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Isotopic composition of precipitation at the station Ljubljana (Reaktor), Slovenia – period 2007–2010

Izotopska sestava padavin na postaji Ljubljana (Reaktor), Slovenija – obdobje 2007–2010

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Abstract

The stable isotopic composition of hydrogen and oxygen (δ^2H and δ^{18}O) and the tritium activity (A) were monitored in monthly collected precipitation at Ljubljana (Reaktor) during the period 2007–2010. Monthly and yearly isotope variations are discussed and compared with those observed over the period 1981–2006 and with the basic meteorological parameters for Ljubljana (Bežigrad) and Ljubljana (Hrastje) stations for the period 2007–2010. The mean values for δ^2H and δ^{18}O, weighted by precipitation amount at Ljubljana (Reaktor), are –59.4 ‰ and –8.71 ‰. The reduced major axis local meteoric water line ($LMWL_{RMA}$) is $\delta^2H = (8.19 \pm 0.22) \times \delta^{18}O + (11.52 \pm 1.97)$, while the precipitation weighted least square regression results in $LMWL_{PWLSR\text{-}Re}$ $\delta^2H = (7.94 \pm 0.21) \times \delta^{18}O + (9.76 \pm 1.93)$. The lack of significant difference in the LMWL slopes indicates a relatively homogeneous distribution of monthly precipitation as well as the small number of low-amount monthly precipitation events with low deuterium excess. The deuterium excess weighted mean value is 10.3 ‰ which indicates the prevailing influence of the Atlantic air masses. The temperature coefficient of δ^{18}O is 0.30 ‰/°C. Tritium activity in monthly precipitation shows typical seasonal variations, with a weighted mean tritium activity in this period of 8.5 TU. No decrease of mean annual activity is observed.

Izvleček

V prispevku obravnavamo rezultate meritev izotopske sestave vodika in kisika (δ^2H in δ^{18}O) ter aktivnosti tricija (A) v mesečnih vzorcih padavin, ki smo jo spremljali na postaji Ljubljana (Reaktor) v obdobju 2007–2010. Analizirali smo mesečne in letne spremembe izotopske sestave padavin ter jih primerjali z nizom podatkov za obdobje 1981–2006 ter z osnovnimi meteorološkimi parametri iz postaj Ljubljana (Bežigrad) in Ljubljana (Hrastje) za obdobje 2007–2010. Srednje tehtane vrednosti δ^2H in δ^{18}O določene ob upoštevanju izmerjene količine padavin na postaji Ljubljana (Reaktor) znašajo –59,4 ‰ in –8,71 ‰. Lokalno padavinsko premico ($LMWL_{RMA}$) lahko zapišemo kot $\delta^2H = (8{,}19 \pm 0{,}22) \times \delta^{18}O + (11{,}52 \pm 1{,}97)$, ob upoštevanju količine padavin pa kot $LMWL_{PWLSR\text{-}Re}$: $\delta^2H = (7{,}94 \pm 0{,}21) \times \delta^{18}O + (9{,}76 \pm 1{,}93)$. Nakloni izračunanih premic so si med seboj podobni, kar nakazuje, da je porazdelitev padavin relativno homogena in da je število mesečnih vrednosti z nizkim devterijevim presežkom majhno. Srednja tehtana vrednost devterijevega presežka znaša 10,3 ‰ in nakazuje prevladujoči vpliv zračnih mas iz Atlantika. Temperaturni koeficient za δ^{18}O pa znaša 0,30 ‰/°C. Tudi podatki o aktivnosti tricija v mesečnih padavinah kažejo sezonske spremembe. Srednja tehtana vrednost znaša 8,5 TU in ne nakazuje padajočega trenda.

Introduction

The Global Network of Isotopes in Precipitation (GNIP) was initiated in 1958 by the International Atomic Energy Agency (IAEA) and the World Meteorological Organisation (WMO), and became operational in 1961. The objective was to make a systematic collection of data on the isotopic composition, i.e. stable isotopes of hydrogen and oxygen and radioactive hydrogen isotope (tritium), of precipitation across the globe to determine temporal and spatial variations of isotope ratios in precipitation. Initially GNIP was focused on monitoring atmospheric thermonuclear test fallout through levels of radioactive tritium and, after 1970, became an observation network of stable hydrogen and oxygen isotope data for hydrologic investigations of water resources. In addition to isotope data for hydrological studies, during its more than 50 years of operation, GNIP has provided an important database for verifying and improving atmospheric circulation models, studying regional,

global and temporal climates, studying the interactions between water in the atmosphere and biosphere, providing baseline information for the authentication of commodities, tracking migratory species and for forensic purposes (INTERNET 1).

The isotopic composition of precipitation in Ljubljana (Slovenia) has been performed by the Jožef Stefan Institute (JSI) since 1981. To begin with, monitoring was performed in cooperation with the Hydrometeorological Survey of Slovenia (now the Slovenian Environmental Agency, SEA), the Ruđer Bošković Institute (RBI; Zagreb, Croatia) and the IAEA. Since 2004 the JSI has also cooperated with Joanneum Research (JR; Graz, Austria). Details of the history of isotope monitoring since the beginning in 1981 until 2006, together with data evaluation, have been reported in VREČA et al. (2008).

Ljubljana station is an interesting location for monitoring isotopic composition of precipitation and has one of the longest continuous records in the area. The data constitute an important input into isotope investigations and were used in evaluations of GNIP data (e. g. ROZANSKI et al., 1993; ICHIYANAGI, 2007; HUGHES & CRAWFORD, 2012), and in many hydrological and hydrogeological investigations (e. g. KRAJCAR BRONIĆ et al., 1998; PEZDIČ, 1999, 2003; BRENČIČ & VREČA, 2006; VREČA et al., 2006, 2008; OGRINC et al., 2008; VODILA et al., 2011; KANDUČ et al., 2012; HORVATINČIĆ et al., 2011; ZAVADLAV et al., 2012; CERAR & URBANC, 2013; MARKOVIĆ et al., 2013; MEZGA et al., 2014).

The main purpose of this paper is to present results concerning the isotopic composition of precipitation at Ljubljana (Reaktor) for the period 2007–2010 and to compare them with those for the long-term 1981–2006 record (VREČA et al., 2008).

Materials and methods

Sampling

Monthly composite precipitation has been sampled at the Reactor Centre of the JSI (46°06'N, 14°36'E; 282 m a.s.l.) in the vicinity of Ljubljana since September 2000 (VREČA et al., 2008). The GNIP station name is Ljubljana (Reaktor) and the GNIP code 1401502. Sampling station Ljubljana (Reaktor) is maintained by the staff of the Department of Environmental Sciences of JSI and is not part of the national meteorological network. Samples were collected from a precipitation gauge as soon as possible after a precipitation event. The volume of collected precipitation was measured in the laboratory and the sample poured into a 5-litre plastic bottle with a tight fitting cap. We removed impurities (e.g. dust, particles) from the composite monthly sample by filtration (Whatman Grade 589, Black Ribbon) before taking aliquots for different isotope analyses. 50 mL was stored for analysis of stable isotopes of hydrogen and oxygen and 1 L (or less if the sample volume was insufficient) for tritium analysis.

