



Slovenian Network of Isotopes in Precipitation (SLONIP) – a review of activities in the period 1981–2015

Slovenska mreža opazovanj izotopske sestave padavin (SLONIP) – pregled aktivnosti v obdobju 1981–2015

Polona VREČA¹ & Neža MALENŠEK²

¹Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia;
e-mail: polona.vreca@ijs.si

²Department of Geology, Faculty of Natural Sciences and Engineering, University of Ljubljana, Aškerčeva
cesta 12, SI-1000 Ljubljana, Slovenia

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Ključne besede: padavine, izotopi, kisik, vodik, tritij, GNIP, SLONIP, Slovenija

Abstract

The first investigations of oxygen and hydrogen isotope composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) and the tritium activity (^3H) in precipitation over Slovenia were performed in the frame of tracer experiments conducted in the period 1972–1975 in the Ljubljanica River drainage basin. The first regular and systematic monitoring of isotope composition of precipitation only began in 1981 in Ljubljana but has been extended during the last 35 years to 30 different locations countrywide. Herein, we present a review of research performed during the period 1981–2015. We collected information about sampling, analytical methods, available data and their evaluation including calculations of local meteoric water lines. Based on the data, we identify gaps in the research and make recommendations for future monitoring in the frame of the Slovenian Network of Isotopes in Precipitation (SLONIP).

Izvleček

Prve raziskave izotopske sestave kisika in vodika ($\delta^{18}\text{O}$ in $\delta^2\text{H}$) ter aktivnosti tritija (^3H) v padavinah na območju Slovenije so potekale v okviru sledilnih poskusov, ki so se v obdobju 1972–1975 izvajali na območju reke Ljubljanice. Prvo redno in sistematično spremljanje izotopske sestave padavin se je pričelo leta 1981 v Ljubljani in bilo zadnjih 35 let izvajano na 30 različnih lokacijah. V prispevku podajamo pregled raziskav, ki so bile v Sloveniji opravljene v obdobju 1981–2015. Zbrali smo podatke o vzorčenju, uporabljenih analiznih postopkih, dostopnih rezultatih in obdelavah podatkov vključno z izračuni lokalnih meteornih premic. Na osnovi zbranih informacij smo identificirali pomanjkljivosti predhodnih raziskav in izdelali priporočila za bodoče raziskave v okviru Slovenske mreže opazovanj izotopske sestave padavin (SLONIP).

Introduction

The importance of systematically collecting data on the water isotope composition of precipitation, i.e. stable isotopes of oxygen (expressed as $\delta^{18}\text{O}$) and hydrogen (expressed as $\delta^2\text{H}$) and the radioactive hydrogen isotope tritium (^3H), in the frame of the Global Network of Isotopes in Precipitation (GNIP) has been steadily increasing since it was initiated by the International Atomic Energy Agency (IAEA) and the World Meteorological Organisation (WMO) in 1958 (INTERNET 1). Initially,

the 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. The GNIP provides also 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 the biosphere, providing baseline information for the authentication of commodities, tracking

migratory species and for forensic purposes. Particularly in the last decade has the demand for accurate spatial and temporal predictions of point, regional, and continental-scale $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in precipitation been increasing (TERZER et al., 2013). This is especially the case for those regions where little or no GNIP data exist. In Slovenia water isotopes in precipitation have been systematically monitored since 1981 only in Ljubljana (PEZDIČ, 1999). In 2000, the need for a much more refined understanding of isotope variations was identified due to geographical diversity, which influences the climate and also the water cycle in Slovenia considerably. Therefore, a programme of collecting new data at a higher spatial density and temporal frequency in different parts of the country has been initiated and was extended several times during the last 15 years. Consequently, the number of sampling locations has grown to a Slovenian Network of Isotopes in Precipitation (SLONIP). Unfortunately, the network is still not a part of a national monitoring programme, such as that operating in European countries, for example, in Switzerland (SCHÜRCH et al., 2003) and Germany (STUMPP et al., 2014).

In the past 35 years, water isotopes in precipitation were monitored in Slovenia by different institutions mostly in the frame of short-term research projects and many isotope data were collected but only partly evaluated and published. The data were used in many hydrological and hydrogeological investigations, as well as in investigations of precipitation, moisture recycling in Alpine regions, identification and characterisation of nitrate pollution sources, in evaluations of GNIP data, investigations of bottled waters (e.g. BRENČIČ et al., 2015; MEZGA, 2014; VREČA et al., 2014, 2015a and references therein) and other studies related to food authentication (BIZJAK BAT et al., 2012).

A growing need for water isotope data and the establishment of the SLONIP database, which could be used in other applications, particularly in water resources research and food authentication, stimulated the authors to review the activities performed in Slovenia in the period 1981–2015. The main aims of this paper are the following: 1) to review the history of isotope in precipitation investigations performed in Slovenia in the period 1981–2015, 2) to summarize the main information about sampling, analytical methods used and basic isotope data for a particular sampling location, 3) to identify the main gaps in the research, and 4) to present general recommendations for future work in the frame of SLONIP.

Materials and methods

We collected available publications: national and international journals, conference papers, PhD theses, and Master theses, reporting data on isotope composition of oxygen and hydrogen in precipitation over Slovenia during the period 1981–2015. We also searched the following databases: Google, Google Scholar, Co-operative Online Bibliographic System and Service – COBISS along with unpublished material including internal reports available at the Jožef Stefan Institute (JSI). The following information were collected:

1. sampling data including location - coordinates, type of sampling station, sampling period, sampling collector, sample treatment including filtration and type of storage bottle.
2. analytical methods used for determining stable oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$) isotope composition.
3. analytical methods used for determining tritium activity (^3H) if available together with stable isotope data.
4. reported isotope data, mean isotope values and local meteoric water lines (LMWLs).

Publications in which isotope composition of precipitation was mentioned but it was not clear where, when or how sampling was performed, which analytical methods were used and reporting limited or no numerical data, were used to prepare a list of the main gaps and general guidelines for future work in the frame of SLONIP.

Results and discussion

History of isotopes in precipitation investigations performed in Slovenia in the period 1981–2015

Water isotopes were applied in Slovenia for the first time in investigations in the frame of extensive underground water tracing performed in the period 1972–1975 in the Ljubljana River drainage basin by the international Association of Tracer Hydrology (GOSPODARIČ & HABIČ, 1976). Samples of precipitation were collected at the Šmarata, Postojna and Logatec meteorological stations. Stable isotopes of oxygen and hydrogen were determined in Munich, Germany and tritium activity in Vienna, Austria. Later, in the early 1980s, isotope ratio mass spectrometer (IRMS) techniques for determining stable oxygen and hydrogen isotope composition in water samples were implemented for the first time also in Slovenia at the JSI. The first systematic monitoring of isotopes in precipitation started in 1981 at the

synoptic station Ljubljana–Bežigrad located at the Hydrometeorological Survey of Slovenia (today Slovenian Environment Agency – ARSO; Fig. 1, Tab. 1, PEZDIČ, 1999; VREČA et al. 2008). In 1993, the collection of precipitation was moved to the JSI (station Ljubljana–IJS) and finally, in September 2000 to the Reactor Centre of the JSI (station Ljubljana–Reaktor) in the vicinity of Ljubljana (Fig. 1, Tab. 1, VREČA et al., 2008). The stable isotope composition of monthly precipitation samples was determined at the JSI and tritium activity was measured at the Ruđer Bošković Institute (RBI) in Zagreb, Croatia (KRAJCAR BRONIČ et al., 1998; PEZDIČ, 1999; VREČA et al., 2008). Data have been regularly reported to the IAEA and published until 1994 in the IAEA Technical Reports Series (IAEA 1986, 1990, 1994), and afterwards on the internet (INTERNET 2). Later, in 2008, a review of all data collected in the period 1981–2006 was performed and sampling history recorded (VREČA et al., 2008). New data and corrections were submitted to the IAEA GNIP database (INTERNET 2). Data collected in the period 2007–2010 were reported and evaluated by VREČA et al. (2014) and the whole 1981–2010 dataset was used for the first time to study the relation between isotope composition of precipitation and atmospheric circulation patterns (BRENČIČ et al., 2015).

