

14°36'E; 282 m a.s.l.) in the vicinity of Ljubljana in September 2000. Location of sampling stations is presented in Figure 1. Meteorological data (precipitation amount, temperature and vapour pressure) are obtained from Ljubljana – Bežigrad meteorological station (46°03'N, 14°31'E; 299 m a.s.l.). Precipitation amount is recorded also at the Reactor Centre since October 2002. Data have been regularly published until 1994 in IAEA Technical Reports Series (1986-1994), and are now available on internet (http://nds121.iaea.org/wiser/). Some previous analyses of isotopic composition of precipitation in Ljubljana have been published by Krajcar Bronić et al. (1998), Pezdič (1999, 2003), Vreča et al. (2005, 2006, 2007), and Ogrinc et al. (2008).

Isotope analyses

The stable isotopic composition of water samples was measured on a Varian MAT 250 mass spectrometer at the Jožef Stefan Institute till the end of 2003. The oxygen isotopic composition ($\delta^{18}O$) was measured by means of the water-CO_2 equilibration technique (Epstein & Mayeda, 1953). The isotopic composition of hydrogen (δ^2H) was determined by means of the H_2 generated by reduction of water over hot zinc. In the beginning a dynamic method was used and after 1988 a static method was applied (Pezdič, 1999). Latter, in 1998, the reduction of water over hot chromium as proposed by Gehre et al. (1996) was applied. Since 2004 stable isotopic composition of water samples is determined at Joanneum Research. The oxygen isotopic composition is determined on a dual inlet Finnigan DELTA^{plus} by means of the fully automated equilibration technique and the isotopic composition of hydrogen is determined on a continuous flow Finnigan DELTA^{plus} XP mass spectrometer with an HEKAtech high-temperature oven by reduction of water over hot chromium (Morrison et al., 2001). All measurements were carried out against laboratory standards that were periodically calibrated against international standards recommended by the IAEA. Measurement precision was better than ±0.1‰ for $\delta^{18}O$ and ±1‰ for δ^2H.

Tritium activity (A) in monthly samples has been determined at the Rudjer Bošković Institute in Zagreb by the gas proportional counting technique. Methane obtained in the reaction of water with Al_4C_3 at 150°C has been used as the counting gas (Horvatinčić, 1980). Gas quality control has been performed by simultaneous monitoring of the count rate above the tritium channel, i.e., above 20 keV (Krajcar Bronić et al, 1986). Results are expressed in Tritium Units (TU), where 1 TU = 0.118 Bq/L, and the limit of detection is 1.5 TU. Tritium in some samples (second half of 2003) was determined at the Isotope Hydrology Section Laboratory at the IAEA by the liquid scintillation counting technique.

Data reduction

Basic descriptive statistics, i.e. mean, minimum value and maximum value, were calculated to describe variation of the data. Deuterium excess (*d*) was also determined. Furthermore, mean $\delta^{18}O$, δ^2H and *d* values weighted by the amount of precipitation were calculated from the monthly data as follows:

$$X = \frac{\sum_i P_i X_i}{\sum_i P_i} \qquad (6)$$

where X denotes the $\delta^{18}O$, δ^2H or d, P the precipitation amount and i the individual monthly precipitation sample. The summations are over all collected samples per year and per month over the period. The minimum required number of data was eight monthly measured samples per year and more than 70 % of total precipitation collected per year.

The two methods of linear correlation between δ^2H and $\delta^{18}O$ usually applied in stable isotope studies have been calculated: the least squares fit (LSF) and the orthogonal regression, known as the reduced major axis (RMA) line (IAEA, 2002). The lines are defined as local meteoric water lines – LMWL.