During the sampling period the tube that connects the rain gauge with the sampling bottle was blocked twice due to particles that accumulated at the top of the tube during severe storms being introduced into the gauge. Consequently, the water sample in May 2007 was exposed to evaporation. In September 2010 precipitation collected was very high, due mostly to heavy precipitation between 17/9/2010 and 19/9/2010. In 48 hours from Friday to Sunday on average from 170 to 180 mm of precipitation fell on the territory of Slovenia, reaching a maximum of 500 mm (DOLINAR et al., 2011). During this event the tube was blocked and approximately one third of sample was assumed not collected. According to information from the automatic meteorological station at the Reactor Centre the amount of precipitation was 360 mm (INTERNET 2) but only 233 mm was registered. In April 2007 the amount of collected water (5 mm) was sufficient only for stable isotope analysis.

Stable isotope analysis

The oxygen isotopic composition ($\delta^{18}O$) was measured by means of the water–CO_2 equilibration technique (EPSTEIN & MAYEDA, 1953) on a dual inlet isotope-ratio mass spectrometer Finnigan DELTA^{plus} by means of the fully automated equilibration technique at JR until February 2007 (see also VREČA et al., 2008). Since then, it has been determined using a continuous flow isotope-ratio mass spectrometer IsoPrime (GV Instruments, UK) coupled to an automatic water-CO_2 equilibration system MultiFlow at the JSI. The isotopic composition of hydrogen was determined on a continuous flow Finnigan DELTA^{plus} XP mass spectrometer with a HEKAtech high-temperature oven, by reduction of water over hot chromium (MORRISON et al., 2001) at JR. All measurements were carried out together with laboratory standards that were calibrated periodically against international standards, as recommended by the IAEA. Measurement precision was better than ±0.1 ‰ for $\delta^{18}O$ and ±1 ‰ for $\delta^{2}H$.

Tritium activity

Tritium activity (A) in monthly samples was determined at the Tritium Laboratory at the Department of Experimental Physics of the RBI. Results are expressed in Tritium Units (1 TU = 0.118 BqL^{-1}). The gas proportional counting technique (GPC) was used until 2007; since 2010, samples have been measured only by the liquid scintillation counting technique (LSC) following electrolytic enrichment (EE), while during 2008 and 2009 both GPC and LSC-EE techniques were used, depending on the available sample quantity. The GPC technique was replaced by the LSC-EE technique for the following reasons: (i) the tritium activity approached natural pre-bomb levels (<5–10 TU), therefore, the measurement of samples without tritium enrichment was not sufficiently precise, and (ii) the GPC technique did not satisfy

requirements for a low detection limit and a high throughput of samples.

For GPC tritium activity measurement, CH_4 was obtained by reaction of water (50 mL) with aluminium carbide at 150 °C (Horvatinčić, 1980), purified and used as a counting gas in a multi-wire GPC. Gas quality control was performed by simultaneous monitoring of the count rate above the tritium channel, i.e., above 20 keV (Krajcar Bronić et al., 1986). The limit of detection (LOD) was 2.5 TU.

The LSC-EE technique consists of electrolytic enrichment of aliquots of 500 mL, distillation before and after the enrichment procedure, and measurement by the Ultra-low-level liquid scintillation counter Quantulus 1220 (Wallac, PerkinElmer). Mixtures of 8 mL of water and 12 mL of scintillation cocktail *Ultima Gold LLT* in plastic vials were used for counting in LSC. The limit of detection of the method is 0.3 to 0.5 TU, depending on measurement duration. If the quantity of sample was not large enough to perform EE, then a direct measurement in LSC Quantulus was performed, the limit of detection then being 6.0 TU (Barešić et al., 2010, 2011; Krajcar Bronić et al., 2013).

Tritium activity in two samples (March 2010 and July 2010) was determined by the Group for radiochemistry at the Department of Environmental Sciences of the JSI following electrolytic enrichment by liquid scintillation counting (LSC-EE) on a Tri Carb 3170 TR/SL Liquid Scintillation Counter (LSC, Canberra Packard) in accordance with method accredited by Slovenian Accreditation since 2009 (accreditation certificate LP-090). The limit of detection was 2.9 TU.

Data reduction

The approach of data reduction described by Vreča et al. (2008) for Ljubljana isotope records 1981–2006 was used. Basic descriptive statistics, i.e. mean, minimum and maximum values were determined. Deuterium excess ($d = \delta^2H - 8\times\delta^{18}O$; Dansgaard, 1964) was calculated to characterize the deviation of isotopic composition of precipitation from the GMWL. As summarized by Harvey (2005), d in precipitation was determined by air/sea interaction processes over the ocean surface during which the value of d is fixed and remains unchanged as air moves across the continents and loses moisture by rainout (Craig & Gordon, 1965; Merlivat & Jouzel, 1979; Gat, 1996). However, d can alter as the air mass moves inland, due to secondary processes such as evaporation from an open surface water body which returns moisture to the air (Gat et al., 1994). In addition, d values can change as precipitation falls through the atmosphere (Gat, 1996; Araguas-Araguas et al., 2000; Peng et al., 2004) or as the precipitation sample sits in the precipitation collector (Harvey, 2005). It was estimated that the initial d values should not be less than 3 ‰ and that lower values should be used with caution unless the source of their evaporative enrichment is known (Harvey, 2005).

Furthermore, mean values weighted by the amount of precipitation collected during sampling at the Reactor Centre were calculated from all monthly data, and then summed over all collected samples per year and per month. Summation was also performed over each season: winter (December, January, February), spring (March, April, May), summer (June, July, August) and autumn (September, October, November). Data for May 2007 and September 2010 were not taken into account due to problems with sampling (see Materials and methods). The minimum required number of data fulfilled the requirement of eight monthly measured samples per year and more than 70 % of total precipitation amount collected per year (IAEA, 1992).

In the previous evaluation of isotopic data from Ljubljana (Vreča et al., 2008) we used meteorological parameters (amount of precipitation and air temperature), obtained from the SEA for meteorological station Ljubljana (Bežigrad; 46°03'N, 14°31'E; 299 m a.s.l.), situated in the city of Ljubljana. A similar approach was used in this study. Meteorological data were obtained from SEA internet database (Internet 3). The mean values, weighted by the amount of precipitation recorded at Ljubljana (Bežigrad), were compared with the mean values weighted by the amount of precipitation collected during sampling at the Ljubljana (Reaktor) site. Oxygen-temperature correlation was calculated using air temperature data provided by SEA from automatic meteorological station Ljubljana (Hrastje; 46°04'N, 14°33'E; 290 m a.s.l.) which is close to Ljubljana (Reaktor). For comparison with the previous data (Vreča et al., 2008) we also calculated the oxygen-temperature correlation, using Ljubljana (Bežigrad) air temperature data, and estimating the temperature difference between the city centre and its outer perimeter using Ljubljana (Bežigrad) and Ljubljana (Hrastje) data.

