# Isotopic composition of precipitation in Portorož (Slovenia)

# Izotopska sestava padavin v Portorožu (Slovenija)

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#### **Abstract**

The stable isotopic composition of hydrogen and oxygen ( $\delta^2H$  and  $\delta^{18}O$ ) and tritium activity ( $^3H$ ) have been monitored in monthly precipitation at Portorož airport meteorological station since October 2000. Here we present a complete set of numerical data and a statistical analysis for the period 2000–2006. Seasonal variations of  $\delta^2H$  and  $\delta^{18}O$  were observed but are much less pronounced than for continental stations of the Northern Hemisphere. The weighted mean  $\delta^2H$  and  $\delta^{18}O$  values are -43 % and -6.6 %, respectively. The relation between hydrogen and oxygen isotopic composition is expressed by the orthogonal Local Meteoric Water Line as  $\delta^2H = (8.05 \pm 0.22) \, \delta^{18}O + (9.35 \pm 1.55)$ , and the temperature coefficient of  $\delta^{18}O$  is 0.13 %/°C. The deuterium excess weighted mean value is 9.8 % and shows some seasonal variations that reflect the variable influence of air masses of different origin (either Atlantic or Mediterranean). Tritium activity in monthly precipitation also showed seasonal variations, with a weighted mean value of 6.9 TU.

## Izvleček

Na meteorološki postaji Letališče Portorož poteka spremljanje izotopske sestave kisika in vodika ( $\delta^2 H$  in  $\delta^{18} O$ ) ter aktivnosti tricija ( $^3 H$ ) v mesečnih vzorcih padavin od oktobra 2000. V prispevku je predstavljen celoten niz pridobljenih podatkov in osnovne statistične obdelave za obdobje 2000–2006. Spreminjanje  $\delta^2 H$  in  $\delta^{18} O$  je sezonsko, a ne tako izrazito kot je značilno za kontinentalne postaje severne poloble. Srednje tehtane  $\delta^2 H$  in  $\delta^{18} O$  vrednosti znašajo -43 ‰ oziroma -6.6 ‰. Odnos med izotopsko sestavo vodika in kisika podajamo kot ortogonalno lokalno padavinsko premico (LMWL) z enačbo  $\delta^2 H$  = (8.05 ± 0.22)  $\delta^{18} O$  + (9.35 ± 1.55), temperaturni koeficient za  $\delta^{18} O$  pa znaša 0,13 ‰/°C. Srednja tehtana vrednost devterijevega presežka (deuterium excess) znaša 9,8 ‰ in se spreminja sezonsko ter odraža vpliv različnih zračnih mas (atlantskih ali sredozemskih). Tudi aktivnost tricija v mesečnih padavinah kaže sezonske spremembe. Srednja tehtana vrednost znaša 6,9 TU.

# Introduction

An improved scientific understanding of the water cycle to better manage water resources under current and future climatic conditions is an internationally recognized goal. Stable isotopes of oxygen (<sup>16</sup>O, <sup>18</sup>O) and hydrogen (<sup>1</sup>H, <sup>2</sup>H), and the radioactive isotope tritium (<sup>3</sup>H), provide unique insights into hydrological and climatic processes on local, regional and global scales, including the role of groundwater in rivers and lakes, groundwater recharge rates, and sources and recycling rates of atmospheric moisture (e.g. Clark & Fritz, 1997, Araguas-Araguas et al., 2000, IAEA/WMO, 2011). Precipitation is of major interest in the hydrological cycle as it is the ultimate source of water to catchments. Therefore, understanding of the

mation of precipitation, as well as a knowledge of temporal and spatial variations in the amount and mode of precipitation are important for basin-wide balance studies (e.g. GAT, 1996). Similarly, understanding how isotopic composition is controlled by the formation of precipitation and knowledge of the temporal and spatial variations in the isotopic composition of precipitation are equally important. 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). In addition, the geographical distribution observed 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 (Dansgaard, 1964).