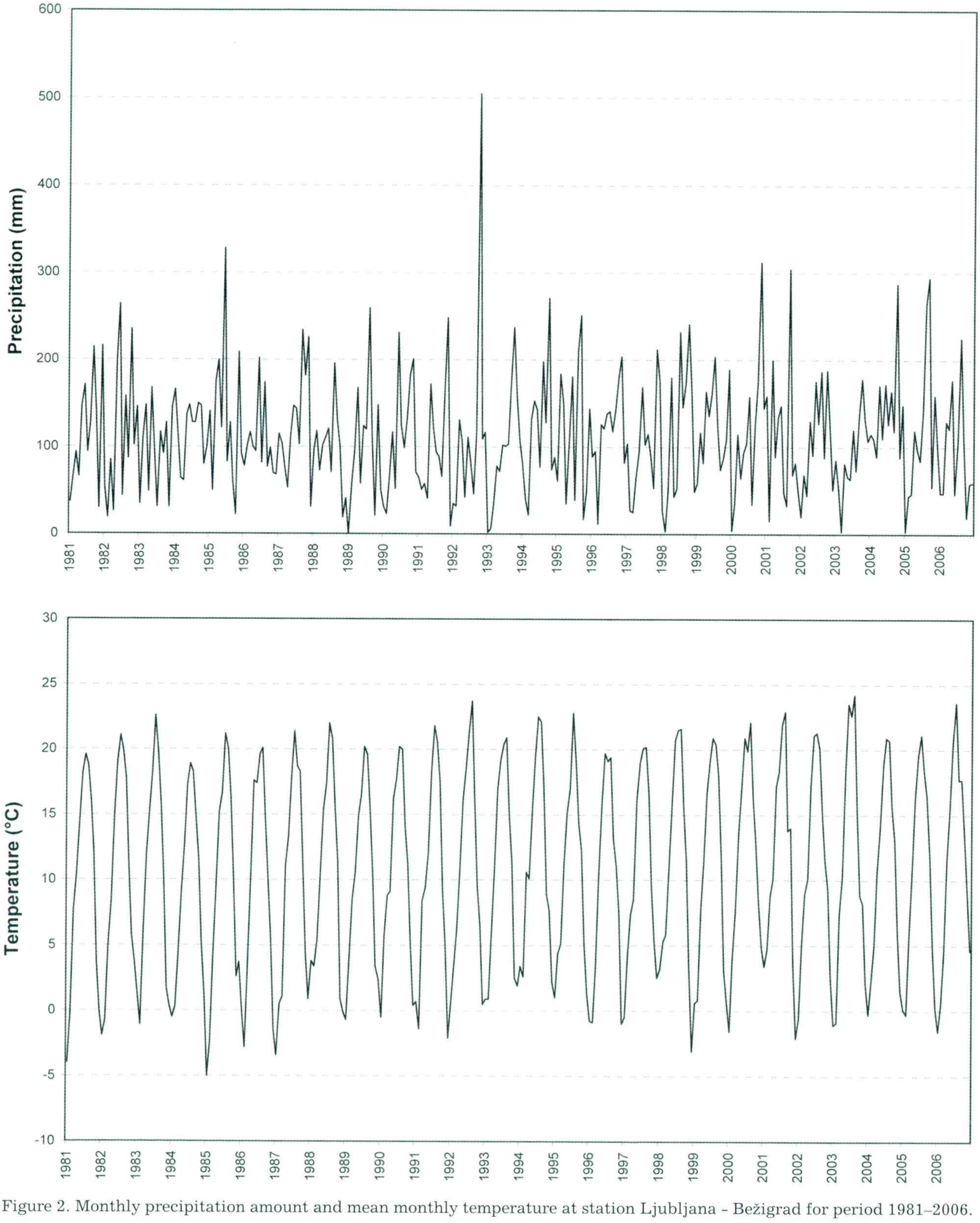

Figure 2. Monthly precipitation amount and mean monthly temperature at station Ljubljana - Bežigrad for period 1981–2006.

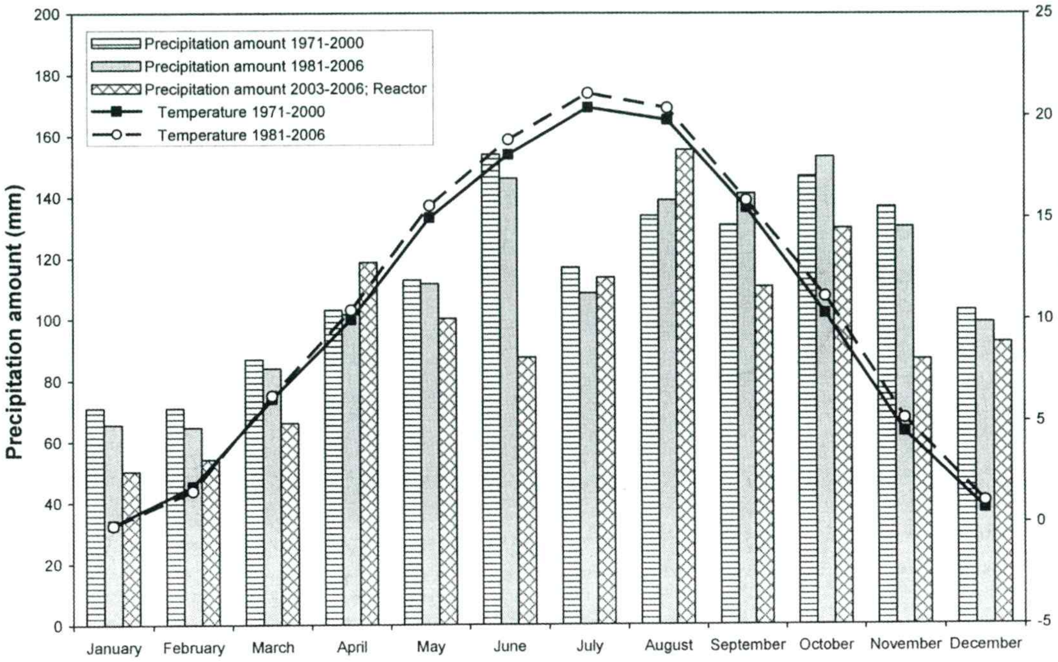

Figure 3. Mean monthly precipitation amount and mean monthly temperature at station Ljubljana - Bežigrad for periods 1971–2000 and 1981–2006. Mean monthly precipitation amount at sampling station Reactor Centre for period 2003–2006 is shown for comparison.

Results and discussion

Precipitation amount and temperature data for Ljubljana - Bežigrad station for the period 1981–2006 are presented graphically in Figure 2. Long-term climatic data show typical continental climate distribution with higher precipitation amounts in summer months with a maximum usually in June and minimum during winter, usually in January. The only month without precipitation in the data set was January 1989. The maximum monthly amount in the data set was recorded in October 1992 (505 mm). The mean precipitation amount for Ljubljana - Bežigrad station in the period 1971–2000 was 1368 mm and during the isotope monitoring period 1981–2006 was 1346 mm. Figure 3 shows mean monthly precipitation amount and temperatures for the period 1981 –2006 compared with the 30-yr-long meteorological period 1971–2000. In addition, mean monthly precipitation amount recorded in the 2003–2006 period at the Reactor Centre is also presented in Figure 3. The observed annual pattern shows generally lower precipitation amount with mean value of 1126 mm at the Reactor Centre then at meteorological station at Ljubljana - Bežigrad.

The long-term temperature maximum is observed in July and the minima in January (Figure 3). During the observation period the maximum monthly temperature was recorded in August 2003 (24.2 °C) and the minimum in January 1985 (–5.0 °C) (Figure 2). The mean temperature for Ljubljana - Bežigrad station in the period 1971–2000 was 10.2 °C and during the isotope monitoring period 1981–2006 the mean temperature was 10.6 °C.

All results of monthly isotopic composition of precipitation obtained from May 1981 to December 2006 are summarized in Table 1 and shown in Figures 4 and 5. Distinctive seasonal variations of δ^{18}O and δ^{2}H characteristic for continental stations are observed (Rozanski et al., 1993). The minimum δ^{18}O value was observed in January 1992 (–19.4 ‰) and the maximum in June 2000 (–2.1 ‰). Variations in δ^{2}H follow the δ^{18}O variations. The minimum δ^{2}H value was also observed in January 1992 (–148 ‰) while the maximum was recorded in May 1990 (–18 ‰). The mean calculated δ^{18}O and δ^{2}H values for observed period are –8.7 ‰ and –60 ‰ (n = 290). Furthermore, deuterium excess variations are presented in Figure 4. The lowest *d* value for individual month was observed in December 1997 (–20 ‰) and the highest in November 2003 (19 ‰). The mean *d* value is 9.4 ‰ but most data vary between 5 and 15 ‰. The lower *d* values probably indicate secondary evaporation processes (e.g. evaporation of falling raindrops in dry atmosphere) (Araguas-Araguas et al., 2000; Peng et al., 2004). Higher values are characteristic of the autumn rainy period and can be attributed to the influence of Mediterranean cyclogenesis that often prevails in the south-western Slovenia during October–December (Vreča et al., 2007) and also in Ljubljana. Values around 10 ‰ can be attributed to air masses from the Atlantic (Gat & Dansgaard, 1972; Rozanski et al., 1993).

