GEOLOGIJA 63/2, 251-270, Ljubljana 2020

https://doi.org/10.5474/geologija.2020.019

Synthesis of past isotope hydrology investigations in the area of Ljubljana, Slovenia

Pregled preteklih izotopskih hidroloških raziskav na območju Ljubljane, Slovenija

Klara NAGODE[1], Tjaša KANDUČ[1], Sonja LOJEN[1], Branka BRAČIČ ŽELEZNIK[2], Brigita JAMNIK[2] & Polona VREČA[1]
[1]Jožef Stefan Institute, Department of Environmental Sciences, Jamova 39, SI-1000 Ljubljana, Slovenia; e-mail: klara.nagode@ijs.si
[2]JP VOKA SNAGA d.o.o., Vodovodna 90, 1000 Ljubljana, Slovenia

Prejeto / Received 5. 5. 2020; Sprejeto / Accepted 2. 11. 2020; Objavljeno na spletu / Published online 7. 12. 2020

Key words: water, stable isotopes, hydrogen, oxygen, carbon, Ljubljansko polje, Ljubljansko barje
Ključne besede: stabilni izotopi, vodik, kisik, ogljik, Ljubljansko polje, Ljubljansko barje

Abstract

Water isotope investigations are a powerful tool in water resources research as well as in understanding the impact that humans have on the water cycle. This paper reviews past hydrological investigations of the Ljubljansko polje and Ljubljansko barje aquifers that supply drinking water to the City of Ljubljana, with an emphasis on hydrogen, oxygen and carbon stable isotope ratios. Information about the methods used and results obtained are summarised, and the knowledge gaps identified. Overall, we identified 102 records published between 1976 and 2019. Among them, 41 reported stable isotope data of groundwater, surface water and precipitation and were further analysed. Isotope investigations of the Ljubljansko barje began in 1976, while groundwater and surface water investigations of the Ljubljansko polje and along the Sava River began as late as 1997. Isotope investigations of carbon started even later in 2003 in the Ljubljansko polje and in 2010 in the Ljubljansko barje. These investigations were performed predominantly in the frame of short-term groundwater research projects at five main wellfields and sites along the Sava River. Almost no large-scale, long-term stable isotope studies have been conducted. The exceptions include groundwater monitoring by the Union Brewery in Ljubljana (2003-2014) and precipitation in Ljubljana since 1981. Since 2011, more detailed surveys of the Ljubljansko barje were performed, and in 2018, the first extensive investigation started at wellfields and objects that form part of the domestic water supply system. Given the number of available studies, we felt that publishing all the numerical data and appropriate metadata would allow for a better understanding of the short and long-term dynamics of water circulation in the urban environment. In the future, systematic long-term approaches, including the appropriate use of isotopic techniques, are needed.

Izvleček

Izotopske raziskave se uporabljajo za proučevanje vodnih virov ter človeškega vpliva na vodni krog. V članku podajamo pregled preteklih izotopskih hidroloških raziskav na območju ljubljanskih vodonosnikov s poudarkom na uporabi razmerij stabilnih izotopov vodika, kisika in ogljika do leta 2019. Zbrali smo podatke o metodah in rezultatih ter identificirali glavne pomanjkljivosti preteklih raziskav. V sklopu pregleda smo zbrali različne vire (skupno 102) z informacijami, ki se nanašajo na karakterizacijo vodonosnikov, pomembnih za oskrbo z vodo na območju mestne občine Ljubljana. Med zbranimi viri je 41 takšnih, ki smo jih podrobneje pregledali, saj poročajo o izotopskih raziskavah podzemne in površinske vode ter padavin. V Sloveniji so bile izotopske raziskave kisika in vodika v podzemni vodi prvič izvedene na Ljubljanskem barju leta 1976, medtem ko so se raziskave na Ljubljanskem polju ter na reki Savi pričele šele 1997. Izotopske raziskave ogljika v podzemni vodi so se pričele kasneje: na Ljubljanskem polju leta 2003 ter na Ljubljanskem barju leta 2010. Spremljanje izotopske sestave se je na obravnavanem območju v preteklosti izvajalo večinoma v sklopu različnih raziskav podzemne vode v glavnih petih črpališčih ter na reki Savi. Raziskave so potekale pretežno v sklopu različnih kratkotrajnih projektov ter so redko vključevale večje območje (npr. Ljubljansko polje in barje). Daljše zvezne izotopske raziskave podzemne vode so potekale od 2003 do 2014 na območju Pivovarne Union, spremljanje padavin pa poteka v Ljubljani od leta 1981. Od leta 2011 so potekale podrobnejše izotopske raziskave na Ljubljanskem barju, leta 2018 pa so bile opravljene prve obsežnejše izotopske raziskave, tako na črpališčih kot tudi objektih, ki so del javnega vodovodnega sistema. Ugotovili smo, da je objavljanje numeričnih podatkov in ustreznih metapodatkov pomembno. Pregled razpoložljivih virov kaže, da bi objava vseh numeričnih podatkov in ustreznih metapodatkov omogočila boljše razumevanje kratke in dolgoročne dinamike kroženja vode v urbanem okolju, zato so v prihodnosti potrebni sistematični dolgoročni pristopi, ki bodo vključevali tudi ustrezno uporabo izotopskih tehnik.

Introduction

As Bowen et al. (2019) states "*Earth's water cycle links solid Earth, biological, and atmospheric systems, and it is both pivotal to the fundamental understanding of our planet and critical to our practical well-being.*" In nature, water is bound in different compartments of the hydrosphere (ice, groundwater, surface water, lakes, soil moisture reservoirs, oceans, and biomass), biosphere, lithosphere and the atmosphere, which form part of a global hydrological cycle. The rapid growth in population, coupled with an increased demand for water by agriculture and industry, are putting pressure on water resources (Mook, 2001). Although the impact that humans are having on the water cycle is indisputable, there is still a lot unknown about how water usage alters regional and global water budgets (Bowen et al., 2019). One of the prerequisites for efficient management of water resources is having reliable information about the quantity and the quality of the resource that is being exploited (Dansgaard, 1954; Craig, 1961).