Tritium is the radioactive isotope of hydrogen (half-life of 12.32 years; Lucas & Unterweger, 2000), which is naturally produced in the upper atmospheric strata by the reaction of cosmic radiation (thermal neutrons) with nitrogen atoms. Tritium reacts in the atmosphere with oxygen to form water and may precipitate on earth as rain and thus reach groundwater. The seasonality of the stratosphere-to-troposphere transport results in the marked seasonal cycle of the tritium content in precipitation (GAT et al., 2001). The natural atmospheric tritium concentration increased about 10<sup>3</sup> times (Ingraham, 1998) after the nuclear weapon tests in the early 1960s. Since 1963 it has been constantly decreasing, partly due to radioactive decay of tritium and partly due to its redistribution in other water reservoirs, such as the oceans (Ingraham, 1998; Gat et al., 2001). The tritium concentration in water is commonly expressed in Tritium Units (TU): 1 TU corresponds to 1 atom <sup>3</sup>H per 10<sup>18</sup> atoms <sup>1</sup>H. Tritium may also be reported in terms of its activity concentration in  $BqL^{-1}$  (1  $TU = 0.118 BqL^{-1}$ ; Ingraham, 1998; Gat et al., 2001).

Some European countries have established networks of stations where the isotopic composition of precipitation and rivers is regularly determined on a monthly basis (e.g. Schürch et al., 2003). In Slovenia, a precipitation and river flow monitoring programme is performed in the framework of the regular activities of the Environmental Agency of the Republic of Slovenia. However, monitoring of the isotopic composition of precipitation and rivers is not yet included in the regular national monitoring programme. It has been performed in the past by different institutions, such as the Jožef Stefan Institute (IJS) at Ljubljana, Kozina and Portorož airport (Krajcar Bronić et al., 1998; Pezdič, 2003; Vreča et al., 2005, 2006, 2007, 2008) and along the River Sava (Ogrinc et al., 2008). The data obtained are partly reported to the International Atomic Energy Agency (IAEA) and included in the Global Network of Isotopes in Precipitation (GNIP) and the Global Network of Isotopes in Rivers (GNIR). Furthermore, the isotopic composition of water is also determined in the framework of other hydrological investigations performed in Slovenia, but the data are not reported to GNIP and GNIR databases.

Monitoring of isotopes in precipitation performed by IJS started in Slovenia in 1981 and was carried out systematically until 2000 only in Ljubljana (Vreča et al., 2008). Due to the geographical diversity which influences the climate of Slovenia considerably (Pučnik, 1980) sampling was extended to two stations in the SW part of Slovenia, namely to the meteorological station at Portorož airport and the precipitation station at Kozina in October 2000 (Vreča et al., 2005, 2006,

2007). Both stations are positioned in an area where large karstic aquifers important for the water supply of SW Slovenia are present. Investigation of the isotopic composition of precipitation in this area is therefore important not only for studying the isotopic patterns of local meteorological conditions, but also for improvement of the knowledge of the isotopic input signal needed for hydrogeological studies of the large karstic springs in the area (VREČA et al., 2007). Data were published only until the end of 2003 (VREČA et al., 2005, 2006, 2007) and were used in different hydrogeochemical investigations of aquifers in Slovenia (Brenčič, 2009), Croatia (Mandić et al., 2008) and in Italy (Cucchi et al., 2008), as well as in investigations of precipitation events (Liotta et al., 2008) and moisture recycling (Froehlich et al., 2008). Unfortunately, since 2004, due to lack of financial support monitoring continues only at Portorož airport.

Therefore, the main purposes of this paper are: 1) to present the 2000–2006 monthly record from Portorož airport, 2) to present a basic statistical evaluation of available data and compare them with data for Ljubljana, and 3) to provide a better background for understanding the hydrological cycle in the SW part of Slovenia.

## Materials and methods

Sampling is performed at the meteorological station of Portorož airport (45°28'N, 13°37'E; 2 m a.s.l.) which is a part of the Slovene national meteorological network and therefore also provides meteorological data necessary for isotope data analyses. Detailed site characteristics of the location were described in Vreča et al. (2007). Monthly composite precipitation samples were collected according to IAEA guidelines for precipitation sampling (IAEA, 1996), available at http:// www-naweb.iaea.org/NAALIHL/publications1. shtml. Samples were collected until October 2002 in a separate rain gauge with a diameter of 16 cm connected with a funnel to a plastic bottle filled with a 0.5 cm film of paraffin oil to prevent evaporation. The collected water was separated from the oil at the end of the month. Since October 2002 the staff of the meteorological station have collected the samples from standard precipitation gauge three times daily. After measuring the amount of precipitation the sample was poured into a 5-litre plastic bottle with a well tight cap to avoid evaporation and kept in a dark place. After bringing the samples to the lab the amount of collected sample was again measured and a 50 mL bottle for the stable isotope analysis was filled. The rest of the water was transferred to 1L bottles (or less if the sample was insufficient) for tritium analysis.