The least squares fit (LSF) regression equation between the isotopic values of individual monthly samples representing LMWL$_{(LSF)}$ for Ljubljana is:

$$\delta^{2}\mathrm{H} = (7.95 \pm 0.08)\delta^{18}\mathrm{O} + (8.90 \pm 0.71); \quad r = 0.99,\ n = 290 \tag{7}$$

The orthogonal (RMA) regression equation between the isotopic values of individual monthly samples representing LMWL$_{(RMA)}$ for Ljubljana is:

$$\delta^{2}\mathrm{H} = (8.06 \pm 0.08)\delta^{18}\mathrm{O} + (9.84 \pm 0.71); \quad r = 0.99,\ n = 290 \tag{8}$$

The LMWLs obtained are close to the Global Meteoric Water Line (Gourcy et al., 2005).

Annual weighted mean δ^{18}O, δ^{2}H and *d* excess values are summarized in Table 2. For comparison, annual means weighted by precipitation

Table 1. Isotopic composition of precipitation in Ljubljana.

Month/ Year	δ²H (‰)	δ¹⁸O (‰)	*d* (‰)	A (TU)
05/81	-54.7	-8.15	10.5	70.0
06/81	-64.0	-9.39	11.1	83.0
07/81	-47.5	-7.19	10.0	54.0
08/81	-30.0	-5.30	12.4	55.0
09/81	-46.3	-7.33	12.3	26.0
10/81	-54.0	-7.66	7.3	18.0
11/81	-86.7	-11.59	6.0	16.0
12/81	-49.7	-7.20	7.9	15.0
01/82	-63.4	-8.83	7.2	14.4
02/82	-105.0	-14.44	10.5	18.7
03/82	-70.3	-9.70	7.3	19.0
04/82	-55.2	-8.33	11.4	32.0
05/82	-54.5	-7.62	6.5	25.0
06/82	-47.0	-6.53	5.2	31.0
07/82	-34.7	-5.11	6.2	51.0
08/82	-49.1	-7.21	8.6	32.0
09/82	-31.0	-5.47	12.8	24.0
10/82	-57.1	-8.43	10.3	20.0
11/82	-101.9	-13.22	3.9	14.0
12/82	-113.2	-14.33	1.4	17.0
01/83	-68.8	-9.68	8.6	27.6
02/83	-104.2	-14.06	8.3	16.2
03/83	-87.6	-11.63	5.4	23.5
04/83	-42.7	-6.47	9.1	20.2
05/83	-60.3	-8.45	7.3	22.9
06/83	-49.8	-7.51	10.3	36.4
07/83	-22.5	-4.17	10.9	61.6
08/83	-34.0	-5.35	8.8	32.9
09/83	-52.7	-7.69	8.8	20.8
10/83	-70.1	-9.81	8.4	20.2
11/83	-40.2	-6.19	9.3	11.7
12/83	-71.7	-10.00	8.3	30.7
01/84	-96.0	-13.11	8.9	21.7
02/84	-104.0	-14.12	9.0	30.9
03/84	-85.0	-11.83	9.6	18.7
04/84	-74.0	-10.67	11.4	30.3
05/84	-52.0	-7.27	6.2	30.7
06/84	-68.0	-9.94	11.5	29.4
07/84	-37.0	-5.73	8.8	41.3
08/84	-40.0	-6.34	10.7	31.9
09/84	-39.0	-6.21	10.7	27.8
10/84	-44.0	-7.06	12.5	39.7
11/84	-66.0	-9.35	8.8	19.0
12/84	-41.0	-6.39	10.1	19.0
01/85	-110.0	-13.78	0.2	-
02/85	-94.0	-12.78	8.2	-
03/85	-104.0	-14.12	9.0	-
04/85	-63.0	-9.03	9.2	-
05/85	-62.0	-8.76	8.1	-
06/85	-54.0	-7.71	7.7	-
07/85	-35.0	-6.09	13.7	-
08/85	-40.0	-6.63	13.0	-
09/85	-33.0	-4.95	6.6	-
10/85	-49.0	-7.63	12.0	-
11/85	-70.0	-10.29	12.3	-
12/85	-76.0	-10.33	6.6	-
01/86	-91.0	-12.17	6.4	-
02/86	-141.0	-18.42	6.4	-
03/86	-84.0	-11.12	5.0	-
04/86	-64.0	-9.57	12.6	-
05/86	-46.0	-7.06	10.5	36.0