Monitoring of water isotopes in precipitation was carried out continuously and systematically by the JSI until 2000 only in Ljubljana (Tab. 1, VREČA et al., 2008). A short-term monthly stable isotope monitoring was performed in 1999 and 2000 also at the ARSO precipitation station in Sela na Krasu (Fig. 1, Tab. 1, DOCTOR, 2002) and at Sinji vrh (Tab. 1, TRČEK, 2003). Due to the geographical diversity, which influences the climate of Slovenia considerably (PUČNIK, 1980) and the large karstic aquifers important for the water supply of SW Slovenia, sampling was extended to two stations, namely to the ARSO synoptic station Portorož airport and the ARSO precipitation station Kozina in October 2000 (Fig. 1, Tab. 1). At both stations stable and radioactive water isotopes were monitored on a monthly basis (VREČA et al., 2005–2007, 2009, 2011, 2015a). Unfortunately, since 2004, due to the lack of financial support monitoring has been continued only at the Portorož airport. First monitoring of stable water isotopes in precipitation in eastern Slovenia started in 2001 in Selniška Dobrava (Fig. 1, Tab. 1, MALI, 2006), and was performed by the staff of the Geological Survey of Slovenia (GeoZS). Afterwards, in 2009 two additional locations were selected by the JSI for monitoring stable oxygen and hydrogen isotope composition in SW and SE Slovenia, one at the

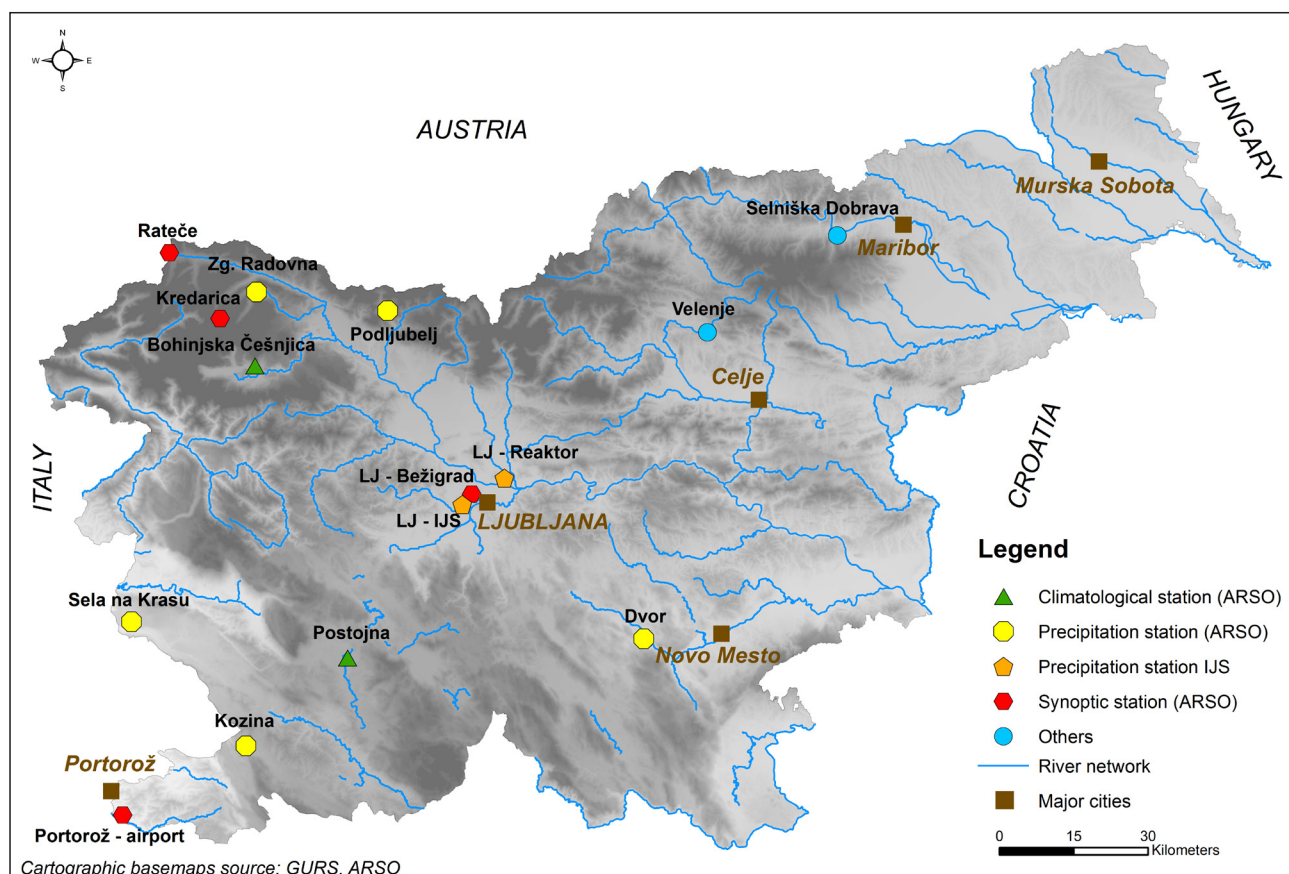


Fig. 1. Slovenian Network of Isotopes in Precipitation (SLONIP) according to sampling station type.

Table 1. Sampling locations and types of sampling station within SLONIP (1 – synoptic station ARSO; 2 – climatological station ARSO; 3 – precipitation station ARSO; 4 – precipitation station at JSI; 5 – others), GNIP code, coordinates and altitude of the sampling station, as well as period of sampling (n.r. – not reported).