Stable water isotopes (^{1}H, ^{2}H, ^{16}O, ^{17}O and ^{18}O) and carbon isotopes (^{12}C and ^{13}C) in the dissolved inorganic carbon (DIC) occur naturally. They can be measured using isotope-ratio mass spectrometry (dual-inlet or continuous-flow) (de Groot, 2004), laser spectroscopy (Wassenaar et al., 2018), or by spectrometric imaging methods (Bowen et al., 2019). An isotope abundance of an element is generally reported in ‰ (per mill = parts per thousand = 10^{-3}) deviations relative to the known isotope abundance of a standard, δ: (Gat, 1996):

$$\delta\ (‰) = (R_{sample}/R_{standard} - 1) \times 10^{3}$$

were R_{sample} and $R_{standard}$ present isotope ratios ($^{2}H/^{1}H$, $^{18}O/^{16}O$, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{34}S/^{32}S$) of a heavy isotope to a light isotope in a sample and an international standard, respectively. Because the numerical values obtained by this equation are small they are expressed in delta notation (δ). Delta values can be negative or positive numbers meaning that the isotope ratio of the sample is lower or higher relative to a standard (Gat, 1996; Meier-Augenstein & Schimmelmann, 2019).

Isotopes are an important tool for studying the water cycle and can be divided into two main categories: environmental isotopes (isotope variations in waters by natural processes) and artificial radioactive isotopes (radioactive isotopes that are injected into the system under investigation) (Kendall & Doctor, 2003). $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ values are important in different applications (Gat, 1996; Clark & Fritz, 1997; Ehleringer et al., 2008; Clark, 2015; Bowen et al., 2019):

- $\delta^{18}O$ and $\delta^{2}H$ can be used as conservative tracers if the isotope signature is unmodified within a study system, i.e., to identify water sources contributing to water sampled at a given place;
- $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ and their variations can enable the identification of important water and carbon cycle processes overlooked by other methods;
- $\delta^{18}O$ and $\delta^{2}H$ can link information on the history of water as it moves through the hydrological cycle.

Isotope methods were introduced into catchment hydrology research to help scientists to understand better the geographical origin of water, recharge and discharge processes, biogeochemical processes and the sources and mechanisms of pollution (Clark & Fritz, 1997; Aggarwal et al., 2005; Bowen et al., 2005; Ehleringer et al., 2008; 2016; Jameel et al., 2016; Du et al., 2019).

Concerns over climate change and the increasing demand for water in urban areas has focused research on water supplies and dynamics within the urban system in order to gain a better understanding of the connections between human populations, climate, and water extraction (Ehleringer et al., 2016; Zhao et al., 2017; Tipple et al., 2017).

Water circulates in nature differently than in urban environments, where the world's population is expected to increase to more than 60 % by 2050. Supplying large urban areas with high-quality drinking water and providing water resources in the long term is a major challenge (Jameel et al., 2016; Ehleringer et al., 2016). In Slovenia, drinking water supply is mainly based on groundwater (around 97 % of the drinking water supply is from groundwater resources) (Uhan & Krajnc, 2003) and in the capital city, Ljubljana, it provides an invaluable drinking water resource (Trček, 2017).

In Slovenia, only tritium and radon analyses are prescribed by drinking water legislation (Official Gazette, No. 74/15), however, if the parametric value for tritium is exceeded, it must be investigated to see if the cause is the presence of artificial radionuclides. Parametric values for specific basic ions, e.g., NO_3^-, SO_4^{2-} and trace elements, e.g., Se, Sb, Pb, Ni, Fe, Cu, Cd, Al, As, B in drinking water have also been established (Official Gazette, Nos. 19/04, 35/04, 26/06, 92/06, 25/09, 74/15, and 51/17), while the regular monitoring of stable isotopes of H, O in water and C and N in different compounds (e.g., HCO_3^-, NO_3^-)

is not required by legislation. Despite quite a large number of isotope analyses performed in the past, to date, there has been no comprehensive research in the use of environmental isotopes in urban water management systems in Slovenia.

Here, we review and synthesize past research involving $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ to advance our understanding of the groundwater characteristics of the Ljubljana aquifers, which can be used as the basis for future investigations. We focus on work conducted over the past 40 years. The main aims of this review were the following:

- make a synthesis of past urban hydrology investigations of the Ljubljansko polje and Ljubljansko barje aquifers with emphasis on the use of $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ until 2019;
- collect information about sampling (location, time, type of sampling site) and the analytical methods used;
- identify the main gaps in the previous investigations and propose future activities.

Site description

The two most important groundwater aquifers for the Slovenia capital Ljubljana and its surroundings are the Ljubljansko polje (LP) and Ljubljansko barje (LB) (Fig. 1). The two aquifers are separated by the Golovec, Grajski hrib and Rožnik hills (Fig. 1) (e.g., Vižintin et al., 2009; Janža, 2015).