Meteorological data (amount of precipitation and temperature) were obtained from the Environmental Agency of the Republic of Slovenia and are available on the internet (http://meteo.arso.gov.si/).

## Isotopic analyses

The stable isotopic composition of water samples was determined on a Varian MAT 250 mass spectrometer at the Jožef Stefan Institute until the end of 2003. The oxygen isotopic composition ( $\delta^{18}$ O) was measured by means of the water-CO, equilibration technique (Epstein & Mayeda, 1953). The isotopic composition of hydrogen ( $\delta^2$ H) was determined by means of the H, generated by reduction of water over hot chromium (Gehre et al., 1996). The stable isotopic composition of water samples collected since the beginning of 2004 to the end of 2006 was determined at Joanneum Research. The oxygen isotopic composition was determined on a dual inlet Finnigan DELTAplus by means of the fully automated equilibration technique and the isotopic composition of hydrogen determined on a continuous flow Finnigan DELTA<sup>plus</sup> XP mass spectrometer with HEKAtech high-temperature oven by reduction of water over hot chromium (Morrison et al., 2001).

Results are reported as  $\delta$  values in units of parts per thousand (%) relative to the V-SMOW (Vienna-SMOW) standard.  $\delta$  values are calculated by:

$$\delta^{Y}Z = (R_r / R_s - 1) \cdot 1000 \tag{1}$$

where  ${}^{\text{Y}}\text{Z}$  is  ${}^{18}\text{O}$  or  ${}^{2}\text{H}$ , R denotes the ratio of the heavy (less abundant) to light (more abundant) isotope (e.g.,  ${}^{2}\text{H}/{}^{1}\text{H}$ ,  ${}^{18}\text{O}/{}^{16}\text{O}$ ), and  $R_x$  and  $R_s$  are the ratios in the sample (x) and standard (s), respectively. All measurements were carried out against laboratory standards that were periodically calibrated against international standards recommended by the IAEA. Measurement precision was better than  $\pm 0.1$  % for  $\delta^{18}\text{O}$  and  $\pm 1$  % for  $\delta^{2}\text{H}$ .

Tritium activity (A) in collected monthly samples was determined at the Rudjer Bošković Institute in Zagreb by the gas proportional counting technique. Methane obtained in the reaction of water with  ${\rm Al_4C_3}$  at 150 °C was used as the counting gas (Horvatinčić, 1980). 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). Results are expressed in Tritium Units (TU), 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 (Vreča et al., 2008).

#### Data reduction

Basic descriptive statistics, i.e. mean, minimum value and maximum value, were calculated to describe variation of the data. Furthermore, mean  $\delta^{18}$ O,  $\delta^2$ H and deuterium excess values (see below) weighted by the amount of precipitation were calculated. The summations were over samples collected per year and per month over the period 2001–2006. During this period March 2002 was very dry with only 0.1 mm precipitation

which was not sufficient for isotope analyses. In addition, the amount of precipitation collected in March 2003 and June 2006 was sufficient only for determination of the stable isotopic composition of oxygen and hydrogen.

Further, to characterize the relation between hydrogen and oxygen isotopes in precipitation and to determine the deviation from Craig's (1961) "Global Meteoric Water Line" (GMWL:  $\delta^2H = 8 \ \delta^{18}O + 10$ ), local meteoric water lines (LMWL) were calculated. Two methods of linear correlation between  $\delta^2H$  and  $\delta^{18}O$  were applied: the least squares fit (LSF) and orthogonal regression, known as the reduced major axis (RMA) line (IAEA, 1981).

Finally, to characterize the deviation of isotopic composition of precipitation from the GMWL, the deuterium excess (d) proposed by Dansgaard (1964) was also calculated as  $d = \delta^2 H - 8\delta^{18}O$ .