Linear correlations between δ^2H and $\delta^{18}O$ were calculated by methods usually applied in stable isotope studies – the ordinary least squares regression (OLSF) and the reduced major axis (RMA) regression (IAEA, 1992; Hughes & Crawford, 2012). Neither OLSF nor RMA take into account the precipitation amount, therefore a new, precipitation weighted least square regression (PWLSR) method, introduced by Hughes & Crawford in 2012, was also applied. The lines are defined as local meteoric water lines ($LMWL_{OLSF}$, $LMWL_{RMA}$ and $LMWL_{PWLSR}$) and were compared with the "Global Meteoric Water Line" (GMWL: $\delta^2H = 8\times\delta^{18}O + 10$) (Craig, 1961).

Results and discussion

Meteorological data: Precipitation and temperature

Variations in precipitation and temperature at Ljubljana (Bežigrad), in precipitation at Ljubljana (Reaktor) and in temperature at Ljubljana (Hrastje) for the period 2007–2010 are presented in Figures 1 and 2. Mean annual temperatures and annual amounts of precipitation in the period 2007–2010 are summarized in Table 1. The annual precipitation amount for Ljubljana (Bežigrad) station varied between 1196 mm in 2007 and 1798 mm in 2010, with a mean value of 1472 mm (Table 1). Precipitation was regularly lower at Ljubljana (Reaktor) , ranging from 1112 mm in 2007 to 1506 mm in 2010, with a mean annual value of 1338 mm (Table 1). At Ljubljana (Reaktor), mean monthly precipitation was lower than at Ljubljana (Bežigrad) in all months (Figure 1). Mean precipitation at Ljubljana (Bežigrad) was higher for January, February, March, July, September and December and lower for other months in 2007–2010 than in 1981–2010 (Figure 1).

The variations in monthly amount of precipitation may indicate some changes in air-mass movement, but the period is too short and more detailed investigations of atmospheric processes (e. g. backward trajectories of precipitating air masses and their rainout history and elementary circulation mechanisms) are needed for reliable conclusions. Monthly variations in precipitation during 2007–2010 are presented in Figure 2. The lowest value was observed in April 2007 and the highest in September 2010. Precipitation was, on average, 134 mm lower at Ljubljana (Reaktor) than at Ljubljana (Bežigrad). The largest differences between the two stations were observed in August 2009, June and August 2010, and can be related to local stormy events during the summer months

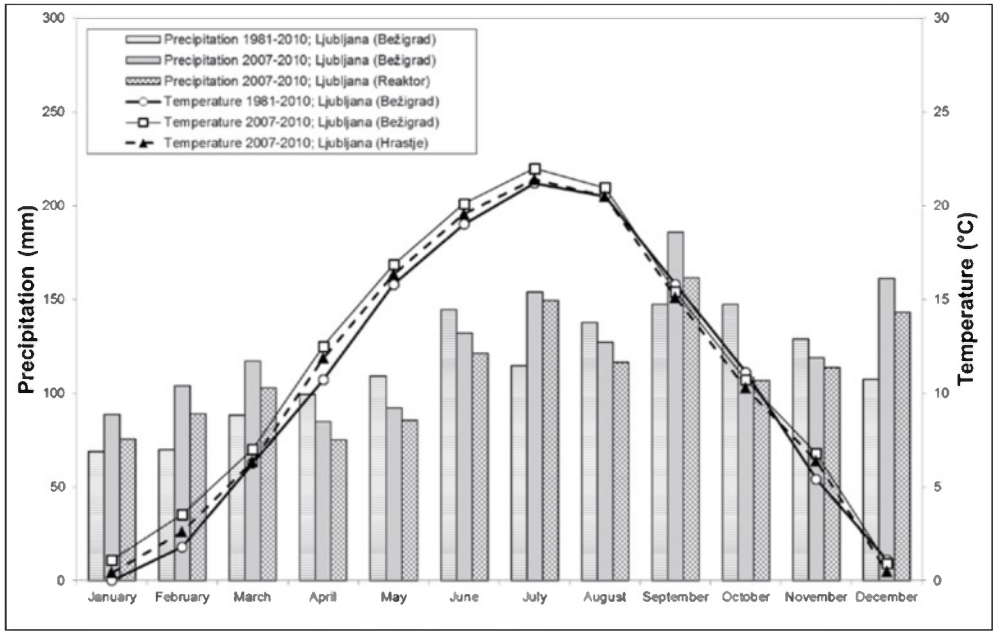


Figure 1. Mean monthly precipitation and mean monthly air temperatures at station Ljubljana (Bežigrad) for periods 1981–2010 and 2007–2010. Mean monthly precipitation at Ljubljana (Reaktor) and mean monthly air temperatures at station Ljubljana (Hrastje) for period 2007–2010 is shown for comparison.

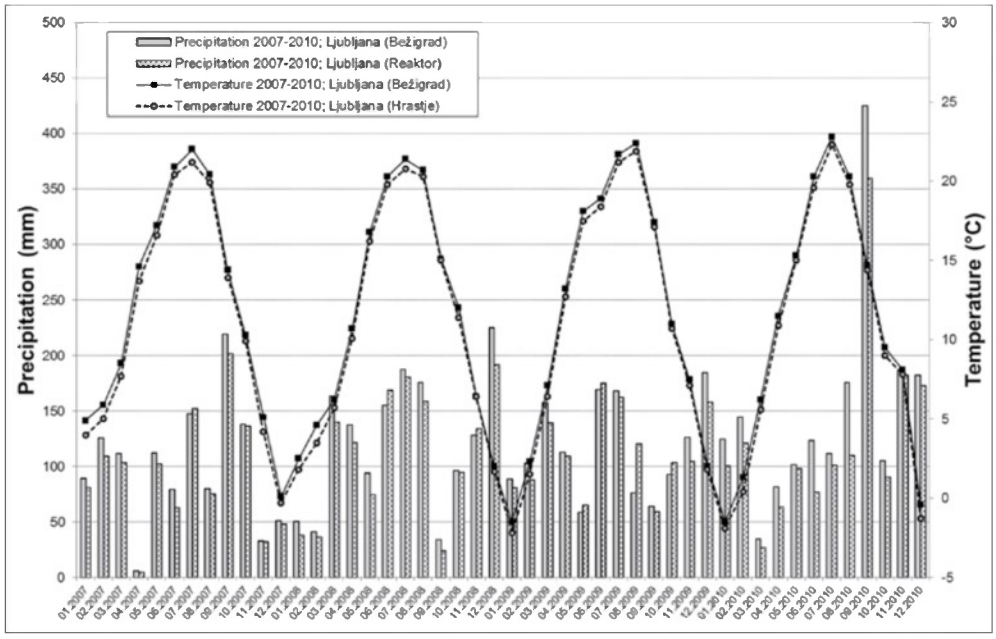


Figure 2. Monthly precipitation and mean monthly air temperatures at station Ljubljana-(Bežigrad), precipitation at Ljubljana (Reaktor) and mean monthly air temperature at station Ljubljana (Hrastje) for period 2007–2010.