Two rivers bound the LP aquifer (Fig. 1) – the Ljubljanica River to the south and the Sava River to the north (Jamnik et al., 2003; Ogrinc et al., 2018). Because of the high velocities (10 m/day) and quite plunder groundwater flow (3–4 m^3/s), the quality of groundwater is good (Jamnik et al., 2003; Jamnik & Žitnik, 2020). Hydrological conditions in the area are characterized by strong interactions between surface water and groundwater and by the high velocities of groundwater flow and pollutant transport: that is, up to 20 m/day (Andjelov et al., 2005; Janža et al., 2005). The LP is located in the eastern part of the Ljubljana basin (Ljubljanska kotlina). It was formed by tec-

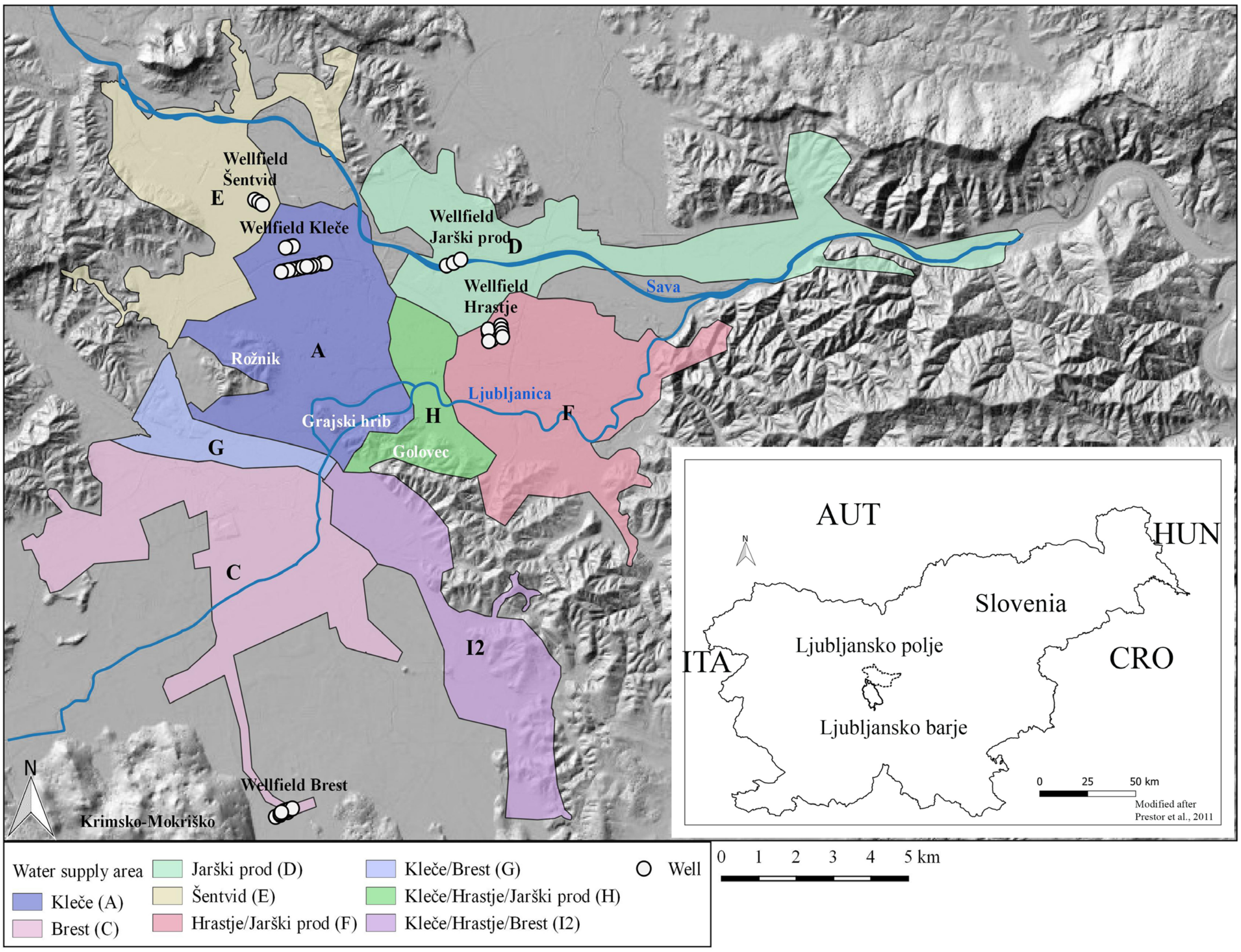

Fig. 1. Locations of the studied area with the main wellfields (Kleče, Hrastje, Brest, Jarški prod and Šentvid) and corresponding water supply areas in the Municipality of Ljubljana (wellfield Hrastje does not represent a unique water supply area). Source of topography: Geodetska uprava RS.

tonic subsidence in the early Pleistocene together with the main neotectonic fault system that runs in an east-west direction. The basin is composed of Permian and Carboniferous slate claystone and sandstone (Žlebnik, 1971). The Pleistocene and Holocene sediments, accumulated by the Sava River, form highly permeable of partially conglomerated sand and gravel.

The thickness of these fluvial sediments increases towards the centre of the LP, where it even exceeds 100 m (Andjelov et al., 2005). The aquifer system has an intergranular porosity, and an unconfined groundwater table, located on 20–25 m below the surface (Vrzel et al., 2018) and can fluctuate up to 10 m (source archive JP VOKA SNAGA d.o.o.). The main recharge of the aquifer comes from infiltration of precipitation and the Sava River, which recharge the aquifer mainly in its north–western part and drains the eastern part of the LP. The LP is also recharged via lateral inflow from the LB multi-aquifer system in the south (Jamnik et al., 2000; Vižintin et al., 2009; Vrzel et al., 2018) as well as from the Kamniško-Bistriško polje (Jamnik & Urbanc, 2000).