#### Results and discussion

Seasonal variations of amount of precipitation and temperature for the period 2000–2006 are presented in Figure 1. During the period 2001–2006 the average amount of precipitation was 944 mm which is lower than during the reference period of 1961–1990 (1046 mm). The decrease in precipitation in this area is similar to the trend observed over the central-western Mediterranean basin (Piervitali et al., 1998). The lowest amount of precipitation was recorded in 2003 (790 mm) and the highest in 2002 (1205 mm). Very low precipitation was recorded in March 2002 (< 1 mm), in March 2003 (4 mm) and in June 2006 (5 mm). The highest precipitation was recorded in August 2006 (325 mm) which was much greater than the monthly mean amount of precipitation (101 mm) in the reference period 1961–90 (Cegnar, 2002). In addition, extremely high precipitation was recorded in autumn 2000 with 241 mm in October and 296 mm in November. The temperature varies seasonally as shown in Figure 1 and its mean value in the investigated period was 13.6 °C, which is 1.1 °C higher than in the reference period of 1961-90 (Cegnar, 2002). The most extreme was the year 2003, with a winter minimum in February (2.4 °C) and a summer maximum in August (26.1 °C); the mean annual temperature was 13.8 °C.

The results for the monthly isotopic composition of precipitation ( $\delta^2 H$ ,  $\delta^{18} O$ , deuterium excess and tritium activity) obtained from October 2000 to December 2006 are summarized in Table 1 and shown in Figures 2 and 3. Seasonal variations of  $\delta^{18} O$  and  $\delta^2 H$  were observed but are less characteristic than for continental stations like Ljubljana (Vreča et al., 2008). The minimum  $\delta^{18} O$  value was observed in February 2005 (-15.2 %) and the maximum in July 2003 (-1.6 %). Variations in  $\delta^2 H$  followed the  $\delta^{18} O$  variations. The minimum  $\delta^2 H$  value was also observed in February 2005 (-106 %), while the maximum was recorded in July 2003 (-8 %). The mean calculated  $\delta^{18} O$  and  $\delta^2 H$  values for the observed period were -6.5 %

Table 1. Isotopic composition of precipitation at Portorož airport ( $d$ – deuterium excess, A – tritium activity, * – the numerical values are below the detection limit, and are given here only for the purpose of statistical evaluation of data).										
Month/ Year	δ <sup>2</sup> H (‰)	δ <sup>18</sup> O (‰)	d (‰)	A (TU)		Month/ Year	δ <sup>2</sup> H (‰)	δ <sup>18</sup> O (‰)	d (‰)	A (TU)
10/0000	FO 1	7.04	10.0	F 0	1	10/0000	94.0	0.07	10.0	г 1