06/86	-66.0	-9.85	12.8	38.7
07/86	-29.0	-5.23	12.8	25.7
08/86	-38.0	-5.83	8.6	17.3
09/86	-44.0	-6.21	5.7	17.7
10/86	-82.0	-11.32	8.6	14.1
11/86	-94.0	-12.12	3.0	8.8
12/86	-101.0	-14.03	11.2	20.6
01/87	-99.0	-13.46	8.7	25.4
02/87	-95.0	-12.74	6.9	22.8
03/87	-72.0	-10.10	8.8	23.1
04/87	-53.0	-7.59	7.7	30.7
05/87	-41.0	-6.27	9.2	36.0
06/87	-52.0	-7.98	11.8	19.3
07/87	-45.0	-7.27	13.2	36.3
08/87	-53.0	-7.99	10.9	25.0
09/87	-46.0	-7.14	11.1	16.5
10/87	-46.0	-7.08	10.6	11.6
11/87	-76.0	-10.88	11.0	12.0
12/87	-91.0	-12.35	7.8	18.3
01/88	-68.0	-9.43	7.4	10.4
02/88	-75.0	-10.84	11.7	10.4
03/88	-70.0	-9.83	8.6	13.5
04/88	-45.0	-7.23	12.8	14.6
05/88	-45.0	-6.79	9.3	24.0
06/88	-45.0	-7.09	11.7	19.8
07/88	-28.0	-5.52	16.2	24.1
08/88	-32.0	-6.19	17.5	18.7
09/88	-45.0	-7.30	13.4	19.8
10/88	-43.0	-7.07	13.6	17.2
11/88	-82.0	-11.74	11.9	22.4
12/88	-90.0	-12.20	7.6	23.8
01/89	-	-	-	-
02/89	-73.0	-10.34	9.7	19.4
03/89	-65.0	-8.98	6.8	16.5
04/89	-62.0	-8.58	6.6	15.5
05/89	-35.0	-5.65	10.2	17.6
06/89	-41.0	-5.72	4.8	25.8
07/89	-48.0	-7.57	12.6	23.6
08/89	-55.0	-8.33	11.6	23.6
09/89	-63.0	-8.89	8.1	-
10/89	-68.0	-9.72	9.8	-
11/89	-64.0	-9.65	13.2	8.3
12/89	-43.0	-6.02	5.2	12.4
01/90	-30.0	-5.32	12.6	11.5
02/90	-98.0	-13.14	7.1	13.7
03/90	-71.0	-9.86	7.9	21.8
04/90	-42.0	-6.53	10.2	16.3
05/90	-18.0	-2.50	2.0	16.4
06/90	-36.0	-5.87	11.0	11.5
07/90	-52.0	-7.32	6.6	25.4
08/90	-48.0	-7.29	10.3	24.8
09/90	-45.0	-7.13	12.0	25.6
10/90	-56.0	-8.45	11.6	10.5
11/90	-79.0	-11.88	16.0	12.8
12/90	-89.0	-12.64	12.1	7.9
01/91	-85.0	-11.60	7.8	7.7
02/91	-106.0	-14.40	9.2	8.4
03/91	-65.0	-9.10	7.8	11.6
04/91	-66.0	-10.00	14.0	8.6
05/91	-73.0	-9.90	6.2	11.9
06/91	-46.0	-6.50	6.0	15.3
07/91	-37.0	-5.50	7.0	13.9
08/91	-41.0	-6.10	7.8	17.5
09/91	-32.0	-4.90	7.2	7.2
10/91	-47.0	-7.40	12.2	9.9
11/91	-88.0	-11.86	6.9	3.6
12/91	-63.0	-8.76	7.1	8.6
01/92	-147.8	-19.40	7.4	-
02/92	-	-	-	-
03/92	-87.7	-10.70	-2.1	14.1
04/92	-41.9	-7.10	14.9	20.4
05/92	-22.9	-4.80	15.5	-
06/92	-51.2	-7.50	8.8	20.3
07/92	-	-	-	-
08/92	-24.5	-4.40	10.7	31.0
09/92	-54.2	-8.00	9.8	8.7
10/92	-67.1	-9.50	8.9	9.0
11/92	-	-8.10	-	14.4
12/92	-	-	-	22.0
01/93	-	-	-	-
02/93	-	-	-	-
03/93	-84.1	-11.80	10.3	-
04/93	-60.0	-8.50	8.0	-
05/93	-44.0	-6.40	7.2	22.0
06/93	-26.8	-4.60	10.0	24.2
07/93	-37.7	-5.80	8.7	20.7
08/93	-36.6	-5.70	9.0	15.7
09/93	-54.5	-8.10	10.3	21.4
10/93	-50.2	-7.50	9.8	8.7
11/93	-86.2	-11.80	8.2	18.1
12/93	-86.8	-11.80	7.6	14.5
01/94	-70.0	-9.60	6.8	4.4
02/94	-58.1	-8.40	9.1	10.1
03/94	-63.0	-8.70	6.6	8.0
04/94	-79.6	-11.10	9.2	12.2