Groundwater is exploited at LP from four wellfields: Kleče, Hrastje, Jarški prod and Šentvid where drinking water is pumped from 16, 10, 3 and 3 wells, respectively (Fig. 1). Anthropogenic conditions of the aquifer are characterized by significant pressures of urbanization, industry, traffic, agriculture and old environmental burdens (Jamnik et al., 2012), which occur within the aquifer recharge area (Trček, 2017). To date, several different sources of pollutants have been detected and investigated. These include dispersed pollution sources where pollutants are consistently present (nitrates from agriculture and sewerage losses, new emerging contaminants in traces – pesticides from agriculture, plasticizers, corrosion and fire inhibitors, pharmaceuticals from sewage system losses (Jamnik et al., 2009) while others originate from past agricultural and industrial activities (atrazine, desethyl-atrazine, chromium (VI), trichloroethene, tetrachloroethene). Also, the characteristics of plumes and multipoint pollution contamination sources were recognized (Brilly et al., 2003; Karahodžič, 2005; Prestor et al., 2017).

The LB aquifer (Fig. 1) extends from the southern part of Ljubljana to the Krimsko-Mokrško hills. The Barje is a depression with a stone bedrock that consists in the southern, western and central parts of Upper Triassic dolomite and Jurassic limestone, and in northern and eastern parts of Triassic and Permo-Carboniferous shaly mudstone, quartz sandstone and conglomerate, characterized by low hydraulic conductivity. The gravel fans are present on the borders of the basins (Mencej, 1988/89; Cerar & Urbanc, 2013). The basin was formed by a tectonic depression and filled by alluvial, marshy and lacustrine sediments during the Pleistocene and Holocene (Mencej, 1988/89). The Ljubljanica River contributes to groundwater storage as well as the Krimsko-Mokrško hills (ARSO, 2012; Cerar & Urbanc, 2013). The wellfield at Brest (Fig. 1) is an important source of drinking water for the southern part of the city of Ljubljana (Bračič Železnik & Globevnik, 2014). It consists of 13 wells of different depths (Bračič Železnik, 2016). Water resources in the area are under significant pressure, and environmental problems include water pollution, increasing water demand, flood and drought risk, reduction in retention capacity, decreasing groundwater levels and terrain subsidence (Bračič Železnik & Globevnik, 2014). However, desethyl-atrazine represents the most severe problem for the further development of the Brest water source (Prestor et al., 2017).

The Ljubljana drinking water supply system

The central Ljubljana water supply system consists of five water supply facilities with altogether active 44 wells and more than 1,100 km long water supply network supplying 330,000 users through 43,000 connections. Water supply network includes different objects (i.e., reservoirs, water treatment locations, pumping stations) (Jamnik & Žitnik, 2020). In the central system, some settlements are continuously supplied with drinking water from a single wellfield (water supply areas A, C, D and E in Fig. 1), and others from two or more wellfields (water supply areas F, G, H and I2 in Fig. 1), depending on water consumption and pressure conditions in the system. Wellfield Hrastje (B) does not represent a unique water supply area (Jamnik & Žitnik, 2020).

The water from the wells is pumped directly to consumers or a reservoir for the short-term, from where it is distributed to the users. Water disinfection devices are built-in into the system; however, water does not undergo technical treatments. It is only chlorinated occasionally. For the Brest wellfield UV disinfection is used (Jamnik & Žitnik, 2020).

Methods

Studies related to the characterization of aquifers important for the domestic water supply in the municipality of Ljubljana were reviewed, with a focus on those studies that used $\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C_{DIC}$ values for the characterization of water sources.

Study selection criteria

First, we considered articles and reports related to the water cycle and domestic water supply investigations for the LP and LB published from 1976 to the present (Fig. 2). In the scope of the review, a comprehensive search of journals was completed based on several keywords related to the Ljubljana aquifers (Ljubljana/Ljubljansko polje, Ljubljansko barje, Ljubljana groundwater, Ljubljana water, Ljubljana water supply). The search included all studies containing information about i) sampling, ii) analytical methods, iii) the parameters determined, and iv) isotope data.

In the second step, we focused on studies reporting the use of $\delta^{18}O$ and $\delta^{2}H$ to measure, describe or establish the characteristics of the LP and LB aquifers. Additionally, we also collected studies involving $\delta^{13}C_{DIC}$. Articles on the modelling of LP and LB and other groundwater parameters, e.g., toxic metals in the groundwater and spring waters, electrical conductivity, and pharmaceuticals, and the quantity and quality conditions of groundwater in the Ljubljana aquifers were beyond the scope of this review (Fig. 2).

Search methods

The databases were searched for relevant literature published before November 2019 and included Google, Google Scholar, Science Direct, Co-operative Online Bibliographic System, and Service – COBISS. Included were national and international journals, conference papers, PhD and Master Theses, reporting data on $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ in an urban water system, precipitation, and the Sava River. Also, the reference section of the articles was searched to identify additional sources. We also inspected the working reports for JP VOKA SNAGA d.o.o. available at Jožef Stefan Institute (JSI) including isotope data. Studies published in both Slovene and English were considered.

Information about i) sampling including location coordinates, type of sampling location (groundwater, spring water, precipitation, river) and sampling period; ii) the analytical methods used for $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ analysis, and iii) $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ data were collected and summarised.

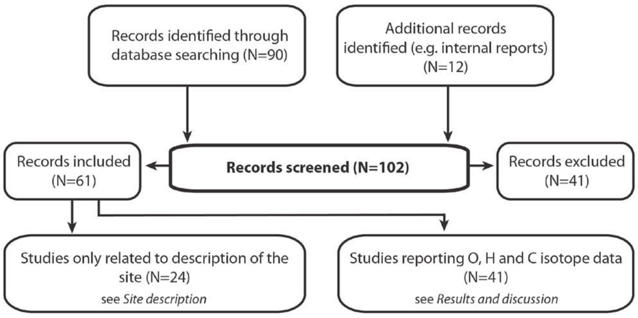

Fig. 2. Flowchart of study selection for detail review synthesis.