(Figure 2). The correlation between monthly precipitation amount (P) at Ljubljana (Reaktor), P_{Re}, and Ljubljana (Bežigrad), P_{Be}, for the period 2007–2010 is:

$$P_{Re} = 0.9 \times P_{Be} + 2.0;\ r = 0.95,\ n = 46 \qquad (1)$$

The warmest year in the period 2007–2010 was 2007 and the coldest 2010 (Table 1). The mean air temperature for Ljubljana (Bežigrad) during the isotope monitoring period 2007–2010 was 11.5 °C, on average 0.7 °C higher than that for 1981–2010 (Table 1). At Ljubljana (Hrastje) the mean air temperature during the period 2007–2010 was 10.9 °C (Table 1). Variations of mean monthly air temperature for Ljubljana (Bežigrad) and Ljubljana (Hrastje) for these four years are shown in Figure 1. The greatest deviations were in January to June. Variations of monthly air temperature for Ljubljana (Bežigrad) and Ljubljana (Hrastje) are shown in Figure 2. At Ljubljana (Bežigrad) the lowest monthly temperatures (–1.5 °C) were observed in January 2009 and 2010 and the highest in July 2010 (22.8 °C) (Figure 2). At Ljubljana (Hrastje) the lowest temperature was observed in January 2009 (–2.2 °C) and the highest in July 2010 (22.3 °C) (Figure 2). Air temperatures at the two stations correlate strongly ($r > 0.99$) and are systematically lower at Ljubljana (Hrastje) by, on average, 0.6 °C, than at Ljubljana (Bežigrad) (Figure 2). The differences in air temperature between Ljubljana (Bežigrad) and Ljubljana (Hrastje) can be explained by an urban heat island effect typical of cities (Mills, 2008).

Stable isotope data (δ^2H, δ^{18}O and d)

Results of monthly isotopic composition of precipitation parameters: δ^2H, δ^{18}O and d together with precipitation amount at the Reactor Centre from January 2007 to December 2010, are summarized in Table 2. Results for May 2007 and September 2010 are reported but not considered in calculations. Results are reported to one decimal point for δ^2H and d values and to two for δ^{18}O.

Variations of monthly isotopic composition of precipitation (δ^2H, δ^{18}O and d) at Ljubljana (Reaktor) in 2007 to 2010 are presented in Figure 3. Seasonal variations of δ^{18}O and δ^2H show patterns typical of continental stations, with maxima in summer and minima in winter (Rozanski et al., 1993). The highest δ^{18}O value was observed in August 2007 (–4.65 ‰) and the lowest in January 2009 (–14.52 ‰). Variations in δ^2H follow those for δ^{18}O, with a maximum δ^2H value of –27.9 ‰ and minimum value of –115.1 ‰ observed in August 2007 and January 2009, respectively. The mean δ^{18}O and δ^2H values for the observed period are –8.57 ‰ and –58.7 ‰ (n = 46), and are similar to those values from 1981 to 2006; i.e., –8.7 ‰ and –60 ‰ (n = 290) (Vreča et al., 2008).

Monthly variations of deuterium excess (d) are presented in Figure 3c. The highest d value for a given month was observed in October 2010 (18.0 ‰). The lowest value was obtained for the sample collected in May 2007 (0 ‰, Table 2, not shown in Figure 3) and confirms evaporation from the rain gauge due to the blocked tube (see Methods). Most d values range between 5 and 15 ‰. The mean value is 9.9 ‰ (n = 46) (Table 2), slightly higher than the mean value of 9.4 ‰ from the period 1981–2006 (Vreča et al., 2008). Values of d around 10 ‰ are typical of those for continental meteoric waters (Craig, 1961) and can be attributed to precipitation of Atlantic origin (Cruz-San et al., 1992).

Analysis of our data shows that d values <5 ‰ correspond to months with low precipitation or to the coldest months, and probably indicate secondary evaporation processes (e.g. evaporation of raindrops falling through a dry atmosphere). The highest values are characteristic of autumn months, especially for November when d values always exceeded 10 ‰, ranging between 13.1 and 17.6 ‰. Higher d values are typical of those for Mediterranean-derived precipitation (Cruz-San et al., 1992; Rozanski et al., 1993). During October and November south-western Slovenia is under the influence of the Mediterranean cyclogenesis (Rakovec & Vrhovec, 2000). The isotopic composition of precipitation in south-western Slovenia (Vreča et al., 2007) and in the central part of the country (Vreča et al., 2006, 2008) reflects the Mediterranean-derived precipitation.

Table 1. Annual amounts of precipitation (P_{Be}, P_{Re}) and mean annual air temperatures (T_{Be}, T_{Hr}) at stations Ljubljana (Bežigrad), Ljubljana (Reaktor) and Ljubljana (Hrastje). n. d. – not determined; * – data for period 2003–2006 (Vreča et al., 2008).

	P_{Be} (mm)	P_{Re} (mm)	T_{Be} (°C)	T_{Hr} (°C)
2007	1196	1112	12.0	11.4
2008	1490	1364	11.6	11.2
2009	1406	1369	11.7	11.2
2010	1798	1506	10.7	10.1
mean value 2007–2010	1472	1338	11.5	10.9
long-term mean value 1981–2010	1362	n. d.	10.8	n. d.
1971–2000	1368	n. d.	10.2	n. d.
1981–2006	1346	1126 *	10.6	n. d.