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$					
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Month/ Year	δ <sup>2</sup> H (‰)	δ¹8O (‰)	d (‰)	A (TU)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	10/2000	-50.1	-7.84	12.6	5.2
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	11/2000	-27.8	-4.63	9.2	6.5
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	12/2000	-75.4	-10.52	8.7	1.9
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	01/2001	-34.4	-4.89	4.7	1.5
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	02/2001	-40.7	-5.45	2.8	5.7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	03/2001	-39.3	-5.25	2.7	5.9
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	04/2001	-21.6	-3.77	8.5	6.8
07/2001         -37.0         -5.68         8.5         12.5           08/2001         -63.5         -8.24         2.4         18.3           09/2001         -48.4         -7.20         9.2         13.2           10/2001         -18.8         -3.64         10.3         9.8           11/2001         -23.7         -4.45         11.8         5.9           12/2001         -45.6         -8.07         18.9         8.1           01/2002         -44.6         -6.06         3.9         0.8*           02/2002         -39.7         -5.58         4.9         0.0*           03/2002         -         -         -         -           04/2002         -41.3         -6.04         7.0         6.4           05/2002         -17.7         -3.15         7.5         6.8           06/2002         -32.6         -5.30         9.8         8.9           07/2002         -39.5         -5.93         7.9         9.0           08/2002         -44.7         -6.84         9.9         3.9           09/2002         -49.1         -7.73         12.7         3.7           10/2002         -23.6 <t< td=""><td>05/2001</td><td>-20.4</td><td>-3.58</td><td>8.3</td><td>16.0</td></t<>	05/2001	-20.4	-3.58	8.3	16.0
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	06/2001	-66.8	-9.53	9.5	15.7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	07/2001	-37.0	-5.68	8.5	12.5
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	08/2001	-63.5	-8.24	2.4	18.3
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	09/2001	-48.4	-7.20	9.2	13.2
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	10/2001	-18.8	-3.64	10.3	9.8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	11/2001	-23.7	-4.45	11.8	5.9
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	12/2001	-45.6	-8.07	18.9	8.1
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	01/2002	-44.6	-6.06	3.9	0.8*
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	02/2002	-39.7	-5.58	4.9	0.0*
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	03/2002	-	-	-	-
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	04/2002	-41.3	-6.04	7.0	6.4
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	05/2002	-17.7	-3.15	7.5	6.8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	06/2002	-32.6	-5.30	9.8	8.9
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	07/2002	-39.5	-5.93	7.9	9.0
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	08/2002	-44.7	-6.84	9.9	3.9
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	09/2002	-49.1	-7.73	12.7	3.7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	10/2002	-23.6	-5.31	18.9	1.4*
01/2003         -68.5         -10.20         13.1         1.6           02/2003         -80.0         -10.65         5.2         2.6           03/2003         -16.9         -3.15         8.4         -           04/2003         -45.6         -6.58         7.0         5.6           05/2003         -20.5         -2.97         3.3         13.2           06/2003         -30.8         -4.47         5.0         11.6           07/2003         -7.7         -1.56         4.9         11.5           08/2003         -20.8         -3.15         4.4         12.1           09/2003         -30.4         -5.62         14.5         5.4           10/2003         -53.5         -8.56         15.0         5.3	11/2002	-24.6	-5.27	17.5	0.0*
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	12/2002	-58.0	-9.06	14.4	0.6*
03/2003         -16.9         -3.15         8.4         -           04/2003         -45.6         -6.58         7.0         5.6           05/2003         -20.5         -2.97         3.3         13.2           06/2003         -30.8         -4.47         5.0         11.6           07/2003         -7.7         -1.56         4.9         11.5           08/2003         -20.8         -3.15         4.4         12.1           09/2003         -30.4         -5.62         14.5         5.4           10/2003         -53.5         -8.56         15.0         5.3	01/2003	-68.5	-10.20	13.1	1.6
04/2003         -45.6         -6.58         7.0         5.6           05/2003         -20.5         -2.97         3.3         13.2           06/2003         -30.8         -4.47         5.0         11.6           07/2003         -7.7         -1.56         4.9         11.5           08/2003         -20.8         -3.15         4.4         12.1           09/2003         -30.4         -5.62         14.5         5.4           10/2003         -53.5         -8.56         15.0         5.3	02/2003	-80.0	-10.65	5.2	2.6
05/2003         -20.5         -2.97         3.3         13.2           06/2003         -30.8         -4.47         5.0         11.6           07/2003         -7.7         -1.56         4.9         11.5           08/2003         -20.8         -3.15         4.4         12.1           09/2003         -30.4         -5.62         14.5         5.4           10/2003         -53.5         -8.56         15.0         5.3	03/2003	-16.9	-3.15	8.4	-
06/2003         -30.8         -4.47         5.0         11.6           07/2003         -7.7         -1.56         4.9         11.5           08/2003         -20.8         -3.15         4.4         12.1           09/2003         -30.4         -5.62         14.5         5.4           10/2003         -53.5         -8.56         15.0         5.3	04/2003	-45.6	-6.58	7.0	5.6
07/2003         -7.7         -1.56         4.9         11.5           08/2003         -20.8         -3.15         4.4         12.1           09/2003         -30.4         -5.62         14.5         5.4           10/2003         -53.5         -8.56         15.0         5.3	05/2003	-20.5	-2.97	3.3	
08/2003     -20.8     -3.15     4.4     12.1       09/2003     -30.4     -5.62     14.5     5.4       10/2003     -53.5     -8.56     15.0     5.3	06/2003	-30.8	-4.47	5.0	11.6
09/2003     -30.4     -5.62     14.5     5.4       10/2003     -53.5     -8.56     15.0     5.3	07/2003	-7.7	-1.56	4.9	11.5
10/2003 -53.5 -8.56 15.0 5.3	08/2003				12.1
	09/2003	-30.4	-5.62	14.5	5.4
11/2003 -30.1 -5.72 15.7 3.5	10/2003	-53.5	-8.56	15.0	5.3
	11/2003	-30.1	-5.72	15.7	3.5

and -43 % (n = 74). Taking into account the data for Ljubljana (VREČA et al., 2008), a continental effect, i.e., a decrease of isotopic composition of precipitation over the continent, of approximately 2% in  $\delta^{18}$ O and 17% in  $\delta^{2}$ H was observed.

Deuterium excess variations are presented in Figure 2. The lowest d value for an individual month was observed in January 2004 (-10 %) and probably indicates secondary evaporation processes (Araguas-Araguas et al., 2000, Peng et al., 2004). The highest d values observed in December 2001 and October 2002 (19 %) are characteristic of the autumn rainy period and can be attributed to the influence of Mediterranean cyclogenesis that often prevails in south-western Slovenia during October-December (VREČA et al., 2007). Values around 10 % can be attributed to air masses from the Atlantic (Gat & Dansgaard, 1972; Rozanski et al., 1993). The calculated mean d value is 9.0 ‰.