Results and discussion

The initial combined search retrieved 102 records (Fig. 2). After removing 41 non-relevant records, the 61 articles remaining were assessed for eligibility. Of these, 24 records were used to summarize site characteristics, while 41 records containing $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ data (Table 1) were reviewed in detail. Some articles were used in both categories. Information about sampling is summarised in subchapter *Sampling*, followed by A*nalytical methods used for determining $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$*. Finally, a summary of the isotope research and the important findings relating to the Ljubljana aquifers is presented.

Sampling

Information collected about the sampling area, sampling locations and type of samples collected in different investigations for isotope analysis is presented in Table 1. Isotope investigations of groundwater were first performed in 1976 at LB (Breznik, 1984) while groundwater and surface water investigations at LP and on the Sava River in Tacen began in 1997 (Urbanc & Jamnik, 1998). The isotope composition of precipitation in Ljubljana has been regularly monitored since 1981 (Pezdič, 1999; Vreča et al., 2008).

At the LP, many investigations were performed at the wellfield Kleče, followed by the wellfields Hrastje, Jarški prod, and Šentvid (Fig. 1, Table 1). Short-term studies were performed at the borehole LMV-1 (located close to the wellfield Kleče). In contrast, long-term investigations were performed in the area of Union Brewery (Table 1). In LB, sampling was mainly conducted in the wellfield Brest (Table 1). Surface waters (e.g., Curnovec, Gradaščica) were also sampled (Urbanc & Jamnik, 2002). On the Sava River, sampling was performed at Tacen, Brod, Črnuče, Šentjakob and Dolsko (see references in Table 1). The Jožef Stefan

Table 1. The list of references related to the isotope investigations performed in the area of Ljubljansko polje (LP), Ljubljansko barje (LB), the Sava River (RS), and precipitation (P). Source of reference: * archive of the JP VOKA SNAGA d.o.o.; ** archive of JSI. (GW = groundwater, P = precipitation, SF = surface water, TW = tap water, VD = well).

Reference	Parameter	Sampling area	Type of sample	Location
Breznik, 1984*	$\delta^{18}O$	LB	GW	Brest
Pezdič, 1998	$\delta^{18}O$, $\delta^{2}H$	LB	P, GW	The southern part of LB
Krajcar Bronić et al., 1998	$\delta^{18}O$, $\delta^{2}H$	LP	P	Ljubljana
Urbanc & Jamnik, 1998	$\delta^{18}O$	LP, RS	GW, SW, P	RS (Tacen), Mostec, Nadgoriški potok, Kleče (V-4, V-6, V-8a, V-11, V-12, V-14, V-15), Šentvid (V-2a), Jarški prod (V-1, V-3), Hrastje (V-1a, V-5, V-8), precipitation-Kleče
Pezdič, 1999	$\delta^{18}O$, $\delta^{2}H$	Ljubljana	P	Ljubljana Bežigrad
Jamnik & Urbanc, 2000	$\delta^{18}O$	LP, RS	GW	Kleče (VIIIa and XII), Hrastje (Ia and V)), Šentvid (IIa) and Jarški prod (I, III), groundwater level stations, precipitation station
Urbanc & Jamnik, 2002	$\delta^{18}O$	LB	GW, SW	Mostec, Gradaščica, Ljubljanica, Curnovec, Holocen aquifer (V-1, V-7, V-9, V-10, V-12, V-13, IŠ-6pl, IŠ-7, IŠ-8, DBP-2, DBP-4, DBP-5, DBP-6, DBP-9). Upper Pleistocene aquifer (Iš-6gl, OP-1, PB-2gl, PB-4, PB-6gl, G-12, PB-1gl, VD-4gl, DBG-2, DBG-4, DBG-5, DBG-6, DBG-9). Lower Pleistocene aquifer (TB-3, B-1, PB-5gl, P-19gl, A-1gl, A-2gl, IŠ-4gl).
Jamnik & Urbanc, 2003	$\delta^{18}O$	LP, LB	GW, P, SW	LP and LB, GeoZS, RS (Tacen)
Pezdič, 2003	$\delta^{18}O$, $\delta^{2}H$	Ljubljana	P	Ljubljana – Bežigrad, Ljubljana – JSI
Andjelov et al., 2005	$\delta^{18}O$, $\delta^{2}H$	LP	GW, SW, P	Nadgoriški potok, Mostec, RS, wells in Kleče (4, 6, 8a, 11, 12, 14, 15), Hrastje (1a, 5, 8), Jarški prod (1, 3), Šentvid (2a)
Brenčič & Vreča, 2005	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$	LP	GW (bottled)	Union Brewery
Trček, 2005	$\delta^{18}O$, ($\delta^{2}H$)	LP	GW, P	Lysimeter Union Brewery
Vreča et al., 2005	$\delta^{18}O$, $\delta^{2}H$	Ljubljana	P	Ljubljana – JSI, Ljubljana – Reaktor
Brenčič & Vreča, 2006	$\delta^{18}O$, $\delta^{2}H$	LP	GW (bottled)	Union Brewery
Trček, 2006	$\delta^{18}O$, $\delta^{2}H$	LP	GW, P	Piezometer Union Brewery
Vreča et al., 2006	$\delta^{18}O$, $\delta^{2}H$	Ljubljana	P	Ljubljana – JSI, Ljubljana – Reaktor
Kanduč, 2006	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$	LP, RS	SW, GW	RS (Brod, Sava Dolsko), LP (Yulon, Hrastje1a, Kleče, vodnjak 17, GeoZS, Kleče 11, Šentvid 2A, Kleče 8a, Hrastje 3, Navje, Petrol - Šmartinska cesta, L.P. Vodovodna, HMZ Hrastje)
Brenčič & Vreča, 2007	$\delta^{13}C_{DIC}$	LP	GW (bottled)	Union Brewery
Ogrinc et al., 2008	$\delta^{18}O$, $\delta^{2}H$	RS	SW, P	RS (Tacen, Dolsko), Ljubljana – Bežigrad, Ljubljana – JSI, Ljubljana – Reaktor
Vreča et al., 2008	$\delta^{18}O$, $\delta^{2}H$	Ljubljana	P	Ljubljana – Bežigrad, Ljubljana – JSI, Ljubljana – Reaktor
Brenčič & Vreča, 2010	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$	LP	GW (bottled)	Union Brewery