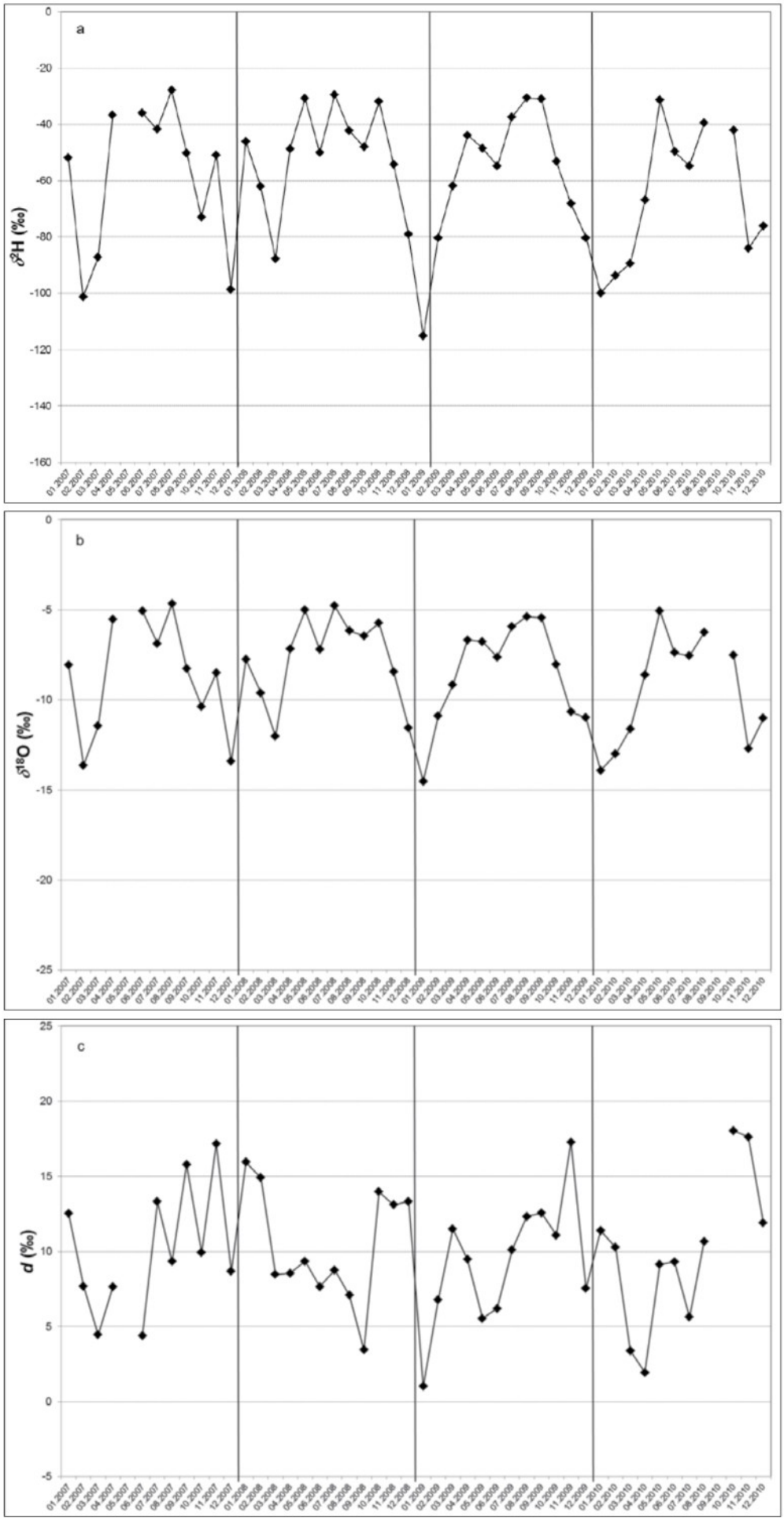


Figure 3. Monthly variations (a) of isotopic composition of hydrogen (δ^2H), (b) oxygen (δ^{18}O) and (c) deuterium excess (*d*), in precipitation at Ljubljana (Reaktor), 2007–2010.

Annual mean $\delta^{18}O$, $\delta^{2}H$ and d values, weighted by amount of precipitation at Ljubljana (Reaktor) and Ljubljana (Bežigrad) for the period 2007–2010, are summarized in Table 3. The differences between weighted annual means at Ljubljana (Reaktor) and Ljubljana (Bežigrad) are within the range of analytical error. The maximum annual weighted mean $\delta^{18}O$ and $\delta^{2}H$ values were observed in 2008, when precipitation was higher during the spring-summer season and represent more than 60 % of the total precipitation in 2008. Changing weather conditions over Europe and the northern Mediterranean during summer months caused stormy weather with high precipitation (Cegnar, 2009) and consequently contributed to the higher weighted mean isotopic composition of precipitation. In addition, January and February were warm and, consequently, the isotopic composition of precipitation was higher than the long term mean values (Vreča et al., 2008). During 2007–2010 the lowest annual weighted mean $\delta^{18}O$ and $\delta^{2}H$ values were observed in 2010 and can be attributed to the lowest mean annual air temperature (Table 1), a cold January and February, with more than 100 mm of precipitation in each month (Figure 2) and air temperatures lower than the long-term records (Cegnar, 2011). 2010 was also characterised by 85 days with snow cover in Ljubljana and the highest annual amount of precipitation (1798 mm at Ljubljana (Bežigrad)). The highest annual weighted mean d value was observed in 2010 and is related mainly to the Mediterranean-derived precipitation in the autumn (Tables 2 and 3). The lowest annual weighted mean d value was observed for 2009. One of the reasons is the very low d value for January 2009 (Table 2), which probably indicates secondary evaporation processes but could not be attributed to sampling.

The weighted mean values for $\delta^{18}O$ and $\delta^{2}H$ are slightly lower than the long-term 1981–2006 values, while the weighted mean d values show an overall increase by 0.8 ‰ (Table 3). However, these differences are within the range of isotope analysis errors and caution is therefore needed in further interpretation. In addition, it has to be noted that the long-term 1981–2006 weighted averages were determined taking into account only precipitation data for Ljubljana (Bežigrad) and that precipitation has only been recorded at Ljubljana (Reaktor) since October 2002.

Seasonal mean $\delta^{18}O$, $\delta^{2}H$ and d values weighted by amount of precipitation at Ljubljana (Reaktor) are summarized in Table 4. The lowest $\delta^{18}O$ and $\delta^{2}H$ values are typical of those in winter and the highest of those in summer. The d values clearly indicate much higher values for autumn when the area is under the influence of Mediterranean-derived precipitation (Vreča et al., 2006).

Table 2. Isotopic composition ($\delta^{2}H$, $\delta^{18}O$, deuterium excess (d) and tritium activity (A)) of precipitation at Ljubljana (Reaktor) for period 2007–2010. n. d. – not determined; P_{Re} – precipitation amount of collected sample; GPC – gas proportional counter, LSC – liquid scintillation counter and electrolytic enrichment, LSC direct – liquid scintillation counter without enrichment, JSI – Jožef Stefan Institute, * – tube blocked, ** – calculated without 05/07 and 09/10 (n = 46).