Table 1. Isotopic composition of precipitation in Ljubljana (continuation).

Month/ Year	δ^2H (‰)	$\delta^{18}O$ (‰)	*d* (‰)	A (TU)
05/94	-52.9	-7.50	7.1	12.8
06/94	-53.3	-7.80	9.1	18.2
07/94	-24.8	-4.20	8.8	28.7
08/94	-38.4	-6.30	12.0	13.0
09/94	-39.8	-6.40	11.4	11.5
10/94	-63.8	-9.30	10.6	14.7
11/94	-83.0	-11.60	9.8	12.2
12/94	-85.1	-11.50	6.9	21.3
01/95	-65.2	-9.70	12.4	10.7
02/95	-72.5	-10.40	10.7	12.5
03/95	-90.3	-12.70	11.3	14.6
04/95	-46.6	-7.80	15.8	23.2
05/95	-56.6	-8.30	9.8	11.9
06/95	-45.5	-6.80	8.9	9.0
07/95	-26.6	-4.30	7.8	19.2
08/95	-52.8	-8.10	12.0	17.4
09/95	-43.1	-7.00	12.9	16.7
10/95	-65.4	-9.20	8.2	23.4
11/95	-73.1	-10.70	12.5	22.2
12/95	-87.0	-12.30	11.4	10.6
01/96	-124.4	-16.70	9.2	-
02/96	-90.0	-12.83	12.6	-
03/96	-89.6	-12.41	9.7	-
04/96	-89.4	-12.46	10.3	-
05/96	-41.3	-6.49	10.6	-
06/96	-	-	-	-
07/96	-32.4	-5.07	8.2	-
08/96	-37.1	-5.95	14.9	-
09/96	-77.7	-10.70	7.9	-
10/96	-52.9	-8.30	13.5	-
11/96	-77.8	-11.62	15.2	-
12/96	-72.7	-10.86	14.2	-
01/97	-79.7	-10.79	6.6	-
02/97	-34.0	-4.75	4.0	-
03/97	-57.3	-8.03	6.9	-
04/97	-79.5	-11.00	8.5	-
05/97	-55.0	-7.62	6.0	-
06/97	-44.1	-6.18	5.3	14.7
07/97	-43.7	-6.37	7.3	26.4
08/97	-57.1	-7.90	6.1	29.2
09/97	-	-	-	
10/97	-46.4	-7.29	11.9	
11/97	-71.7	-10.46	12.0	9.2
12/97	-98.4	-9.81	-19.9	6.8
01/98	-61.1	-8.75	8.9	-
02/98	-51.5	-7.60	9.3	19.4
03/98	-49.2	-7.60	11.6	-
04/98	-53.9	-7.95	9.7	8.5
05/98	-44.1	-5.97	3.7	16.8
06/98	-40.9	-6.52	11.3	5.7
07/98	-40.9	-6.53	11.3	-
08/98	-49.7	-7.46	10.0	11.4
09/98	-47.5	-7.28	10.7	5.9
10/98	-	-	-	-
11/98	-	-	-	-
12/98	-53.3	-8.07	11.3	5.8
01/99	-	-	-	-
02/99	-	-	-	8.7
03/99	-60.7	-8.82	9.9	8.9
04/99	-56.0	-8.25	10.0	8.3
05/99	-36.4	-5.41	6.9	8.9
06/99	-36.9	-5.40	6.3	15.0
07/99	-55.1	-7.78	7.1	12.6
08/99	-	-	-	28.9
09/99	-31.1	-4.35	3.7	4.9
10/99	-43.5	-6.80	10.9	4.8
11/99	-92.9	-13.34	13.8	6.5
12/99	-78.1	-10.81	8.4	4.2
01/00	-	-	-	-
02/00	-100.4	-12.84	2.3	-
03/00	-65.6	-8.75	4.5	11.2
04/00	-	-	-	-
05/00	-33.0	-4.72	4.8	-
06/00	-26.4	-2.12	-9.4	15.3
07/00	-59.5	-7.12	-2.5	-
08/00	-37.9	-5.48	6.0	5.8
09/00	-48.3	-6.86	6.5	-
10/00	-63.1	-9.21	10.6	12.3
11/00	-45.4	-7.10	11.5	5.7
12/00	-90.3	-12.34	8.4	1.4
01/01	-51.0	-7.51	9.0	3.9
02/01	-47.7	-6.80	6.6	8.8
03/01	-51.5	-7.63	9.6	7.9
04/01	-56.2	-8.24	9.7	8.4
05/01	-26.6	-4.24	7.3	16.6
06/01	-51.0	-6.93	4.5	14.1
07/01	-37.5	-5.35	5.3	8.5
08/01	-40.8	-5.77	5.3	9.6
09/01	-62.4	-9.22	11.4	9.4
10/01	-40.5	-6.46	11.2	8.8
11/01	-60.9	-9.39	14.3	10.1
12/01	-89.3	-13.04	15.1	10.1
01/02	-86.1	-11.80	8.3	4.1
02/02	-53.4	-7.76	8.6	4.1
03/02	-35.3	-5.37	7.7	3.8
04/02	-61.5	-8.86	9.4	9.1
05/02	-38.2	-5.98	9.6	6.4
06/02	-28.6	-4.66	8.7	3.7
07/02	-36.2	-5.65	9.0	11.4
08/02	-54.0	-7.91	9.3	6.8
09/02	-73.9	-10.60	10.8	6.8
10/02	-58.9	-8.86	11.9	4.1
11/02	-54.3	-8.15	11.0	0.6
12/02	-95.1	-12.75	6.9	5.7
01/03	-120.1	-15.71	5.6	4.3
02/03	-127.3	-16.33	3.3	12.8
03/03	-70.7	-8.93	0.8	-
04/03	-76.1	-10.72	9.7	9.1
05/03	-42.8	-6.23	7.0	9.3
06/03	-22.3	-3.61	6.6	13.6
07/03	-31.2	-5.05	9.3	11.0
08/03	-23.1	-3.96	8.6	11.9
09/03	-62.5	-9.25	11.5	9.2
10/03	-61.3	-9.74	16.6	7.6
11/03	-49.5	-8.61	19.4	5.5
12/03	-62.0	-9.93	17.5	5.7
01/04	-100.0	-14.00	12.0	6.1
02/04	-91.2	-13.30	15.2	14.8
03/04	-92.8	-12.86	10.1	7.2
04/04	-69.0	-10.06	11.5	14.2
05/04	-62.7	-9.16	10.6	14.6
06/04	-50.9	-7.79	11.4	17.0
07/04	-32.0	-5.42	11.4	12.5
08/04	-27.1	-4.91	12.2	17.0
09/04	-56.0	-8.51	12.1	4.4
10/04	-44.6	-6.89	10.6	6.5
11/04	-78.4	-11.69	15.1	6.5
12/04	-78.3	-11.48	13.6	7.1
01/05	-94.3	-13.33	12.4	-
02/05	-132.5	-18.34	14.2	8.9
03/05	-61.6	-9.16	11.7	13.4
04/05	-58.2	-8.38	8.8	9.1
05/05	-46.9	-6.86	8.0	12.7
06/05	-32.2	-4.94	7.3	12.4
07/05	-45.7	-7.09	11.0	13.7
08/05	-52.0	-7.82	10.5	12.7
09/05	-62.4	-8.70	7.2	12.8
10/05	-59.7	-8.73	10.2	10.8
11/05	-93.4	-14.07	19.1	9.1
12/05	-76.6	-11.32	14.0	9.7
01/06	-	-	-	-
02/06	-28.9	-5.05	11.5	6.8
03/06	-105.3	-14.13	7.7	7.3
04/06	-52.1	-7.61	8.8	8.0
05/06	-65.1	-9.51	11.0	11.8
06/06	-35.3	-5.21	6.4	11.5
07/06	-	-	-	-
08/06	-57.6	-8.75	12.4	11.2
09/06	-24.1	-4.96	15.6	6.6
10/06	-34.6	-6.24	15.3	5.4
11/06	-68.7	-10.00	11.3	7.5
12/06	-67.7	-10.51	16.4	6.9