Vreča et al., 2011**	$\delta^{18}O$, $\delta^{13}C_{DIC}$	LB	GW, SW	V-1A, V-2A, V-3A, V-4A, V-5, V-7, V-8, and V-9, P-23/10
Brenčič, 2011*	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$	LB	GW, SW	V-1A, V-2A, V-3A, V-4A, V-5, V-7, V-8, and V-9, P-23/10
Urbanc et al., 2012	$\delta^{18}O$	LP, LB	GW, SW	VD Kleče (4, 8a, 11, 14, 17), VD Hrastje (1a, 3), VD Brest (1, 1a, 2a, 3, 4a, 5, 7, 9), VD Jarški prod (1, 3), VD Šentvid (1a)
Cerar & Urbanc, 2013	$\delta^{18}O$	LP, LB	GW, SW, P	LP aquifer, the northern part of LB, the middle part of LB, the southern part of LB – Brest and Iški Vršaj, GeoZS
Vreča et al., 2013**	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$	LB	GW	VD-3a
Mezga, 2014	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$	LP	GW	LMV-1
Mezga et al., 2014	$\delta^{18}O$, $\delta^{2}H$	LP	GW	LMV-1
Vreča et al., 2014	$\delta^{18}O$, $\delta^{2}H$	Ljubljana	P	Ljubljana – Reaktor
Vreča et al., 2015**	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$	LB	GW	VD-3a
Vreča & Malenšek, 2016	$\delta^{18}O$, $\delta^{2}H$	LP	P	Ljubljana – Bežigrad, Ljubljana – JSI, Ljubljana – Reaktor, Kleče
Trček, 2017	$\delta^{18}O$, ($\delta^{2}H$)	LP	GW, P	Union Brewery
Bračič Železnik et al., 2017	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$	LB	GW, SW	VD Brest-3a
Vrzel et al., 2018	$\delta^{18}O$, $\delta^{2}H$	LP, RS	GW, SW, P	RS (Šentjakob), Kleče (8, 11, 12), Hrastje (3, 8), Jarški prod (1, 3), Ljubljana – Reaktor, GeoZS
Ogrinc et al., 2018	$\delta^{18}O$, $\delta^{2}H$	RS	SW	RS (Dolsko)
Vreča et al., 2019a**	$\delta^{18}O$, $\delta^{2}H$	LP, LB, RS	GW, SW, TW	VD Kleče (2, 3, 4, 6, 7, 8a, 9, 10, 11, 12, 13, 14, 15, 16, 17), VD Hrastje (1a, 2, 2a, 3, 4, 5, 6, 7, 8), VD Brest (1, 2, 2a, 3, 4, 4a 5, 6, 7, 8, 9), Jarški prod (1, 2, 3), VD Šentvid (1a, 2a, 3), joint exits from water pumping stations, reservoirs, drinking water fountains, tap water in public and private buildings, RS (Šentjakob, Črnuče, Brod)
Vreča et al., 2019b	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$	LB, LP, RS	GW, SW, TW	VD Kleče (2, 3, 4, 6, 7, 8a, 9, 10, 11, 12, 13, 14, 15, 16, 17), VD Hrastje (1a, 2, 2a, 3, 4, 5, 6, 7, 8), VD Brest (1, 2, 2a, 3, 4, 4a 5, 6, 7, 8, 9), Jarški prod (1, 2, 3), VD Šentvid (1a, 2a, 3), joint exits from water pumping stations, reservoirs, drinking water fountains, tap water in public and private buildings, RS (Šentjakob, Črnuče, Brod)
Vreča et al., 2019c**	$\delta^{18}O$, $\delta^{2}H$	LB, LP	TW	Vrtec Miškolin enota Zajčja Dobrava; Vrtec Pedenjped, enota Zadvor; Vrtec Visji gaj, enota Kozarje Bencinski servis Agip; Vrtec Hansa Christiana Andersena, enota Marjetica; Vrtec Vodmat; Vrtec Mladi rod, enota Kostanjčkov vrtec; Vrtec Mojca, enota Rozle; OS IG - podruznica Iška vas
Vreča et al., 2019d**	$\delta^{18}O$, $\delta^{2}H$	LB, LP	TW	Tap water at location Jože Stefan Institute
Vreča et al., 2019e **	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$	LB	GW	PB – 24b/19
Vreča et al., 2019f **	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$	LB	GW	PB – 24a/19, PB – 24c/19

Institute (JSI) has recorded the isotope composition of precipitation since 1981. Samples of precipitation were first collected at the synoptic station Ljubljana–Bežigrad located at the Hydrometeorological Survey of Slovenia (today Slovenian Environment Agency – ARSO), later at the JSI (station Ljubljana–JSI) and finally at the Reactor Centre of the JSI (station Ljubljana–Reaktor) (Pezdič, 2003; Vreča et al., 2006; Vreča & Malenšek, 2016). Precipitation was collected for a short period in the areas of wellfield Kleče, Union Brewery and at Geological Survey of Slovenia (GeoZS) (see references Table 1).

The first stable water isotope survey of tap water in Slovenia, according to our best knowledge, was performed in 2014 (Vreča et al., 2019c). In this survey, tap water samples were collected for O and H isotope analysis at 105 locations around Slovenia, nine of them at locations in Ljubljana and its vicinity (Vreča et al., 2019c).