Month/ Year	$\delta^{2}H$ (‰)	$\delta^{18}O$ (‰)	d (‰)	A (TU)	P_{Re} (mm)	Method of tritium activity measurement
01/07	–51.9	–8.05	12.5	9.1	81	GPC
02/07	–101.3	–13.62	7.7	4.7	109	GPC
03/07	–87.2	–11.45	4.4	6.4	103	GPC
04/07	–36.7	–5.54	7.6	n. d.	5	-
05/07	–51.2*	–6.38*	–0.1*	20.1*	102*	LSC direct
06/07	–36.0	–5.05	4.4	11.1	63	GPC
07/07	–41.7	–6.88	13.3	11.3	153	GPC
08/07	–27.9	–4.65	9.3	6.2	76	GPC
09/07	–50.3	–8.26	15.8	10.6	202	GPC
10/07	–73.1	–10.37	9.9	4.3	137	GPC
11/07	–50.9	–8.51	17.2	4.6	32	GPC
12/07	–98.6	–13.41	8.7	6.3	48	GPC
01/08	–46.1	–7.76	15.9	3.6	38	GPC
02/08	–62.1	–9.62	14.9	7.8	36	GPC

Month/ Year	δ^2H (‰)	$\delta^{18}O$ (‰)	d (‰)	A (TU)	P_{Re} (mm)	Method of tritium activity measurement
03/08	–87.7	–12.02	8.5	6.7	140	GPC
04/08	–48.7	–7.16	8.6	4.3	122	GPC
05/08	–30.8	–5.02	9.3	9.1	75	GPC
06/08	–50.0	–7.21	7.6	20.3	169	GPC
07/08	–29.5	–4.78	8.8	13.5	181	LSC
08/08	–42.3	–6.17	7.1	9.3	159	LSC
09/08	–48.1	–6.44	3.5	9.6	24	GPC
10/08	–31.9	–5.73	14.0	8.3	94	LSC
11/08	–54.3	–8.43	13.1	4.5	134	GPC
12/08	–79.0	–11.54	13.3	5.0	192	GPC
01/09	–115.1	–14.52	1.0	13.0	81	GPC
02/09	–80.3	–10.89	6.8	1.6	89	GPC
03/09	–61.8	–9.16	11.5	1.6	140	GPC
04/09	–43.9	–6.67	9.5	13.8	109	LSC
05/09	–48.5	–6.76	5.5	21.8	65	GPC
06/09	–54.8	–7.62	6.2	13.6	175	GPC
07/09	–37.4	–5.94	10.1	11.9	162	GPC
08/09	–30.6	–5.37	12.3	9.0	121	GPC
09/09	–31.0	–5.44	12.5	4.8	60	GPC
10/09	–53.3	–8.04	11.1	2.0	104	GPC
11/09	–68.1	–10.67	17.3	5.1	105	GPC
12/09	–80.3	–10.98	7.5	7.7	158	GPC
01/10	–99.9	–13.91	11.4	5.7	101	LSC
02/10	–93.7	–13.00	10.3	6.6	121	LSC
03/10	–89.4	–11.60	3.4	9.4	27	LSC, JSI
04/10	–66.9	–8.60	1.9	10.0	64	LSC
05/10	–31.3	–5.05	9.1	11.1	98	LSC
06/10	–49.7	–7.38	9.3	12.7	77	LSC
07/10	–54.8	–7.55	5.6	11.2	101	LSC, JSI
08/10	–39.4	–6.26	10.7	9.6	110	LSC
09/10	–52.4*	–6.97*	3.4*	6.5*	360*	LSC
10/10	–42.1	–7.51	18.0	6.1	91	LSC
11/10	–84.1	–12.71	17.6	5.1	183	LSC
12/10	–76.2	–11.01	11.9	5.6	173	LSC
min**	–115.1	–14.52	1.0	1.6	5	
max**	–27.9	–4.65	18.0	21.8	202	
mean**	–58.7	–8.57	9.9	8.3	106	
n	46	46	46	45	46	

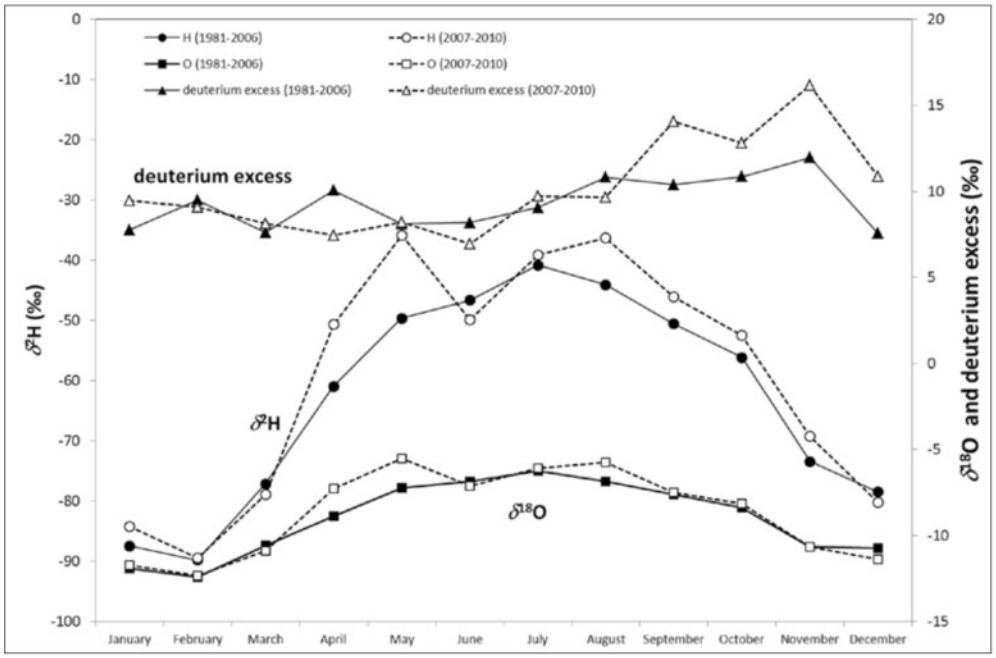


Figure 4. Monthly weighted mean δ^2H (in legend H), δ^{18}O (in legend O) and deuterium excess for periods 1981–2006 (Vreča et al., 2008) and 2007–2010.

Monthly mean δ^{18}O, δ^2H and d values, weighted by precipitation amount at Ljubljana (Reaktor), are summarized in Table 5 and presented in Figure 4, where they are compared with the 1981–2006 values (Vreča et al., 2008). The higher δ^{18}O and δ^2H values in spring and summer months, due to higher air temperatures, constitute a typical seasonal variation. The lowest values are observed in February, similarly to those for the period 1981–2006, and are related to snow as the prevailing type of precipitation. The highest positive deviations from long-term calculations are observed for April, May and August and can be attributed to higher temperatures and lower amounts of precipitation during sampling period 2007–2010. d values range around 10.3 ‰ (Table 5) with the lowest values in June (7.0 ‰) and the highest in November (16.2 ‰). The observed pattern is one of higher d values in autumn precipitation, with values above 10 ‰, and also above mean values for the long-term period 1981–2006, indicating the greater influence of Mediterranean air masses over the region during the observation period (Figure 4).