Location ^x (x ... type of station)		GNIP code	Coordinates		Altitude (m a.s.l.)	Sampling period
			N	E		
1a	Ljubljana–Bežigrad ¹	1401500	46°03'56"	14°30'45"	299	1981–1992
1b	Ljubljana–IJS ⁴	1401500	46°02'31"	14°29'16"	292	1993–08/2000
1c	Ljubljana–Reaktor ⁴	1401500	46°05'41"	14°35'50"	282	09/2000–
2	Portorož airport ¹	1410501	45°28'31"	13°36'58"	2	10/2000–
3	Kozina ³	1411001	45°36'15"	13°55'54"	486	10/2000–12/2003
4	Dvor ³	1411801	45°48'12"	14°57'41"	195	2009–2012
5	Postojna ²	1411200	45°45'58"	14°11'34"	533	2009–
6	Kredarica ¹	1400800	46°22'45"	13°50'57"	2514	03/2010–
7	Rateče ¹	1400700	46°29'50"	13°42'47"	864	03/2010–
8	Bohinjska Češnjica ²	1400601	46°17'39"	13°56'32"	595	03/2010–06/2014
9	Zgornja Radovna ³	1400801	46°25'42"	13°56'36"	750	04/2010–
10	Podljubelj ³	1401001	46°23'48"	14°17'17"	740	03/2010–06/2014
11	Velenje ⁵	-	46°21'36"	15°07'43"	433	09/2012–05/2015
12	Murska Sobota ¹	-	46°39'08"	16°11'29"	189	2015–
13	Kleče ⁵	-	n.r.	n.r.	n.r.	1997–1998
14	Blatnik ⁵	-	n.r.	n.r.	n.r.	1998–1999
15	Ponikve ⁵	-	n.r.	n.r.	n.r.	1998–1999
16	Sinji vrh ⁵	-	n.r.	n.r.	n.r.	1999–2000
17	Sela na Krasu ³	-	45°49'15"	13°37'38"	270	08/1999–10/2000
18	Selniška Dobrava ⁵	-	46°32'	15°28'	295	1/2001–10/2005
19	Union brewery, Ljubljana ⁵	-	n.r.	n.r.	n.r.	07/2003–06/2005
20	Postojna cave ⁵	-	n.r.	n.r.	n.r.	2004–2005
21	Rogaška Slatina ⁵	-	n.r.	n.r.	n.r.	2008–2010
22	Postojna Karst Research Institute ⁵	-	n.r.	n.r.	n.r.	03/2010–02/2011
23	Ilirska Bistrica ⁵	-	n.r.	n.r.	1043	03/2011–02/2012
24	Snežnik ⁵	-	n.r.	n.r.	1300	03/2011–03/2012

ARSO climatological station Postojna (Fig. 1, Tab. 1, Lojen, personal communication) and the second at the ARSO precipitation station Dvor (Fig. 1, Tab. 1, ZAVADLAV, 2013). Because none of the sampling locations was situated in the mountainous, north-western part of Slovenia that represents an important water resource, we established in 2010 additional isotope monitoring of precipitation at five ARSO meteorological stations in the Julian

Alps and Karavanke including the following: Kredarica, Rateče, Bohinjska Češnjica, Zgornja Radovna and Podljubelj (Fig. 1, Tab. 1, VREČA et al., 2013). At all five locations stable and radioactive water isotopes (VREČA et al., 2013, 2015b; VREČA, 2015) were monitored until July 2014. Since then, monitoring has been continued at Kredarica, Rateče and Zgornja Radovna. In autumn 2012 monitoring of oxygen and hydrogen isotope

composition in Velenje was established (Fig. 1, Tab. 1, KANDUČ et al., 2014) and in 2015 also in north-eastern Slovenia at the ARSO synoptic station Murska Sobota (Lojen, personal communication).

Oxygen and hydrogen in precipitation were monitored monthly also at the Union brewery in Ljubljana during the period 2003–2005 by TRČEK (2005, 2006), at the Postojna cave in the period 2004–2005 by KOGOVŠEK & URBANC (2007), at

Rogaška Slatina during the period 2008–2010 by TRČEK & LEIS (2011) and at Ilirska Bistrica and Snežnik during 2011–2012 (MANČE et al., 2014). In addition, the staff of the GeoZS performed monitoring at Klariči, Korentan, Ptuj and at their institute in Ljubljana (Urbanc, personal communication). Only the isotope composition of oxygen was monitored at Ljubljana (Kleče) in the period 1997–1998 by URBANC & JAMNIK (1998), at Blatnik and Ponikve in the period 1998–1999 by

Table 2. Sampling and analytical methods. HDPE – high-density polyethylene bottles with sealing caps, 50 and 500 mL; PE – polyethylene bottles with sealing caps; b-gl. – borosilicate glass bottles with double caps, 30 or 50 mL; b-pl. – plastic bottle; IRMS – isotope ratio mass spectrometer; CO₂ equil. – water-CO₂ equilibration technique; Zn red. to H₂ – zinc reduction method; Cr red. to H₂ – chromium reduction method; LAS – laser absorption spectroscopy; H₂ equil. – water-H₂ equilibration technique; GPC – gas proportional counting; LSC-EE – electrolytic enrichment liquid scintillation counting; filt. 589/1 – sample filtered through Grade 589/1; filt. 589/3 – sample filtered through Grade 589/3; n.d. – not determined, n.r. – not reported. For sampling collectors see Figure 2.

Location		Sampling collector	Sample bottles and analytical methods			References
			$\delta^{18}\text{O}$	δH	^3H	
1a	Ljubljana–Bežigrad	b	PE IRMS CO ₂ equil.	PE IRMS Zn red. to H ₂	PE GPC	PEZDIČ, 1999, 2003
1b	Ljubljana–IJS	a	PE IRMS CO ₂ equil.	PE IRMS Zn red. to H ₂ IRMS Cr red. to H ₂	PE GPC	VREČA et al., 2008
1c	Ljubljana–Reaktor	a	filt. 589/1 PE, b-gl. IRMS CO ₂ equil.	filt. 589/1 PE, b-gl. IRMS Cr red. to H ₂	HDPE GPC, LSC-EE	VREČA et al., 2014
2	Portorož airport (until 2002)	d	PE IRMS CO ₂ equil.	PE IRMS Cr red. to H ₂	n.d. GPC	VREČA et al., 2005– 2007, 2009, 2011, 2015a
	Portorož airport (since 2002)	b	filt. 589/1 b-gl. IRMS CO ₂ equil.	filt. 589/1 b-gl. IRMS Cr red. to H ₂	HDPE GPC, LSC-EE	
3	Kozina	b	filt. 589/1 PE, b-gl. IRMS (CO ₂ equil.)	filt. 589/1 PE, b-ql. IRMS Cr red. to H ₂	HDPE GPC, LSC-EE	VREČA et al., 2005– 2007, 2009
4	Dvor	b	filt. 589/3 HDPE IRMS CO ₂ equil.	filt. 589/3 HDPE LAS	n.d.	ZAVADLAV, 2013 JSI unpublished data
5	Postojna	b	HDPE IRMS CO ₂ equil. HDPE, b-gl. LAS	HDPE, b-gl. LAS	n.d.	ZAVADLAV et al., 2012 MANDIČ, 2013 JSI unpublished data
6	Kredarica	b	filt. 589/1 b-gl. IRMS CO ₂ equil. filt. 589/1 HDPE, b-gl. LAS	filt. 589/1 HDPE, b-gl. LAS	filt. 589/1 HDPE LSC-EE	VREČA et al., 2012, 2015 JSI unpublished data
7	Rateče	b				
8	Bohinjska Češnjica	b				
9	Zgornja Radovna	b				
10	Podljubelj	b				
11	Velenje	other	IRMS CO ₂ equil.	IRMS H ₂ equil.	n.d.	KANDUČ et al., 2014
12	Murska Sobota	b	b-gl. Analysis in progress	b-gl. Analysis in progress	n.d.	Lojen, personal communication
13	Kleče	n.r.	IRMS CO ₂ equil.	n.d.	n.d.	URBANC & JAMNIK, 1998
14	Blatnik	n.r.	IRMS CO ₂ equil.	n.d.	n.d.	LAPANJE, 2000
15	Ponikve	n.r.	IRMS CO ₂ equil.	n.d.	n.d.	LAPANJE, 2000

Table 2. Sampling and analytical methods – continued.