To assess the usefulness of environmental isotopes, scientists have been performing systematic monitoring of the Ljubljana drinking water supply system since 2018. The first detailed sampling campaign was carried out between 06/09/18 and 29/11/18 at 103 locations; 41 wells in five water supply facilities, seven joint exits from the water pumping station, 22 reservoirs, two water treatment locations, 13 fountains, and 19 taps (see Table 1). In addition, samples were collected on the Sava River at Brod, Črnuče and Šentjakob (Vreča et al., 2019a; Vreča et al., 2019b). The first 24-hour experiment was performed in the basement of the main building at the Jožef Stefan Institute in Ljubljana with emphasis on the hourly isotope variability of tap water in April 2019 (Vreča et al., 2019d).

From Table 1, the following sampling locations were identified:

- **Wellfields** – Kleče (11 wells), Hrastje (5 wells), Brest (12 wells), Jarški prod (2 wells), and Šentvid (1 well)
- **The Sava River** – five locations: Brod, Črnuče, Dolsko, Šentjakob and Tacen
- **Precipitation** – six locations: synoptic station Ljubljana–Bežigrad, JSI-Ljubljana, Ljubljana-Reaktor, Union Brewery, wellfield Kleče, and GeoZS
- **Other locations** – piezometers and spring water from the LB, lysimeter and piezometers at Union Brewery, groundwater in LMV-1, tap water and different objects of the drinking water supply system.

Analytical methods used for determining stable oxygen, hydrogen and dissolved inorganic carbon isotope composition

Results of $\delta^{18}O$, $\delta^{2}H$ were reported relative to VSMOW (e.g., Urbanc & Jamnik, 1998; Brenčič & Vreča, 2006; Vrzel et al., 2018), while $\delta^{13}C_{DIC}$ was reported relative to the VPDB (e.g., Brenčič & Vreča, 2006; Kanduč, 2006; Vreča et al., 2019e). Isotope ratio mass spectrometers (IRMS) were used for the determination of $\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C_{DIC}$ in water except for some precipitation samples collected at the Ljubljana–Reaktor which were measured by off-axis integrated cavity output laser spectroscopy, OA-ICOS (Vreča et al. 2017).

Oxygen isotope composition ($\delta^{18}O$) is reported in 40 records (Table 1). In all past investigations, the authors reported that the $\delta^{18}O$ was determined by the water-CO_2 equilibration technique (Epstein & Mayeda, 1953; Avak & Brand, 1995) using different IRMS, namely the dual inlet Varian Mat 250 at the JSI (Pezdič, 1998; Urbanc & Jamnik, 1998; Jamnik & Urbanc 2000; Andjelov et al., 2005; Vreča et al. 2005; 2006; 2008; Ogrinc et al., 2008), Finnigan DELTA^{plus} at the Joanneum Research (JR) in Graz, Austria (Brenčič & Vreča 2006; Trček, 2017), Finnigan MAT 250 at the Hydroisotop GmbH laboratory in Schweitenkirchen, Germany (Cerar & Urbanc, 2013; Mezga et al., 2014; Mezga, 2014; Vreča et al., 2015), and a continuous flow IsoPrime (GV Instruments) at the JSI (Bračič Železnik et al., 2017; Ogrinc et al., 2018; Vrzel et al., 2018; Vreča et al., 2014). Trček (2005; 2006) reported that analysis was performed at the Institute of Groundwater Ecology (GSF) in Neuherberg, Germany, but does not state the type of IRMS used for the analysis. The $\delta^{18}O$ analysis of precipitation collected by the JSI at the Ljubljana–Reaktor was performed from February 2007 to the end of 2014, using a continuous flow IRMS IsoPrime (GV Instruments) connected to equilibration system MultiFlow Bio (Vreča et al., 2014). Samples collected since 2015 were measured on a dual inlet Finnigan MAT DELTA^{plus} with CO_2-H_2O equilibrator HDOEQ48 (Vreča et al., 2019a; 2019b; 2019d; 2019e; 2019f).

Hydrogen isotope composition ($\delta^{2}H$) is reported in 32 records using different analytical methods, which included H_2 generated by the reduction of water over hot zinc (Pezdič, 1999), H_2 equilibrated with the water samples using a Pt-catalyst (Horita et al., 1989), reduction on Cr at 800 °C (Gehre et al., 1996; Morrison et al., 2001) or with an OA-ICOS (Wassenaar et al., 2014). Measurements were performed on different IRMS including a dual inlet Varian Mat

250 at the JSI (Pezdič, 1998; Vreča et al., 2005; 2006; 2008; Ogrinc et al., 2008; 2018; Vrzel et al., 2018), Finnigan DELTA^{plus} XP at the Joanneum Research (JR) in Graz, Austria (Brenčič & Vreča, 2006; Vreča et al., 2014; Trček, 2017), Finnigan MAT 251 at the Hydroisotop GmbH laboratory in Schweitenkirchen, Germany (Vreča et al., 2011; 2013; 2015; Mezga et al., 2014; Bračič Železnik et al., 2017). Samples collected from 2015 onwards were measured on the dual inlet Finnigan MAT DELTA^{plus} with CO_2-H_2O equilibrator HDOEQ48 at the JSI (Vreča et al., 2019a; 2019b; 2019d; 2019e; 2019f). Some precipitation samples collected at the Ljubljana–Reaktor were measured at the Isotope Hydrology Laboratory at the International Atomic Energy Agency (IAEA) on a Los Gatos Research OA-ICOS (Vreča et al. 2017).

The carbon isotope composition in the dissolved inorganic carbon ($\delta^{13}C_{DIC}$) is reported in 13 records and was determined using CO_2 collected after the reaction of the water sample with 100 % H_3PO_4 on a continuous flow Europa 20-20 IRMS with ANCA-TG separation module for trace gas analysis (Brenčič & Vreča, 2005; 2007; 2010; Mezga, 2014; Vreča et al., 2019a) or a continuous flow IsoPrime or IsoPrime 100 IRMS with equilibration system MultiFlow Bio at the JSI (Brenčič, 2011, Bračič Železnik et al., 2017; Vreča et al., 2011; 2013; 2015; 2019e; 2019f).