The LSF regression equation between the isotopic values of individual monthly samples representing LMWL<sub>(LSF)</sub> for Portorož is:

Month/ Year	δ²Η (‰)	δ¹8O (‰)	d (%)	A (TU)
12/2003	-34.6	-6.07	13.9	5.1
01/2004	-92.6	-10.30	-10.2	6.6
02/2004	-46.2	-6.84	8.5	6.7
03/2004	-75.4	-9.77	2.8	6.3
04/2004	-44.3	-6.05	4.1	9.9
05/2004	-44.3	-6.49	7.6	11.8
06/2004	-39.7	-6.16	9.6	11.3
07/2004	-16.5	-3.35	10.3	17.2
08/2004	-21.8	-3.81	8.7	17.3
09/2004	-36.5	-5.48	7.3	10.5
10/2004	-34.5	-5.79	11.8	1.6
11/2004	-58.3	-9.04	14.0	7.0
12/2004	-55.7	-8.37	11.2	7.9
01/2005	-77.9	-10.88	9.2	3.0
02/2005	-105.9	-15.18	15.5	7.8
03/2005	-31.4	-5.47	12.4	3.3
04/2005	-36.5	-5.37	6.5	3.6
05/2005	-47.4	-5.94	0.2	8.8
06/2005	-34.4	-5.22	7.4	7.4
07/2005	-28.0	-4.52	8.1	9.8
08/2005	-37.6	-5.78	8.6	10.7
09/2005	-44.2	-6.47	7.6	9.3
10/2005	-49.0	-7.43	10.4	10.9
11/2005	-67.1	-10.22	14.7	5.4
12/2005	-39.6	-6.87	15.3	6.2
01/2006	-82.3	-11.54	10.0	6.3
02/2006	-74.2	-10.47	9.6	1.4*
03/2006	-61.4	-8.25	4.6	6.1
04/2006	-31.3	-4.48	4.5	9.5
05/2006	-49.9	-6.96	5.8	8.5
06/2006	-66.5	-8.95	5.1	-
07/2006	-16.9	-3.48	10.9	14.7
08/2006	-36.5	-6.14	12.7	5.6
09/2006	-34.8	-5.44	8.7	7.0
10/2006	-10.6	-3.46	17.0	3.6
11/2006	-44.2	-7.08	12.4	4.7
12/2006	-46.0	-7.17	11.4	1.1*

$$\delta^{2}H = (7.82 \pm 0.23) \, \delta^{18}O + (7.84 \pm 1.57);$$
  
 $r = 0.97, \, n = 74$  (2)

The RMA regression equation between the isotopic values of individual monthly samples representing LMWL<sub>(RMA)</sub> for Portorož is:

$$\delta^{2}H = (8.05 \pm 0.22) \, \delta^{18}O + (9.35 \pm 1.55);$$
  
 $r = 0.97, \, n = 74$  (3)

The LMWLs obtained are close to the Global Meteoric Water Line (Gourcy et al., 2005) and also to LMWLs for Ljubljana (Vreča et al., 2008).

The annual weighted mean  $\delta^{18}$ O,  $\delta^{2}$ H and dexcess values for the period 2001-2006 are summarized in Table 2. The minimum annual weighted mean  $\delta^{18}$ O and  $\delta^{2}$ H values were observed in 2006 and the maximum in 2002. The lowest annual weighted mean d excess value was observed in 2001 and the highest in 2003. At a given location, the weighted average annual  $\delta^{18}$ O and  $\delta^{2}$ H values of precipitation remain fairly constant

Table 2. Annual weighted mean  $\delta^2 H$ ,  $\delta^{18}O$ , deuterium excess (d) values (in ‰) and tritium activity (A in TU), \* denotes for n=11.