Location		Sampling collector	Sample bottles and analytical methods			References
			$\delta^{18}\text{O}$	$\delta^2\text{H}$	^3H	
16	Sinji vrh	c	n.r.	n.r.	n.d.	TRČEK, 2003
17	Sela na Krasu	b	HDPE IRMS CO ₂ equil.	HDPE IRMS Cr red. to H ₂	n.d.	DOCTOR, 2002
18	Selniška Dobrava	c	b-pl. IRMS CO ₂ equil.	b-pl. IRMS Cr red. to H ₂	n.d.	MALI, 2006, MALI & URBANC, 2009
19	Union brewery, Ljubljana	n.r.	n.r.	n.r.	n.d.	TRČEK, 2005, 2006
20	Postojna cave	c	n.r.	n.r.	n.d.	KOŠOVŠEK & URBANC, 2007
21	Rogaška Slatina	n.r.	n.r.	n.r.	n.r.	TRČEK & LEIS, 2011
22	Postojna Karst Research Institute	d	n.r.	n.d.	n.d.	MANDIČ, 2013
23	Ilirska Bistrica	d	IRMS CO ₂ equil.	IRMS H ₂ equil.	n.d.	MANCE et al., 2014
24	Snežnik	d	IRMS CO ₂ equil.	IRMS H ₂ equil.	n.d.	MANCE et al., 2014

LAPANJE (2000), and at the Karst Research Institute in Postojna (ZRC SAZU) from June 2010 to February 2011 by MANDIČ (2013). Detailed data (i.e. coordinates) about these locations are not reported. The monitoring of tritium in precipitation, surface and groundwater is performed at other locations in Slovenia in the frame of national programmes approved by the Slovenian Nuclear Safety Administration (KOVAČIČ, 2015 and references therein). Results of these investigations are not discussed in this paper.

To summarize, isotope composition of monthly precipitation was monitored in the period 1981–2015 at 30 different locations in Slovenia, however none of the monitoring operated continuously at the same location during the last 35 years. Data about sampling and analytical methods used for determining isotope composition ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and ^3H , if measured) are summarized in Tables 1 and 2 while the mean isotope values and LMWLs are presented in Table 3.

Sampling of precipitation for isotope analysis in Slovenia

Basic data about 26 locations are summarized in Table 1, which includes all available information like coordinates, sampling period, type of sampling station and GNIP code in case that the station is already or will be included in the worldwide database. Information about type of sampling collector and water sample treatment (filtration, types of storage bottle used) are

presented in Table 2. The 15 locations with known coordinates (except Murska Sobota) are shown in Figure 1 and different types of sampling collectors are presented schematically in Figure 2.

The longest isotope record is available for Ljubljana (Fig.1, Tab. 1) and is maintained by the staff of the Department of Environmental Sciences of the JSI. Samples are collected from the precipitation collector (type a in Fig. 2) as soon as possible after the precipitation event (VREČA et al., 2014). Many stations (Fig. 1, Tab. 1) are part of the Slovenian national meteorological network maintained by the staff of ARSO where precipitation samples are collected from the collector (type b in Fig. 2, Tab. 2) either three times (synoptic stations) or once per day (climatological and precipitation stations). Details about sampling at Selniška Dobrava are described in MALI (2006). They collected precipitation from a system connected by a tube to a glass bottle (type c in Fig. 2). Similar collectors with an isolated vessel buried in the soil were used at Sinji vrh (TRČEK, 2003), at the Postojna cave (KOŠOVŠEK & URBANC, 2007) and at four stations maintained by the GeoZS (Urbanc, personal communication). The high-density polyethylene (HDPE) collectors containing paraffin oil to prevent evaporation during sampling were used at four locations (Fig. 2d, Tab. 2), at Portorož until 2002 (VREČA et al., 2011), at Sela na Krasu (DOCTOR, 2002) and at Ilirska Bistrica and Snežnik (MANCE et al., 2014). The collected water was separated from the oil at the end of the month. At Postojna (MANDIČ, 2013)

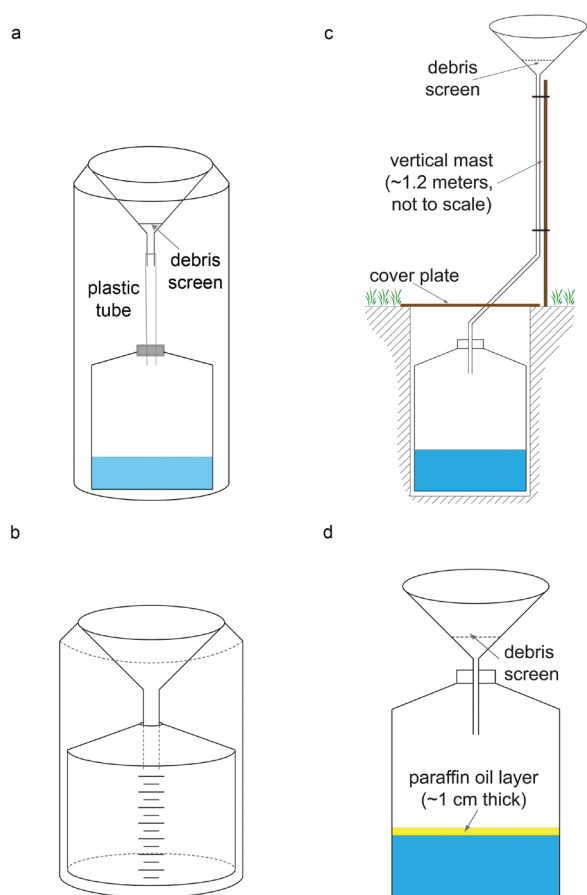


Fig. 2. Different types of collectors used for sampling of precipitation in Slovenia. a – collector used at Jožef Stefan Institute, b – collector used at meteorological stations, c – buried totalizer, d – totalizer with paraffin oil layer. Schematic presentations of type b, c and d collectors kindly provided by S. Terzer, IAEA.

precipitation was sampled also on the roof of the ZRC SAZU and integrated monthly samples were collected in a HDPE container with added paraffin oil. Walls of the collector were completely covered with aluminium foil and Styrofoam to achieve temperature stability and to prevent growth of algae. According to IAEA guidelines (INTERNET 3) approximately 0.5 cm film of paraffin is recommended. However, a thicker paraffin layer (approximately 1 cm) will be recommended in updated guidelines as shown schematically for sampling collector type d in Figure 2 (Terzer, personal communication). In Velenje HDPE collector was used (KANDUČ et al., 2014). For Kleče, Blatnik, Ponikve, the Union brewery and Rogaska Slatina details about how the samples were collected are not given.