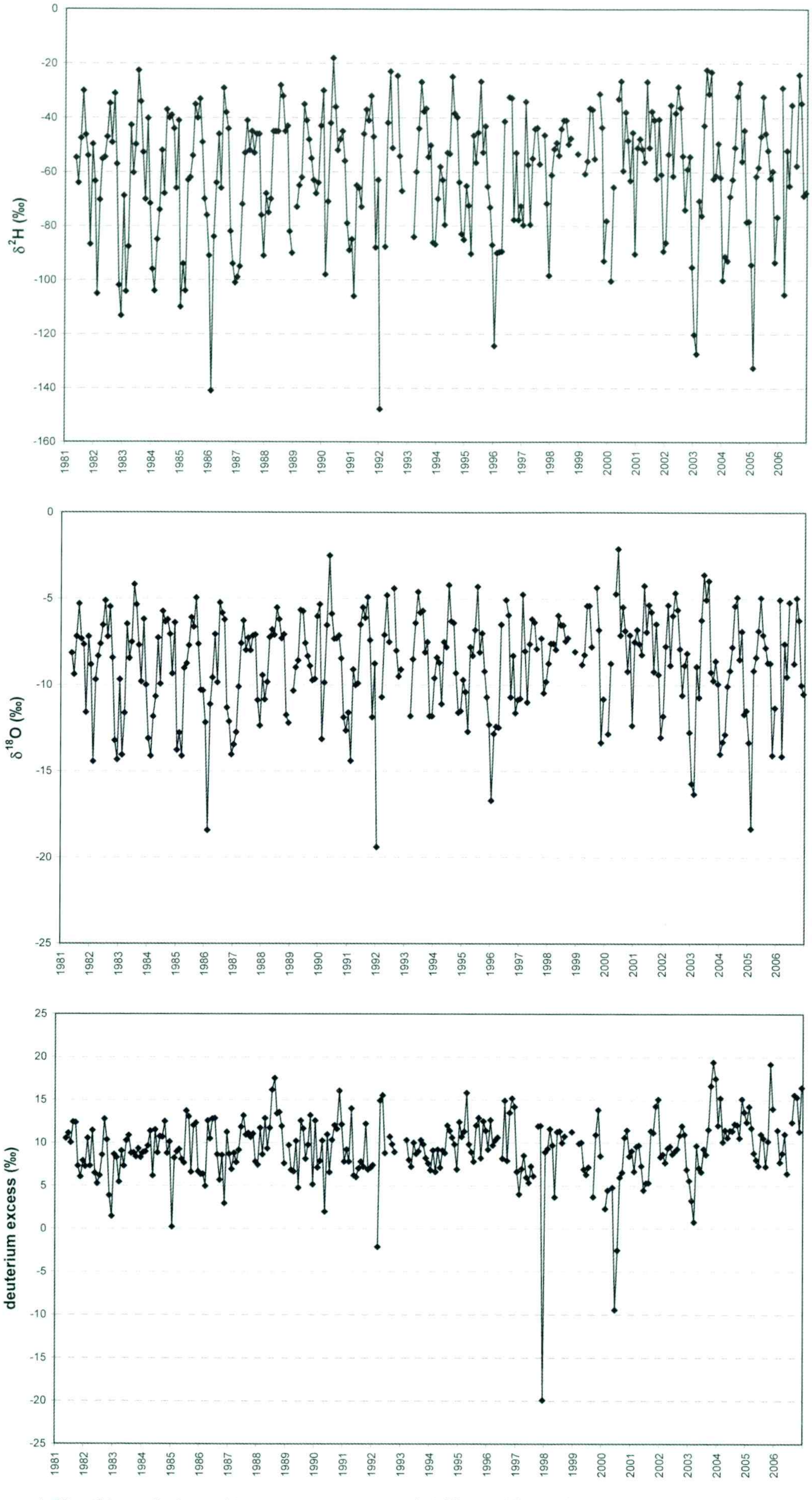

Figure 4. Monthly variations of isotopic composition of a) δ^2H, b) δ^{18}O and c) deuterium excess, 1981-2006.

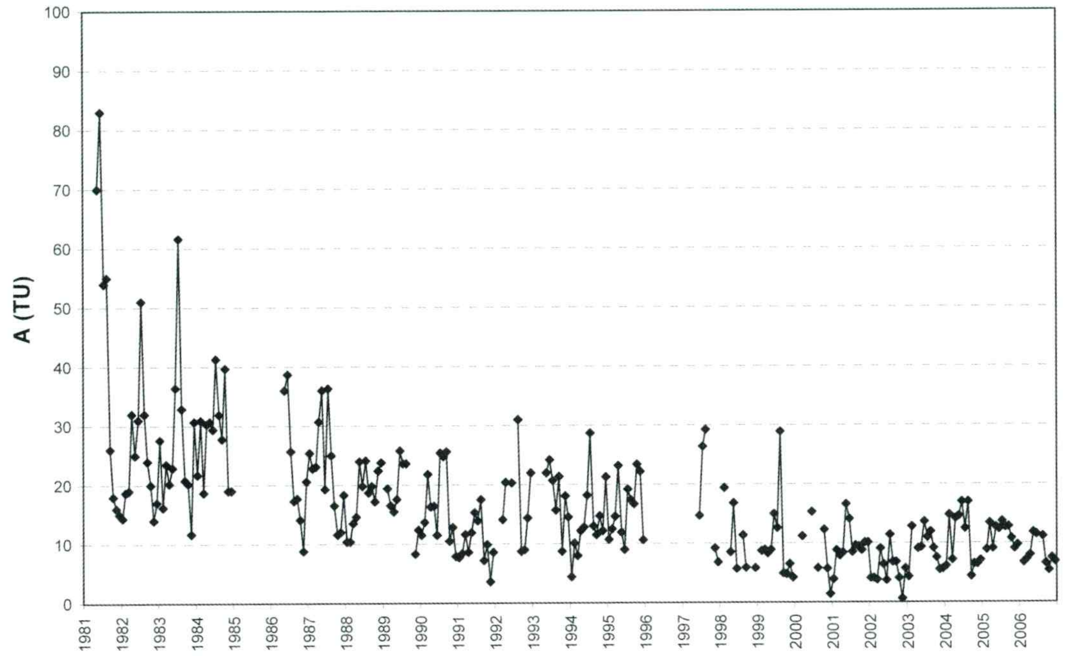

Figure 5. Monthly variations of tritium activity A (in TU), 1981–2006.

amount recorded in the 2003–2006 period at the Reactor Centre are also presented. The difference between weighted annual means of δ^2H and δ^{18}O at Ljubljana - Bežigrad and Reactor Centre are in the range of analytical error. The minimum annual weighted mean δ^{18}O and δ^2H values were observed in 1986 and the maximum in 1998. The lowest annual weighted mean *d* excess value was observed 1997 and is due to extremely low *d* value recorded for December. The highest annual weighted mean *d* excess value was observed in 1988. Annual weighted mean δ^{18}O, δ^2H and *d* values for the whole period 1981–2006 are –8.6 ‰, –59 ‰ and 9.5 ‰, respectively.

Monthly weighted mean δ^{18}O, δ^2H and *d* values are summarized in Table 3 and presented in Figure 6. The long-term monthly means show a distinctive seasonal variation with highest δ^{18}O and δ^2H values in July, when the highest mean temperature is recorded. The lowest values are observed in February when snow is the prevailing type of precipitation. The *d* value varies around 9.3 ‰ with the lowest values in December and the highest in November. The observed pattern (Figure 6) shows generally higher *d* values in autumn precipitation with means above 10 ‰ and can be attributed to the influence of Mediterranean air masses over the region during this period. Previous investigations showed that Mediterranean air masses probably contribute up to 26% of precipitation in Ljubljana (Vreča et al., 2006).