Year	n	$\delta^2 H$	$\delta^{18}O$	d	A
2001	12	-41.4	-6.15	7.8	9.7
2002	11	-37.0	-6.05	11.4	4.0
2003	12	-42.0	-6.70	11.6	5.4*
2004	12	-45.4	-6.71	8.3	8.6
2005	12	-46.2	-7.01	9.9	7.6
2006	12	-47.5	-7.16	9.8	5.9*
	min	-47.5	-7.16	7.8	4.0
	max	-37.0	-6.05	11.6	9.7
	mean	-43.2	-6.63	9.8	6.9

from year to year 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 (Ingraham, 1998). However, the annual weighted mean  $\delta^{18}{\rm O}$  and  $\delta^2{\rm H}$  values for Portorož show a decreasing trend since 2002. Annual weighted mean  $\delta^{18}{\rm O}$ ,  $\delta^2{\rm H}$  and d values for the whole period 2001–2006 are -6.6 %, -43 % and 9.8 %, respectively and are similar to the mean values.

Monthly weighted mean  $\delta^{18}$ O,  $\delta^{2}$ H and d values are summarized in Table 3. The  $\delta^{18}O$  and  $\delta^{2}H$  values show seasonal variation with the highest values in July, when also the highest mean temperature for the period 2001–2006 was recorded. The lowest values were observed in January and February when the lowest temperatures were recorded. 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 (Ingraham, 1998). The d value varies around 9.3 % with the lowest values in March and the highest in November. The observed pattern shows much higher d values in autumn precipitation, with weighted means between 13.5 and 15.1 ‰, and can be attributed to the influence of Mediterranean air masses over the region during this period (VREČA et al., 2006, 2007). In contrast, the low d values in winter and spring precipitation with weighted means between 5.1 and 8.7 % probably indicate the influence of At-

Table 3. Monthly weighted mean  $\delta^2 H$ ,  $\delta^{18}O$ , deuterium excess (d) values (in ‰) and tritium activity (A in TU), \* denotes for n=4, \*\* denotes for n=5.

Month	n	$\delta^2 H$	$\delta^{18}O$	d	A
January	6	-59.8	-8.23	6.1	3.0
February	6	-59.1	-8.31	7.4	3.5
March	5	-49.9	-6.87	5.1	5.6*
April	6	-38.5	-5.62	6.4	6.6
May	6	-36.5	-5.30	5.9	10.2
June	6	-43.8	-6.57	8.7	11.3**
July	6	-26.3	-4.38	8.7	12.5
August	6	-37.1	-5.96	10.5	7.4
September	6	-44.3	-6.88	10.7	8.5
October	6	-35.1	-6.13	13.9	4.6
November	6	-42.6	-7.21	15.1	3.8
December	6	-45.8	-7.40	13.5	5.6
	min	-59.8	-8.3	5.1	3.0
	max	-26.3	-4.4	15.1	12.5
	mean	-43.2	-6.57	9.3	6.9

lantic air masses and secondary evaporation processes (Araguas-Araguas et al., 2000; Peng et al., 2004). Previous estimations showed that Mediterranean air masses probably contribute between 26 and 45% of precipitation in Portorož (Vreča et al., 2006); however, the mixing of different air masses and rapidly changing meteorological conditions in this area influence the isotopic composition considerably (Vreča et al., 2007).

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 (Schotterer et al., 1996). The correlation between  $\delta^{18}$ O in monthly samples and mean monthly temperature (Figure 4) for the period October 2000 to December 2006 is:

$$\delta^{18}O = 0.19 \text{ T} - 9.14 \text{ (n = 74, r = 0.54)}$$
 (4)

The correlation between monthly weighted mean  $\delta^{18}O$  values and mean monthly temperature (Figure 4) for the period 2001–2006 is:

$$\delta^{18}O = 0.13 \text{ T} - 8.33 \text{ (n = 12, r = 0.79)}$$
 (5)

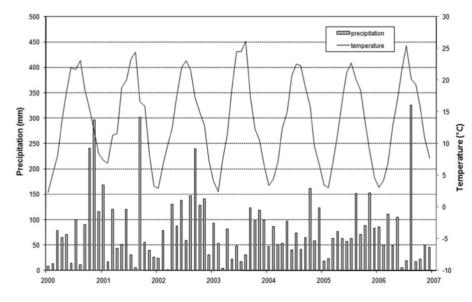


Figure 1.
Monthly precipitation and mean monthly temperature at Portorož airport for period 2000–2006.