At the laboratory impurities (e.g. dust, particles) were removed from the samples collected at the stations Ljubljana-Reaktor, Portorož, Kredarica, Rateče, Bohinjska Češnjica, Zgornja Radovna and Podljubelj by filtration through 12–25 μm

pore size ashless filter papers (Grade 589/1 Black Ribbon, Whatman, UK) before taking aliquots for the different isotope analyses (VREČA et al., 2014, 2015a). ZAVADLAV (2013) reports filtration of samples through 2 μm pore size ashless filters (Grade 589/3, Whatman, UK). For other sampling stations filtration of samples is not reported. Samples were stored either in polyethylene, HDPE or in borosilicate glass bottles (Tab. 2).

Analytical methods used for determining stable oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$) isotope composition

Oxygen isotope composition ($\delta^{18}\text{O}$) was determined at all locations and in all cases the $\delta^{18}\text{O}$ was measured using the water- CO_2 equilibration technique (EPSTEIN & MAYEDA, 1953; AVAK & BRAND, 1995, Tab. 2). However, different IRMS were used including either a dual inlet Varian MAT 250 at JSI (URBANC & JAMNIK, 1999; PEZDIČ, 1999; LAPANJE, 2000; VREČA et al., 2008, 2011), Finnigan DELTA^{plus} at the Joanneum Research (JR) in Graz, Austria (MALI, 2006; MANDIČ, 2013; VREČA et al., 2008, 2011), Thermo Finnigan DELTA^{plus} XP at the University of Rijeka (UR), Croatia (MANČE et al., 2014) or a continuous flow IsoPrime IRMS at the JSI (Lojen, personal communication; ZAVADLAV, 2013; ZAVADLAV et al., 2012; VREČA et al., 2013, 2014, 2015a; VREČA, 2015). DOCTOR (2002) and TRČEK (2003, 2005, 2006) report that analyses were performed at the Institute of Groundwater Ecology (GSF) in Neuherberg, Germany but do not state the type of IRMS used for analysis. KOGOVŠEK & URBANC (2007), TRČEK & LEIS (2011) report just that analyses were performed at the JR in Graz, Austria and KANDUČ et al. (2014) at the National Institute of Geophysics and Volcanology (INVG) in Palermo, Italy. Investigations at Murska Sobota started in 2015 and sample analysis is in progress at the JSI. Samples collected by the GeoZS at four locations around Slovenia were analysed at the JSI (Urbanc, personal communication).

For certain samples (Tab. 2), $\delta^{18}\text{O}$ was determined by off-axis integrated cavity output laser absorption spectroscopy (LAS) (OA-ICOS, Los Gatos Research, Mountain View CA, United States of America) at the IAEA Isotope Hydrology Laboratory (IHL) in Austria according to the analytical protocol of WASSENAAR et al. (2014).

Hydrogen isotope composition ($\delta^2\text{H}$) was determined at 25 locations using different analytical methods. These included H_2 generated by reduction of water over hot zinc – Zn (PEZDIČ, 1999), reduction of water over hot chromium – Cr (GEHRE et al., 1996; MORRISON et al., 2001) or by water- H_2 equilibration using platinum – Pt

(HORITA et al., 1989; COPLEN et al., 1991, Tab. 2). Measurements were performed on different IRMS like the dual inlet Varian MAT 250 at JSI (PEZDIČ, 1999; VREČA et al., 2008, 2011) or the Finnigan DELTA^{plus} XP at the JR (MALI, 2006; VREČA et al., 2008, 2011, 2014, 2015a) and at the UR (MANCE et al., 2014). DOCTOR (2002) reports that the chromium reduction method (GEHRE et al., 1996) was used at the GSF, however similar as in TRČEK (2003, 2005, 2006) no information about the type of IRMS used for analysis is reported. KOGOVŠEK & URBANC (2007) and TRČEK & LEIS (2011) report just that the analyses were performed at JR in Austria, while KANDUČ et al. (2014) report that analyses were performed at the INVG. Investigations at Murska Sobota started in 2015 and sample analysis is in progress at the JSI. Samples collected by GeoZS at four locations around Slovenia are analysed at the JSI (Urbanc, personal communication).

For certain samples (Tab. 2), $\delta^2\text{H}$ was determined also by LAS at IAEA IHL according to the analytical protocol of WASSENAAR et al. (2014).

Results are reported as δ values in per mill (‰) relative to the Vienna-SMOW standard (COPLEN et al., 2002). Methods used in different laboratories are described in more detail in PEZDIČ (1999), MALI (2006) and MANDIČ (2013). The authors usually report that measurements were carried out together with laboratory standards calibrated periodically against international standards, as recommended by the IAEA and that the measurement precision was better than ± 0.1 ‰ for $\delta^{18}\text{O}$ and ± 1 ‰ for $\delta^2\text{H}$. In some cases, better precision was reported (e.g. TRČEK & LEIS, 2011).

Analytical methods used for determining tritium activity (^3H) if available together with stable isotope data

Tritium activity was monitored in the frame of SLONIP activities only at 11 locations (Tab. 2). Analyses of samples from Ljubljana, Portorož and Kozina were performed at the RBI either by the gas proportional counting (GPC) technique (KRAJCAR BRONIČ et al., 1998; VREČA et al., 2006, 2008, 2011 and references therein) or by the liquid scintillation counting technique (LSC) following electrolytic enrichment (EE) (VREČA et al., 2014, 2015a and references therein). In samples collected in the second half of 2003 in Ljubljana, Portorož and Kozina, ^3H activity was determined at the IHL after EE by the LSC technique (VREČA et al., 2006) while samples collected after 2010 were analysed after EE by LSC at the JSI (VREČA et al., 2014, 2015a, 2015b). TRČEK & LEIS (2011) report only that ^3H measurements were performed in the Isotope laboratory HYDROSYS in Hungary.

Meteorological data

The most rational approach for monitoring isotopes in precipitation is to perform sampling at meteorological stations that are part of a national network such as the Swiss National Network for the observation of Isotopes in the Water Cycle – NISOT (SCHÜRCH et al., 2003). Therefore, the JSI cooperates with the staff of ARSO meteorological stations where meteorological data like precipitation and air temperature, are available from the ARSO database (INTERNET 4). We performed in the past isotope monitoring at 11 different ARSO stations (Tab.1, Fig. 1) and since 2015 sampling has been performed at six ARSO stations (Tab. 1). Unfortunately, air temperature data were not available for the majority of isotope monitoring stations including the ARSO precipitation stations: Sela na Krasu, Kozina, Dvor, Zgornja Radovna and Podljubelj, and therefore it was not possible to determine the relation between isotope composition and temperature. Precipitation data in numerical form (expressed in mm) for other than ARSO stations, except precipitation for Ljubljana-Reaktor (VREČA et al., 2014) are not reported. However, precipitation data are presented graphically by TRČEK (2003, 2006), KOGOVŠEK & URBANC (2007), and MALI & URBANC (2009).