Local meteoric water lines

The local meteoric water lines (LMWLs) for the period 2007–2010 were calculated using different types of linear regression analysis. The OLSF regression line ($LMWL_{OLSF}$) for Ljubljana (Reaktor) is:

$$\delta^2H=(8.05\pm0.22)\times\delta^{18}O+(10.36\pm2.02);r=0.98,n=46 \quad (2)$$

The reduced major axis regression line ($LMWL_{RMA}$) is:

$$\delta^2H=(8.19\pm0.22)\times\delta^{18}O+(11.52\pm1.97);r=0.98,n=46 \quad (3)$$

For the precipitation amount recorded at Ljubljana (Reaktor) the PWLSR line ($LMWL_{PWLSR\text{-}Re}$) is:

$$\delta^2H=(7.94\pm0.21)\times\delta^{18}O+(9.76\pm1.91);r=0.99,n=46 \quad (4)$$

For the precipitation amount recorded at Ljubljana (Bežigrad), the PWLSR line ($LMWL_{PWLSR\text{-}Be}$) differs only slightly from $LMWL_{PWLSR\text{-}Re}$ (4):

$$\delta^2H=(7.93\pm0.21)\times\delta^{18}O+(9.68\pm1.93);r=0.99,n=46 \quad (5)$$

The LMWLs obtained are close to the long term LMWLs for the period 1981–2006 (Vreča et al., 2008) and also to the GMWL of Craig (1961) and to that calculated from the GNIP database for the period 1961–2000 by Gourcy et al. (2005). The absence of significant difference between the PWLSR slope and either the OLSF or the RMA slope indicates a relatively homogeneous distribution of monthly precipitation amounts as well as a small number of small monthly precipitation with low deuterium excess (Hughes & Crawford, 2012). The slope of all LMWLs is close to 8, so it is possible to equate the intercept with the deuterium excess concept (Gat, 2005).

Oxygen – temperature correlation

The linear correlation between δ^{18}O in monthly samples and mean monthly air temperature at Ljubljana (Hrastje), T_{Hr}, for the period 2007–2010 is:

$$\delta^{18}O = 0.30\times T_{Hr} - 11.80 \ (r = 0.82, n = 46) \quad (6)$$

The linear correlation between δ^{18}O in monthly samples and mean monthly air temperature at Ljubljana (Bežigrad), T_{Be}, for the period 2007–2010 is:

$$\delta^{18}O = 0.30\times T_{Be} - 11.99 \ (r = 0.82; n = 46) \quad (7)$$

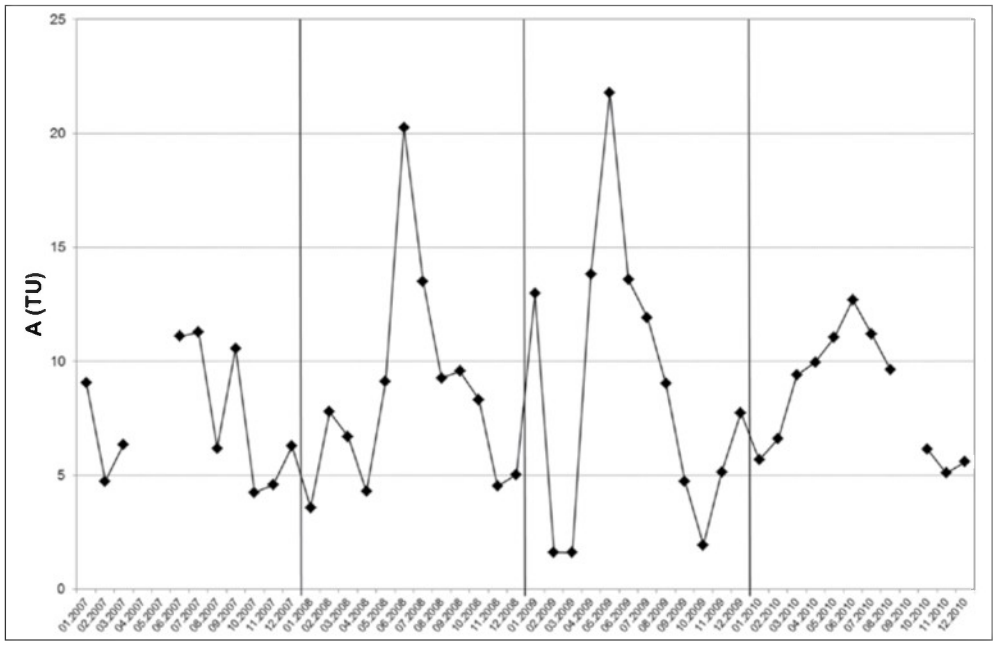


Figure 5. Monthly variations of tritium activity A (in TU) in precipitation at Ljubljana (Reaktor), 2007–2010.

The correlations obtained differ only slightly in their intercept values, have the same slope (0.30 ‰/°C) as that for the long term record (1981–2006; Vreča et al., 2008) and are typical of continental stations (Rozanski et al., 1993). For comparison, the long-term precipitation data for GNIP station Zagreb, Croatia, led to an average isotope temperature gradient of 0.33 ‰/°C (Krajcar Bronić et al., 1998; Vreča et al., 2006) and, for Debrecen, Hungary, of 0.32 ‰/°C for the period 2001–2009 (Vodila et al., 2011), while Mezga et al. (2014) estimated an average isotope temperature gradient of 0.25 ‰/°C for groundwater in Slovenia.

Tritium activity

Results of monthly tritium activity (A) of precipitation are summarized in Table 2 in which the technique used to determine tritium activity in a particular sample is indicated. Amount of precipitation weighted mean annual, seasonal and monthly values are summarized in Tables 3, 4 and 5. Variations of tritium activity in monthly precipitation at Ljubljana (Reaktor) during the sampling period 2007–2010 are presented in Figure 5. Seasonal fluctuations typical of continental/ inland stations of the Northern hemisphere (Rozanski et al., 1991) are observed, with lower ^{3}H activities in autumn and winter and higher ones in spring and summer (Table 4). Maximal values are observed between May and July, mostly in June, and minimal between October and March (Table 5). The tritium activity distributions for 2008 and 2009 show the pronounced maxima in summer typical of the Northern hemisphere (Rozanski et al., 1991). The annual precipitation amounts and average air temperatures were very similar during these two years (Table 1). In contrast, much lower maxima were observed in 2007 and 2010 and can be attributed to warm summer periods with less precipitation. The seasonal fluctuations of tritium activity observed for the present short period 2007–2010 are the same as for the long-term period 1981–2006 (Vreča et al., 2008). However, the long-term data show a seasonal structure superposed on the basic decrease in mean annual tritium activities (Krajcar Bronić et al., 1998, 2006; Vreča et al. 2008), while data recorded since 1998 show no significant decrease of mean annual values. The mean tritium activity for the period 1998–2010 is 9.1 TU while, in the studied period, it is 8.3 TU (Table 2). Observations similar to those in our study are valid for the nearest continental GNIP station Zagreb, where mean annual tritium activities measured since 1996 cluster around 9 TU (Krajcar Bronić et al., 2006). Compared with the Ljubljana data, mean values for Zagreb precipitation are 8.6 TU and 9.0 TU for periods 1998–2010 and 2007–2010, respectively. Thus, no decrease in mean annual tritium activity is observed in the studied period, and the seasonal (Table 4) and monthly (Table 5) weighted mean values can be applied also for tritium activity.