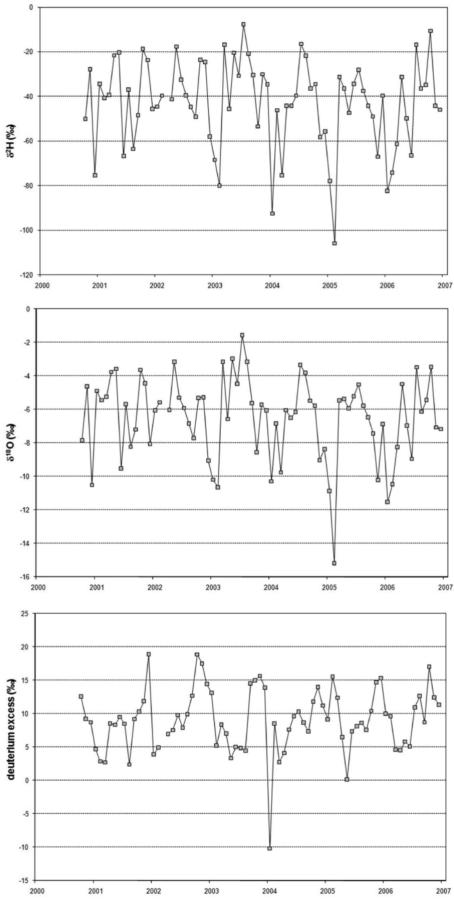


Figure 2. Monthly variations of isotopic composition of  $\delta^2H,\,\delta^{18}O$  and deuterium excess, 2000–2006.

The temperature coefficients of 0.19~%/°C and 0.13~%/°C, respectively, are much lower than that of 0.29~%/°C obtained for Ljubljana and are typical of maritime stations with smaller tempe-

rature variations during the year and a mean temperature higher than  $10^{\circ}\text{C}$  (Rozanski et al., 1993; Vreča et al., 2006).

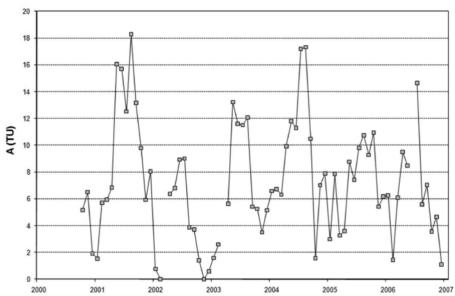


Figure 3. Monthly variations of tritium activity A (in TU), 2000–2006.

Tritium activity in monthly precipitation (Figure 3) shows seasonal variation typical of the Northern Hemisphere (Rozanski et al., 1991). Monthly activities vary between < 1.5 TU and 18.3 TU; maximum activity is usually observed in the summer months, and minimum in the late autumn or winter (Figure 3, Table 3). The highest monthly weighted mean tritium activity is observed in July and the minimum in January. The mean annual tritium activity is 7.2 TU and the weighted mean annual tritium activity 6.9 TU and varies between 4.0 TU and 9.7 TU in the period 2001-2006, but without an observable trend. Since the ban of atmospheric nuclear and thermonuclear bomb-tests, the tritium activity in precipitation showed a basic decreasing trend with a superimposed seasonal structure. However, during the last two decades (approximately), the mean annual values in Zagreb and Ljubljana (Krajcar Bronić et al., 1998; Vreča et al., 2006, 2008) remained stable/constant, at values of about 9 TU. The values observed at Portorož are lower than for Ljubljana and are typical of stations close to the sea (VREČA et al., 2006, 2008).

## **Conclusions**

Results for the isotopic composition of oxygen and hydrogen ( $\delta^{18}O$ ,  $\delta^{2}H$  and  ${}^{3}H$ ) are presented and evaluated for monthly precipitation collected at Portorož airport for the period October 2000 to December 2006. Basic descriptive statistics (i.e. mean, minimum and maximum value), weighted means of the amount of precipitation and local meteoric water lines were calculated. The data obtained provide a better background for understanding the hydrological cycle in SW Slovenia than previously available from three-year long observations.

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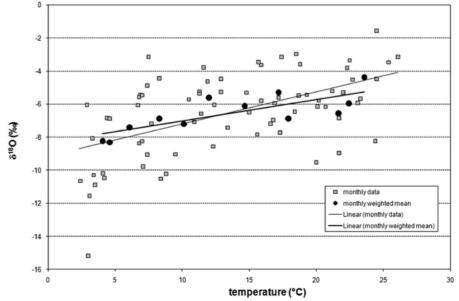


Figure 4. Relation between  $\delta^{18}O$  and local surface air temperature for monthly samples collected in the period 2000–2006 and monthly weighted mean  $\delta^{18}O$  values for the period 2001–2006.

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