Data reduction

Most publications report basic descriptive statistics (mean $\delta^{18}\text{O}$, $\delta^2\text{H}$) while deuterium excess (d -excess) as defined by DANSGAARD (1964) is not always calculated and reported. Even less publications report values weighted by the amount of precipitation and consequently the influence of precipitation amount at a particular location is not determined. As recommended by the IAEA (1992), the summations have to be calculated over all collected samples per year and per month over the period. The minimum required number of data is eight monthly measured samples per year and more than 70 % of total precipitation collected per year. For example, in Selniška Dobrava (MALI, 2006) these requirements were not fulfilled, many monthly data are missing and therefore caution is needed in future calculations and interpretations.

Reporting isotope data, mean isotope values and local meteoric water lines

Numerical data are evaluated and published for Ljubljana and Portorož until the end of 2010, and for the period 2011–2015 evaluation of the data is in progress. For Sela na Krasu (DOCTOR, 2002), Kozina (VREČA et al., 2005; GNIP database), Selniška Dobrava (MALI, 2006) and Velenje

(KANDUČ et al., 2015) data are reported for the whole sampling period, while for Dvor only oxygen data for 2009 – 2010 are reported (ZAVADLAV, 2013). Evaluation of data collected by the JSI for the stations Kredarica, Rateče, Bohinjska Češnjica, Zgornja Radovna, Podljubelj, Dvor and Postojna for the whole sampling period is in progress. Figure 3 shows the number of evaluated or partly evaluated data for Ljubljana and the different regions of Slovenia. In the eastern part of the country, there is a deficiency of numerical data and the new data from Murska Sobota will help fill this data gap for NE part of the country.

Arithmetic and weighted means together with LMWLs as reported in publications are presented in Table 3. Complete data are only available for Ljubljana, Portorož and Kozina. Mean isotope composition of oxygen and hydrogen together with d -excess are reported for 13 locations, while tritium and weighted mean values are reported only rarely (Tab. 3). Arithmetic or weighted means can be further used for geostatistical evaluation of the data and modelling the geospatial distribution of water isotopes in precipitation. VREČA et al. (2010) reported the first presentation of such a map for oxygen isotope composition of precipitation over Slovenia in 2010. The spatial distribution

of $\delta^{18}\text{O}$ in precipitation has been explained by a simple multiple regression model, based on the meteorological (temperature) and geographic factors (latitude and elevation) and a continuous digital map of the $\delta^{18}\text{O}$ distribution over Slovenia has been generated using GIS tools. Further evaluations of the data are in progress and will take into account data collected during the last 35 years. The review shows that the data sets, available for Slovenia during the same period, do not always overlap and therefore in spatial modelling, these gaps, have to be taken into account adequately. This is particularly important in the preparation of reliable geospatial maps and in their future implementation in water resources research, food authentication and other applications in Slovenia.

Authors report rarely local meteoric water lines (LMWL) and only in a few cases details about regression analysis are given (Tab. 3, VREČA et al. 2008, 2011, 2014, 2015a). For Ljubljana many different LMWLs are reported but users have to be aware of the details about different lines which are all close to the Global Meteoric Water Line (GMWL) defined by CRAIG (1961). Differences among the LMWLs are due to the different observation periods, number of data, or the type of regression calculations. These factors should be

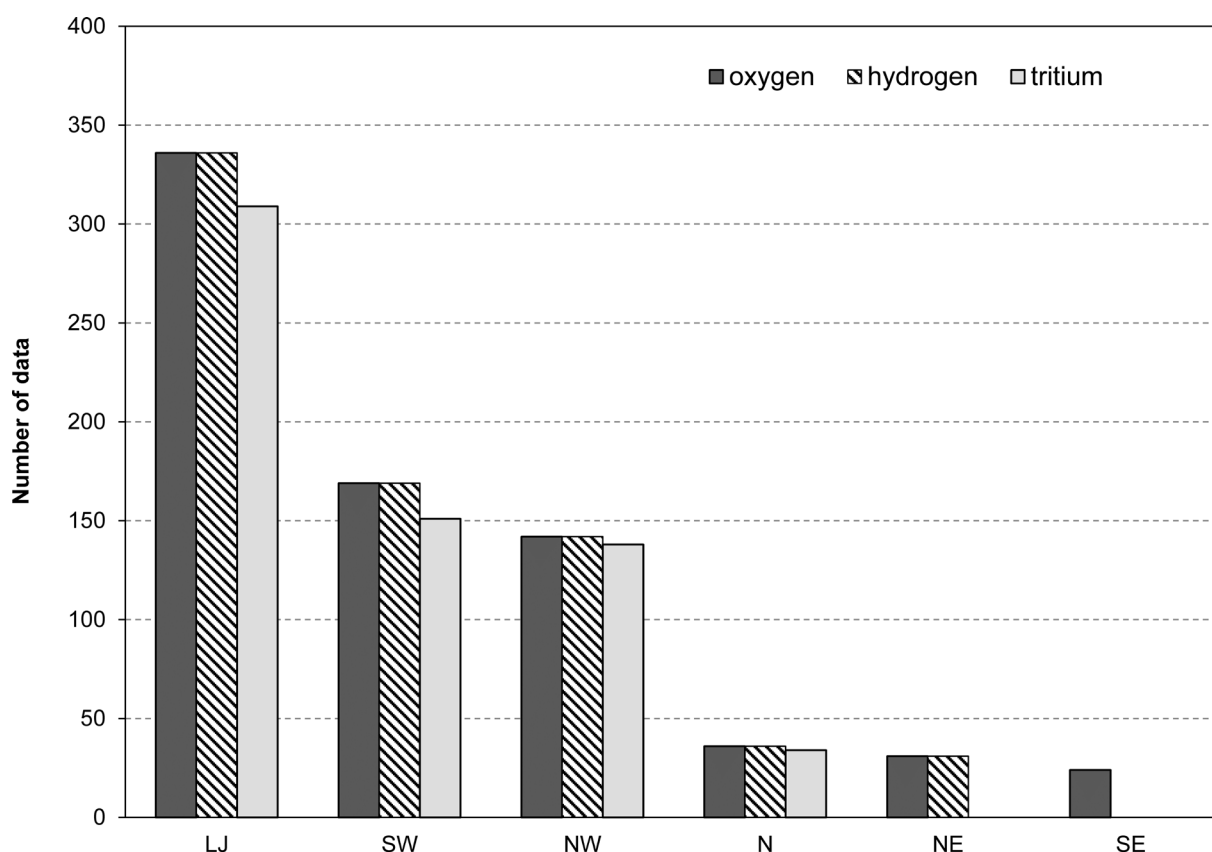


Fig. 3. Number of oxygen ($\delta^{18}\text{O}$), hydrogen ($\delta^2\text{H}$) and tritium (^3H) monthly data evaluated for Ljubljana (LJ) and different regions of Slovenia: south-western (SW – locations 2, 3 and 17 in Table 1), north-western (NW – locations 6 to 9 in Table 1), northern (N – location 10 in Table 1), north-eastern (NE – locations 11 and 18 in Table 1) and south-eastern (SE – location 4 in Table 1) part of Slovenia.

Table 3. Local meteoric water lines (LMWLs), arithmetic and weighted mean isotope values. LSF – least squares fit, RMA –reduced major axis regression (called also orthogonal regression), OLSF – ordinary least square regression, PWLSR – precipitation weighted least square regression, * – calculated from the available numeric data, n.d. – not determined, n.r. – not reported.