The correlation between δ^{18}O in collected monthly samples and mean monthly temperature at Ljubljana - Bežigrad ($T_{\text{Bežigrad}}$) is:

$$\delta^{18}\text{O} = 0.29\ T_{\text{Bežigrad}} - 11.86\ (n = 290,\ r = 0.75) \quad (9)$$

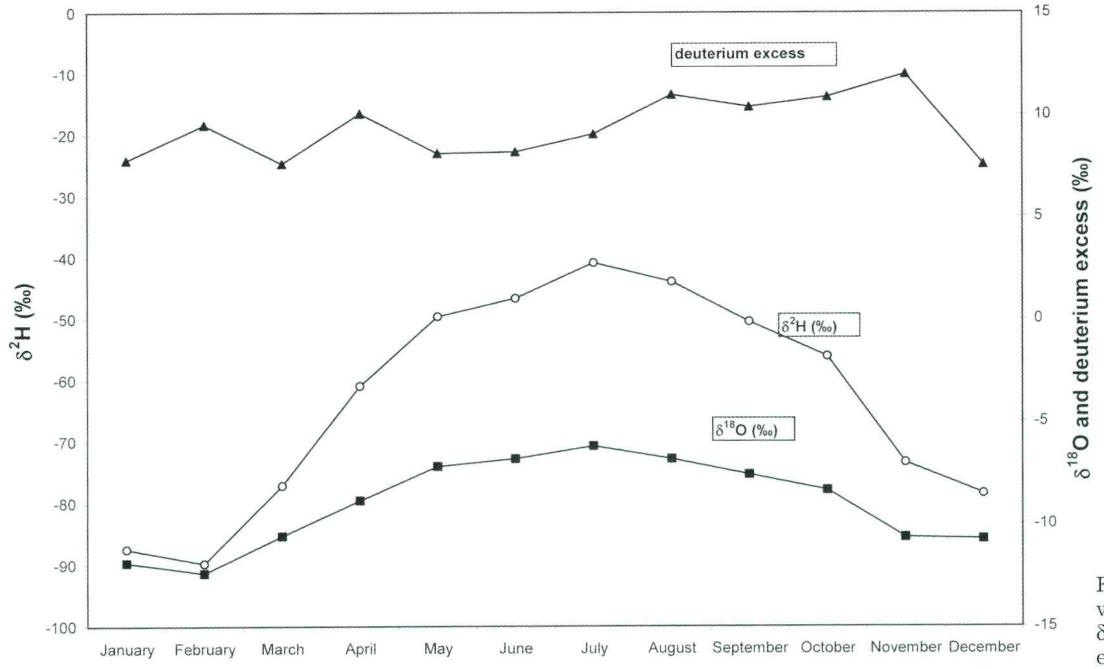

Figure 6. Monthly weighted mean δ^2H, δ^{18}O and deuterium excess values.

Table 2. Annual weighted mean δ^2H, $\delta^{18}O$ and deuterium excess (d) values (in ‰). Re denotes annual mean weighted by precipitation amount at Reactor Centre.

Year	n	δ^2H	$\delta^{18}O$	d	δ^2H_{Re}	$\delta^{18}O_{Re}$	d_{Re}
1981	8	-50.9	-7.63	10.1			
1982	12	-62.3	-8.66	7.0			
1983	12	-64.4	-9.07	8.2			
1984	12	-60.7	-8.82	9.8			
1985	12	-67.7	-9.55	8.7			
1986	12	-70.7	-9.96	9.0			
1987	12	-60.8	-8.90	10.4			
1988	12	-50.2	-7.84	12.5			
1989	11	-56.1	-8.18	9.4			
1990	12	-53.8	-8.10	10.9			
1991	12	-63.5	-8.94	8.0			
1992	8	-63.2	-8.97	8.5			
1993	10	-56.0	-8.13	9.0			
1994	12	-57.7	-8.40	9.5			
1995	12	-60.9	-9.02	11.3			
1996	11	-67.0	-9.85	11.8			
1997	11	-65.2	-8.59	3.6			
1998	10	-47.7	-7.25	10.3			
1999	9	-55.7	-8.02	8.4			
2000	10	-55.4	-7.64	5.7			
2001	12	-52.3	-7.71	9.4			
2002	12	-52.0	-7.70	9.6			
2003	12	-59.6	-8.93	11.9	-59.7	-8.99	12.2
2004	12	-61.0	-9.12	11.9	-60.0	-8.97	11.8
2005	12	-62.1	-9.11	10.7	-61.2	-8.99	10.7
2006	10	-59.2	-8.82	11.3	-61.2	-9.01	10.9
	min	-70.7	-9.96	3.6			
	mean	-59.1	-8.57	9.5			
	max	-47.7	-7.25	12.5			

Table 3. Monthly weighted mean δ^2H, $\delta^{18}O$ and deuterium excess (d) values (in ‰).

Month	n	δ^2H	$\delta^{18}O$	d
January	20	-87.4	-11.90	7.8
February	22	-89.8	-12.41	9.5
March	25	-77.2	-10.60	7.6
April	24	-60.9	-8.88	10.1
May	26	-49.6	-7.22	8.1
June	25	-46.6	-6.85	8.2
July	24	-40.8	-6.23	9.1
August	25	-44.0	-6.87	11.0
September	25	-50.5	-7.61	10.4
October	25	-56.2	-8.38	10.9
November	24	-73.4	-10.67	12.0
December	25	-78.5	-10.75	7.6
	min	-89.8	-12.41	7.6
	mean	-62.9	-9.03	9.3
	max	-40.8	-6.23	12.0

Tritum activity in monthly precipitation (Figure 5) shows seasonal variation typical for the continental station of the Northern Hemishepere. Maximum activity is observed usually in early summer, mostly in June or July, and minima in winter, mostly in January. The seasonal variations are superposed to the general decreasing trend of the mean annual tritium activities. The mean annual tritium activities decrease between 1981 and 1995 with a half-life of about 6 years (which is in accordance with the half-life of tritium in the stratosphere, as explained in the Introduction), and varies slightly around 9.3 TU after 1998.

Conclusions

The results of isotopic composition of oxygen and hydrogen ($\delta^{18}O$, δ^2H and ^3H) are presented and evaluated for monthly precipitation collected in the 25-yeas period at Ljubljana. The presented results are important for further scientific and practical applications in hydrology and hydrogeology, and climatology. Observed seasonal fluctuations are significant and typical for continental stations. The Local Meteoric Water Line is close to Global Meteoric Water Line and the deuterium excess shows the predominant influence of Atlantic air masses in Ljubljana. However, higher d values are observed in autumn and indicate the influence of Mediterranean air masses. Observed tritium activity distribution is typical for the Northern Hemisphere.