A relatively good correlation between deuterium excess and tritium activity has been obtained for the mean monthly data with a slope of –0.38 ‰/ TU ($r = 0.48$, $n = 12$). This confirms the seasonal fluctuations typical of continental/inland stations with the highest d values in autumn months when tritium activity is low, and lower d during summer when tritium activity has its seasonal maximum (Table 4). This finding corroborates the previous conclusion that, in autumn, Ljubljana receives a relatively higher share of the precipitation formed by moisture evaporated from the Adriatic and Mediterranean Seas.

Conclusions

The results of the isotopic composition of oxygen and hydrogen, and of tritium activity ($\delta^{18}O$, $\delta^{2}H$ and A) of precipitation collected at Ljubljana (Reaktor) in the period 2007–2010 are

Table 3. Annual weighted mean δ^2H, $\delta^{18}O$, deuterium excess (d) values (in ‰) and tritium activity (A in TU). Subscript Be denotes annual mean values weighted by amount of precipitation at Ljubljana (Bežigrad); Re denotes annual mean values weighted by amount of precipitation at Ljubljana (Reaktor); * denotes for n = 10; n. d. – not determined.

Year	n	δ^2H_{Be}	$\delta^{18}O_{Be}$	d_{Be}	A_{Be}	δ^2H_{Re}	$\delta^{18}O_{Re}$	d_{Re}	A_{Re}
2007	11	–61.4	–9.01	10.7	7.9*	–61.2	–9.00	10.8	7.9*
2008	12	–53.1	–7.90	10.1	8.9	–52.5	–7.83	10.1	9.2
2009	12	–60.1	–8.68	9.3	8.5	–58.2	–8.44	9.3	8.8
2010	11	–66.2	–9.66	11.0	8.1	–67.4	–9.83	11.2	7.8
min		–66.2	–9.66	9.3	7.9	–67.4	–9.83	9.3	7.8
max		–53.1	–7.90	11.0	8.9	–52.5	–7.83	11.2	9.2
2007–2010 mean		–60.0	–8.78	10.3	8.3	–59.4	–8.71	10.3	8.5
1981–2006 weighted mean (Vreča et al., 2008)		–59.1	–8.57	9.5	n. d.	n. d.	n. d.	n. d.	n. d.

Table 4. Seasonal weighted mean δ^2H, $\delta^{18}O$, deuterium excess (d) values (in ‰) and tritium activity (A in TU) for period 2007–2010. Subscript Re denotes monthly mean values weighted by amount of precipitation at Ljubljana (Reaktor); * denotes for n = 10.

Season	n	δ^2H_{Re}	$\delta^{18}O_{Re}$	d_{Re}	A_{Re}
Winter	12	–83.9	–11.74	10.0	6.3
Spring	11	–59.1	–8.38	7.9	8.4*
Summer	12	–41.6	–6.31	8.8	12.2
Autumn	11	–57.4	–8.98	14.4	6.0

Table 5. Monthly weighted mean δ^2H, $\delta^{18}O$, deuterium excess (d) values (in ‰) and tritium activity (A in TU) for period 2007–2010. Subscript Re denotes monthly mean values weighted by amount of precipitation at Ljubljana (Reaktor); * denotes for n = 3.

Month	n	δ^2H_{Re}	$\delta^{18}O_{Re}$	d_{Re}	A_{Re}
January	4	–84.2	–11.71	9.5	8.3
February	4	–89.5	–12.32	9.1	4.9
March	4	–78.9	–10.87	8.1	5.1
April	4	–50.6	–7.26	7.5	9.1*
May	3	–35.8	–5.51	8.2	13.4
June	4	–49.9	–7.10	7.0	15.4
July	4	–39.1	–6.10	9.8	12.1
August	4	–36.2	–5.74	9.7	8.8
September	3	–46.1	–7.52	14.1	9.3
October	4	–52.5	–8.16	12.8	5.0
November	4	–69.2	–10.67	16.2	4.9
December	4	–80.2	–11.38	10.9	6.1
min		–89.5	–12.32	7.0	4.9
max		–35.8	–5.51	16.2	15.4
2007–2010 mean		–59.4	–8.71	10.3	8.5

presented and compared with the long-term data from the period 1981–2006. The observed seasonal fluctuations of $\delta^{18}O$ and $\delta^{2}H$ are significant and typical of continental stations. The local meteoric water lines (LMWLs) were calculated by applying three different types of regression analysis – in addition to the previously used ordinary least squares regression (OLSF) and the reduced major axis (RMA) regression analyses that do not take into account the amount of precipitation. A new precipitation weighted least square regression (PWLSR) method was also applied. All three LMWLs have similar slopes and intercepts, very high correlation coefficients ($r \geq 0.98$) and are close to Craig's GMWL, indicating a homogeneous distribution of monthly precipitation and a small number of low-amount precipitation events with low d values. The deuterium excess, with a weighted mean value of 10.3 ‰, shows the predominating influence of Atlantic air masses in Ljubljana. However, much higher d values are observed in autumn (mean 14.4 ‰) and indicate the influence of Mediterranean air masses. The observed tritium activity distributions show patterns typical of the Northern Hemisphere, with pronounced maxima in summer, and no decrease in mean annual tritium activity is observed.

The results presented are important for further scientific and practical applications in hydrology and hydrogeology, and in climatology. The LMWLs obtained can be useful above all in investigating those hydrological systems in Slovenia that are fed directly by precipitation and in enabling the range of input parameters to be defined. However, as stressed by Gat (2005), any application beyond that is limited because of rain events associated with air masses of different origins. Taking into account the characteristic geographic diversity of Slovenia, which influences considerably the climate and the isotopic composition of precipitation, a more detailed investigation of the complete isotope data set (1981–2010) for Ljubljana needs to be performed, taking into consideration the atmospheric circulation patterns over Slovenia. In addition, it is necessary to separate those clusters of data with different air mass origins and different isotope distributions and to determine LMWLs for particular clusters. In such a way it would be possible to verify whether the calculated composite best-fit line for isotope data from Ljubljana represents a range of input parameters as a whole or is just an artefact.

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