Location	Sampling period	LMWL	Arithmetic mean				Weighted mean				References
			$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	<i>d</i> (‰)	^3H (TU)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	<i>d</i> (‰)	^3H (TU)	
Ljubljana	n.r.	$r = 0.99, n = 90$ $\delta^2\text{H} = (8.197 \pm 0.276) \times \delta^{18}\text{O} + (10.834 \pm 2.468)$	-8.5	-60	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	PEZDIČ, 1999
Ljubljana	1982–1994	$r = 0.99, n = 90$ $\delta^2\text{H} = 8.83 \times \delta^{18}\text{O} + 16.5$	n.r.	n.r.	n.r.	n.r.	-8.73	-60.6	n.r.	n.r.	PEZDIČ, 2003
Ljubljana	1981–1996	$r = 0.99, n = 149$ $\delta^2\text{H} = (8.1 \pm 0.1) \times \delta^{18}\text{O} + (11.1 \pm 0.8)$	-9.3	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	KRAJČAR BRONIĆ et al., 1998
Ljubljana	1981–2006	LSF: $r = 0.99, n = 290$ $\delta^2\text{H} = (7.95 \pm 0.08) \times \delta^{18}\text{O} + (8.90 \pm 0.71)$ RMA: $r = 0.99, n = 290$ $\delta^2\text{H} = (8.06 \pm 0.08) \times \delta^{18}\text{O} + (9.84 \pm 0.71)$	-8.7 n=290	-60 n=290	9.4 n=290	16.4 n=264	-8.57 n=290	-59.1 n=290	9.5 n=290	n.d.	VREČA et al., 2008 # - period 1998-2006
Ljubljana	2001–2003	RMA: $r = 0.99, n = 36$ $\delta^2\text{H} = (8.0 \pm 0.2) \times \delta^{18}\text{O} + (9.2 \pm 1.8)$	-8.3 n=36	-57 n=36	9.3 n=36	8.1 n=35	-8.1 n=36	-55 n=36	10.3 n=36	8.0 n=35	VREČA et al., 2006
Ljubljana	2007–2010	OLSF: $r = 0.98, n = 46$ $\delta^2\text{H} = (8.05 \pm 0.22) \times \delta^{18}\text{O} + (10.36 \pm 2.02)$ RMA: $r = 0.98, n = 46$ $\delta^2\text{H} = (8.19 \pm 0.22) \times \delta^{18}\text{O} + (11.52 \pm 1.97)$ PWLSR: $r = 0.99, n = 46$ $\delta^2\text{H} = (7.94 \pm 0.21) \times \delta^{18}\text{O} + (9.76 \pm 1.91)$	-8.6 n=46	-59 n=46	9.9 n=46	8.3 n=45	-8.7 n=46	-59 n=46	10.3 n=46	8.5 n=45	VREČA et al., 2014
Portorož airport	2001–2003	RMA: $r = 0.96, n = 35$ $\delta^2\text{H} = (7.7 \pm 0.4) \times \delta^{18}\text{O} + (7.3 \pm 2.2)$	-5.8 n=35	-38 n=35	9.2 n=35	6.9 n=34	-6.3 n=35	-40 n=35	10.3 n=35	6.3 n=34	VREČA et al., 2006

Location	Sampling period	LMWL	Arithmetic mean				Weighted mean				References
			$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	<i>d</i> (‰)	^3H (TU)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	<i>d</i> (‰)	^3H (TU)	
Portorož airport	2001–2006	LSF: $r = 0.97$, $n = 74$ $\delta^2\text{H} = (7.82 \pm 0.23) \times \delta^{18}\text{O} + (7.84 \pm 1.57)$	-6.5 $n=74$	-43 $n=74$	9.0 $n=74$	7.2 $n=71$	-6.6 $n=71$	-43 $n=71$	9.8 $n=71$	6.9 $n=71$	VREČA et al., 2011 VREČA et al., 2015a
		RMA: $r = 0.97$, $n = 74$ $\delta^2\text{H} = (8.05 \pm 0.22) \times \delta^{18}\text{O} + (9.35 \pm 1.55)$									
		PWLSR: $r = 0.96$, $n = 71$ $\delta^2\text{H} = (7.80 \pm 0.27) \times \delta^{18}\text{O} + (8.52 \pm 1.85)$									
Portorož airport	2007–2010	OLSF: $r = 0.98$, $n = 47$ $\delta^2\text{H} = (7.96 \pm 0.28) \times \delta^{18}\text{O} + (7.15 \pm 1.81)$	-6.1 $n=47$	-41 $n=47$	7.4 $n=47$	7.2 $n=47$	-6.28 $n=47$	-41.6 $n=47$	8.6 $n=47$	6.4 $n=47$	VREČA et al., 2015a
		RMA: $r = 0.98$, $n = 47$ $\delta^2\text{H} = (8.14 \pm 0.25) \times \delta^{18}\text{O} + (8.28 \pm 1.64)$									
		PWLSR: $r = 0.99$, $n = 47$ $\delta^2\text{H} = (7.87 \pm 0.28) \times \delta^{18}\text{O} + (7.97 \pm 1.87)$									
Kozina	2001–2003	RMA: $r = 0.97$, $n = 36$ $\delta^2\text{H} = (7.7 \pm 0.3) \times \delta^{18}\text{O} + (9.6 \pm 2.2)$	-7.2 $n=36$	-46 $n=36$	11.6 $n=36$	5.6 $n=33$	-7.8 $n=36$	-50 $n=36$	12.2 $n=36$	5.4 $n=33$	VREČA et al., 2006 VREČA et al., 2007
Kredarica	04/2010–03/2013	Data analysis in progress	-11.3 $n=36$	-76 $n=36$	14.5 $n=36$	7.9 $n=36$	n.d.	n.d.	n.d.	7.9 $n=36$	VREČA, 2015 VREČA et al., 2015b
Rateče	04/2010–03/2013	Data analysis in progress	-10.6 $n=35$	-74 $n=35$	11.1 $n=35$	7.5 $n=35$	n.d.	n.d.	n.d.	7.6 $n=35$	
Bohinjska Češnjica	04/2010–03/2013	Data analysis in progress	-8.7 $n=36$	-59 $n=36$	10.6 $n=36$	7.4 $n=33$	n.d.	n.d.	n.d.	6.8 $n=33$	
Zgornja Radovna	04/2010–03/2013	Data analysis in progress	-9.7 $n=36$	-66 $n=36$	11.5 $n=36$	7.5 $n=34$	n.d.	n.d.	n.d.	7.3 $n=34$	
Podljubelj	04/2010–03/2013	Data analysis in progress	-9.4 $n=36$	-65 $n=36$	9.7 $n=36$	7.8 $n=34$	n.d.	n.d.	n.d.	7.6 $n=34$	