Acknowledgement

The work of J. Pezdič who initiated monitoring of isotopic composition of precipitation in Ljubljana and of all colleagues who helped during last 27 years with sampling and analyses is greatly acknowledged. Special thanks are due to S. Žigon, Z. Trkov, S. Lindbichler, B. Obelić, N. Horvatinčić, J. Barešić and A. Rajtarić for their valuable help. The project was financially supported predominantly by the Ministry of Higher Education, Science and Technology and Slovenian Research Agency (P0–0531–0106, P1–0143, BI–HR/01–03–11) during the last eight years. We are grateful also to L. Gourcy and staff of the Isotope Hydrology Section Laboratory of IAEA for performing some tritium activity measurements and for all valuable information provided during the IAEA CRP F31002 (RC 11267).

References

Araguas-Araguas, L., Fröhlich, K. & Rozanski, K. 2000: Deuterium and oxygen-18 isotope composition of precipitation and atmospheric moisture. Hydrological Processes 14: 1341–1355.

Clark, I. & Fritz, P. 1997: Environmental isotopes in hydrology, CRC Press, 328p.

Craig, H. 1961: Isotope variations in meteoric waters. Science 133: 1702–1703.

Craig, H. & Gordon, L. 1965: Deuterium and oxygen-18 in the ocean and the marine atmosphere. In Stable Isotopes in Oceanographic Studies and Paleotemperatures. Tongiorgi E. (Ed.), Spoleto, 9–130.

Dansgaard, W. 1964: Stable isotopes in precipitation. Tellus 16: 436–468.

Epstein, S. & Mayeda, T.K. 1953: Variations of ^{18}O content of waters from natural sources. Geochimica et Cosmochimica Acta 4: 213–224.

Gat, J.R. & Dansgaard, W. 1972: Stable isotope survey of the freshwater occurrences in Israel and the Jordan Rift Valley. Journal of Hydrology 16: 177–211.

Gat J.R. 1996: Oxygen and hydrogen isotopes in the hydrologic cycle. Annual Review of Earth and Planetary Sciences 24: 225–262.

Gat, J.R., Mook, W.G. & Meijer, H.A.J. 2001: Atmospheric water. In: Environmental Isotopes in the Hydrological cycle, Vol. II. Edited by W.G. Mook, IAEA and UNESCO, Technical documents in Hydrology, No. 39, Vol. II, UNESCO Paris, p. 63–74.

Gehre, M., Hoefling, R., Kowski, P., Strauch, G. 1996: Sample preparation device for quantitative hydrogen isotope analysis using chromium metal. Analytical Chemistry 68: 4414–4417.

Gourcy, L.L., Groening, P.K. & Aggarwal, P.K. 2005: Stable oxygen and hydrogen isotopes in precipitation. In: Aggarwal, P.K., Gat, J.R., Froehlich, K. (Eds.) Isotopes in the water cycle: past, present and future of a developing science. Dordrecht: Springer, 39–51.

Iaea 1986, 1990, 1994: Environmental Isotope Data Nos. 1–10: World Survey of Isotope Concentration in Precipitation, Technical Reports Series Nos. 264, 311, 371.

Iaea 2002: Statistical treatment of data on environmental isotopes in precipitations. IAEA, Vienna.

Iaea/Wmo 2008: Global Network of Isotopes in Precipitation. The GNIP Database, Accessible at: http://nds121.iaea.org/wiser/

Horvatinčić, N. 1980: Radiocarbon and tritium measurements in water samples and application of isotopic analyses in hydrology. Fizika 12 (S2), pp. 201–218.

Ingraham, N.L. 1998: Isotopic variations in precipitation. In Isotope tracers in catchment hydrology. Kendall C., McDonnell J.J. (Eds.), Elsevier, 87–118.

Krajcar Bronić, I., Obelić, B., Srdoč, D. 1986: The simultaneous measurement of tritium activity and the background count rate in a proportional counter by the Povinec method: Three years experience at the Ruđer Bošković Institute. Nuclear Instruments and Methods in Physics Research B17, 498–500.

Krajcar Bronić, I., Horvatinčić, N., Obelić, B. 1998: Two decades of environmental isotope records in Croatia: Reconstruction of the past and prediction of the future levels, Radiocarbon 40: 399–416.

Lucas, L.L. & Unterweger, M.P. 2000: Comprehensive review and critical evaluation of the half-life of tritium. J. Res. Natl. Stand. Technol. 105: 541–549.

Morrison, J., Brockwell, T., Merren, T., Fourel, F. & Phillips A.M. 2001: On-line high-precision stable hydrogen isotopic analyses on nanoliter water samples. Analytical Chemistry 73: 3570–3575.

Ogrinc, N., Kanduč, T., Stichler, W. & Vreča, P. 2008: Spatial and seasonal variations in δ^{18}O and δD values in the river Sava in Slovenia. Journal of Hydrology 359: 303–312.

Peng, H., Mayer, B., Harris, S. & Krouse, H. R. 2004: A 10-yr record of stable isotope ratios of hydrogen and oxygen in precipitation at Calgary, Alberta, Canada. Tellus 56B: 147–159.

Pezdič, J. 1999: Izotopi in geokemijski procesi. Naravoslovnotehniška fakulteta, Oddelek za geologijo, 269 pp.

Pezdič, J. 2003: Isotope fractionation of long term precipitation averages in Ljubljana (Slovenia). RMZ – Materials and Geoenvironment (Ljubljana) 50: 641–650.

Pučnik, R. 1980: Velika knjiga o vremenu. Cankarjeva založba, Ljubljana, 368 pp.

Rozanski, K., Araguas-Araguas, L. & Gonfiantini, R. 1993: Isotopic patterns in modern global precipitation. Geophys. Monogr. 78: 1–36.

Schotterer, U., Oldfield, U. & Froehlich, K. 1996: GNIP – Global Network for Isotopes in Precipitation, IAEA, 48p.

Vreča, P., Kanduč, T., Žigon, S. & Trkov, Z. 2005: Isotopic composition of precipitation in Slovenia. In *Isotopic composition of precipitation in the Mediterranean basin in relation to air circulation patterns and climate*, L. Gourcy (Ed.), pp. 157–172, IAEA-TECDOC-1453, IAEA, Vienna.

Vreča, P., Krajcar Bronić, I., Horvatinčić, N. & Barešić, J. 2006: Isotopic characteristics of precipitation in Slovenia and Croatia: Comparison of continental and maritime stations. Journal of Hydrology 330: 457–469.

Vreča, P., Brenčič, M. & Leis, A. 2007: Comparison of monthly and daily isotopic composition of precipitation in the coastal area of Slovenia. Isotopes in Environmental and Health Studies 43: 307–321.