Location	Sampling period	LMWL	Arithmetic mean				Weighted mean				References
			$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	<i>d</i> (‰)	^3H (TU)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	<i>d</i> (‰)	^3H (TU)	
Sela na Krasu	08/1999–10/2000	OLSF: $r = 0.99$, $n = 12$ $\delta^2\text{H} = (7.22 \pm 0.31) \times \delta^{18}\text{O} + (6.62 \pm 2.15)$	-6.44 $n=12$	-39.9 $n=12$	11.7 $n=12$	n.d.	-6.71 $n=12$	-41.8 $n=12$	11.9 $n=12$	n.d.	DOCTOR, 2002*
		RMA: $r = 0.99$, $n = 12$ $\delta^2\text{H} = (7.28 \pm 0.28) \times \delta^{18}\text{O} + (7.05 \pm 1.97)$	-6.50 $n=10$	-40.1 $n=10$	11.9 $n=10$	n.d.	-6.47 $n=10$	-40.0 $n=10$	11.8 $n=10$	n.d.	
Sela na Krasu	08/1999–07/2000 (96% of annual precipitation)	n.d.	-6.50 $n=10$	-40.1 $n=10$	11.9 $n=10$	n.d.	-6.47 $n=10$	-40.0 $n=10$	11.8 $n=10$	n.d.	DOCTOR, 2002*
Selniška Dobrava	11/1999–10/2000 (80% of annual precipitation)	n.d.	-7.08 $n=9$	-44.5 $n=9$	12.1 $n=9$	n.d.	-7.31 $n=9$	-46.2 $n=9$	12.2 $n=9$	n.d.	
		$r = 0.99$ $\delta^2\text{H} = 7.296 \times \delta^{18}\text{O} + 1.8373$	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.
Selniška Dobrava	01/2010–10/2005	OLSF: $r = 0.99$, $n = 31$ $\delta^2\text{H} = (7.33 \pm 0.17) \times \delta^{18}\text{O} + (1.85 \pm 1.60)$	-8.71 $n=31$	-61.97 $n=31$	7.69 $n=31$	n.d.	n.d.	n.d.	n.d.	n.d.	MALI, 2006*
		RMA: $r = 0.99$, $n = 31$ $\delta^2\text{H} = (7.39 \pm 0.17) \times \delta^{18}\text{O} + (2.35 \pm 1.55)$	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	
Union brewery, Ljubljana	2003–2005, I. phase	n.r.	-9.07	-67.00	10.45	n.d.	n.d.	n.d.	n.d.	n.d.	TRČEK, 2006
	2003–2005, II. phase	n.r.	-8.12	-56.95	11.72	n.d.	n.d.	n.d.	n.d.	n.d.	
Postojna cave	2004–2005	n.r.	-9.0	n.r.	n.r.	n.d.	n.d.	n.d.	n.d.	n.d.	KOGOVIŠEK & URBANČ, 2007
Rogaška Slatina	2008–2010	$r = 0.99$ $\delta^2\text{H} = 8.44 \times \delta^{18}\text{O} + 14.74$	n.r.	n.r.	n.r.	n.r.	n.d.	n.d.	n.d.	n.d.	TRČEK & LEIS, 2011

taken into account in future applications. In the case of LMWLs reported by PEZDIČ (1999, 2003), TRČEK (2003), MALI (2006) and TRČEK & LEIS (2011) for Sinji vrh, Selniška Dobrava and Rogaška Slatina it is not clear how the lines were calculated. According to the IAEA (1992) and HUGHES & CRAWFORD (2012), the linear correlations between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ can be calculated by the methods usually applied in stable isotope studies – either by the ordinary least squares regression (OLSF, previously called least squares fit – LSF) or the reduced major axis (RMA, called also orthogonal) regression. More recently, HUGHES & CRAWFORD (2012) introduced the precipitation weighted least squares regression (PWLSR) method, which takes into account precipitation in a particular month. The lines are defined as local meteoric water lines ($\text{LMWL}_{\text{OLSF}}$, LMWL_{RMA} and $\text{LMWL}_{\text{PWLSR}}$) and can be significantly different (HUGHES & CRAWFORD, 2012). Such an approach was in Slovenia used only by VREČA et al. (2014, 2015a) for the 2007–2010 isotope records at Ljubljana and Portorož and should be in the future used in all such investigations.

For Sela na Krasu numerical data and precipitation amount are reported and it was possible to perform additional calculations (Tab. 3). Similarly, we calculated the LMWLs for Selniška Dobrava based on data reported by MALI (2006). In both cases caution is needed in further use of the reported data and LMWLs. At Sela na Krasu sampling was performed for less than two years which is insufficient to obtain representative information about a particular location. At Selniška Dobrava sampling was performed for almost five years but only 31 monthly data are available, among them 11 collected in Autumn–Winter and 20 in Spring–Summer. Such a distribution of collected precipitation samples causes a bias of the mean values towards more positive isotope values.

Conclusions

Based on all collected information, we prepared a list of the main gaps in the research and general recommendations for future work in the frame of SLONIP. The list of main gaps includes limited information about sampling location (e.g. missing coordinates), sampling mode (e.g. type of collector, sampling period, sampling frequency, sample treatment and sample storage), and methods (e.g. instrumentation, quality control, measurement uncertainty). Different researchers have used different approaches and only rarely have the IAEA guidelines (INTERNET 3) been strictly followed. Often additional meteorological data and data evaluations are also missing. During the

last 35 years isotope techniques and evaluation approaches have also changed and developed. The main problem is that only a limited amount of data collected at a particular station is publically available and in many cases numerical data is only presented in graphical form. In addition, only part of the data set provided by the JSI is available in the international GNIP database. This is mainly due to the lengthy and expensive measurements in the past, limited and old infrastructure and insufficient financial support in the frame of short-term projects. For this reason, the JSI has cooperated with different laboratories like the RBI from Croatia and the JR and the IAEA from Austria to collect isotope data, and other researchers from Slovenia have often cooperated with foreign laboratories. In 2015 the infrastructure at the JSI was upgraded and now enables independent continuation of monitoring of water isotopes in precipitation in Slovenia. At the JSI we intend to continue with sampling and analysing the monthly precipitation at seven locations in the frame of SLONIP and will focus on more rapid publication and accessibility of the data.

General recommendations for future work in the field of isotope in precipitation monitoring are in detail presented in the IAEA/GNIP precipitation sampling guide (INTERNET 3) and have been greatly improved during the last few years (update in progress). In addition, we recommend that Slovenian researchers collect samples at the ARSO stations maintained daily by the staff of the station, filtration of samples through ashless filter papers (Grade 589/1 Black Ribbon) and the storage of samples in doubly capped borosilicate glass bottles for stable isotope analysis and in HDPE bottles for tritium analysis. When researchers send samples to laboratories we also suggest they communicate with the lab in advance regarding the sampling and storage of samples and to collect all details about measurements (i.e. type of instrument, calibration and procedure, quality control, reference materials used, measurement uncertainty). Finally, it is very important to report numerical data and evaluate data according to IAEA guidelines (1992) and HUGHES & CRAWFORD (2012) and to clearly describe how the data is evaluated.

Development in the field of isotope hydrology has brought a lot of new but complex knowledge. Therefore, it is very important to collect all listed information and report it properly, particularly because nowadays precipitation isotope data are used widely in temporal and spatial investigations of the atmo-, hydro-, bio- and geosphere. Due to the importance of water isotope data it is clear that inappropriate sampling, storage, analyses

and finally data evaluation can lead to wrong interpretations, for instance of spatial and temporal predictions of water isotope values at different scales.

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