Only a few articles reported the analytical errors (Trček, 2005; 2006; Brenčič & Vreča, 2006; 2007; Ogrinc et al., 2008; 2018; Vreča et al., 2008; 2018; Cerar & Urbanc, 2013; Mezga et al., 2014). Most publications report basic descriptive statistics or isotope ranges and only in a few cases, whole datasets are publicly available (e.g., Brenčič & Vreča, 2006; 2007; Vreča et al., 2008; 2014; Vrzel et al., 2018).

History of the stable isotope research in the catchment area of Ljubljana aquifers

Here we present a summary of the 41 records (Table 1) related to the past stable isotope investigations in the area of LP and LB aquifers. Articles usually report the use of $\delta^{18}O$ and δ^2H in water resources investigations; however, it is interesting, that the $\delta^{13}C_{DIC}$ was determined in only 13 records.

Ljubljansko barje

The first isotope investigations in the area of Ljubljana aquifers were performed in 1976 (Breznik, 1984), as part of the hydrological research into the Brest wellfield between 1974 and 1976. Water samples were collected at the LB aquifer, from the Iška River and other springs in the vicinity. No precise sampling locations with coordinates were reported, and no information was given about the collection of the samples or where the analyses were performed. They reported values for $\delta^{18}O$ between -9.94 and -8.90 ‰ and -65.8 and -58.9 ‰ for δ^2H. From the tritium isotope data, Breznik (1984) concluded that the recharge rate of the lower aquifer is very low.

Samples from the southern part of LB were collected in early spring and autumn in 1993. Nineteen sampling points for groundwater and river base flow measurements were established for the determination of groundwater recharge and storage capacity (Pezdič, 1998). Unfortunately, the sampling locations are presented only graphically, and the author gives no exact coordinates or location names. Precipitation was collected in Ljubljana for the determination of $\delta^{18}O$ and δ^2H values. Pezdič (1998) reported $\delta^{18}O$ values of springs and surface river water of -9.65 and -8.82 ‰, while δ^2H values ranged from -67.4 to -61.2 ‰. The weighted means of $\delta^{18}O$ and δ^2H in precipitation for the year 1993 were -8.07 ‰ and -55.6 ‰, respectively. The author concluded that the contribution of local precipitation was small and infrequent; however, local precipitation could recharge nearby aquifers (Pezdič, 1998).

After 1997, Urbanc & Jamnik (2002) performed more detailed investigations of the LB in which the chemical and isotope composition of groundwater was studied. Isotope investigations combined with hydrogeochemical methods were used to obtain hydrogeological data on the properties of water in individual aquifers: the Holocene aquifer and the upper and the lower Pleistocene aquifers. The authors, however, do not provide any sampling information or at which institute the analyses were conducted. Also, location names are shown only on maps. Surface water and groundwater in wells, piezometers and boreholes (Table 1) were sampled between November 1999 and February 2002. The authors report mean values for $\delta^{18}O$ in surface waters and based on the isotope data, the mean altitude of individual water recharge areas (exact numbers were not provided). The $\delta^{18}O$ values of groundwater in the Holocene aquifer were -8.9 to -8.6 ‰, -9.6 to -8.6 ‰ in the upper Pleistocene aquifer, and -9.5 to -9.2 ‰ in the lower Pleistocene aquifer. Again, values were mainly presented graphically, and numerical values were given only for the lower Pleistocene aquifer (Urbanc & Jamnik, 2002).

Since 2010, many isotope investigations at wellfield Brest were performed. In 2011, $\delta^{18}O$, δ^2H

and $\delta^{13}C_{DIC}$ values were determined in water samples collected during a pumping test from a 200 m deep well (VD Brest-3a) to determine the recharge dynamics, origin and age of groundwater in the dolomite. The investigation began on the 23/05/11 when a step-test was performed, followed by a one-month-long pumping test. In the third step, the rising of water was investigated. Testing finished on 24/06/11 (Brenčič, 2011). The $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ were also determined in seven wells at Brest and in one observation well (P-23/10). The values of $\delta^{18}O$ ranged between -9.98 and -9.61 ‰ and $\delta^{2}H$ between -64.9 and -61.1 ‰. $\delta^{13}C_{DIC}$ values were between -12.8 and -11.8 ‰. The isotope composition of springs near wellfield Brest was also determined. Isotope values were between -9.56 and -6.21 ‰ for $\delta^{18}O$, between -64.4 and -58.8 ‰ for $\delta^{2}H$ and between -9.42 and -18.65 ‰ for $\delta^{13}C_{DIC}$ (Brenčič, 2011). By performing the pumping test, mixing of water from different aquifers, namely, shallow water from the upper Holocene aquifer and a lower Pleistocene aquifer in well VD Brest-3a, was confirmed. A certain amount of deep-water was also present; however, the exact amount was unknown, and its characteristics were not determined. The isotope composition of the water also varied during the pumping test, indicating that the fraction of water of different origin had changed (Brenčič, 2011; Vreča et al., 2011; Bračič Železnik et al., 2017). In 2013 (from 21/05/13 to 31/05/13), the pumping test was repeated in well VD Brest-3a. The $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ values ranged from -9.46 and -9.05 ‰, -65.9 and -63.4 ‰, and -14.5 and -12.3 ‰, respectively (Vreča et al., 2013; Bračič Železnik et al., 2017).

In 2015, another pumping test in well VD Brest-3a was performed and the $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ values varied between -9.78 and -9.06 ‰, -65.4 and -61.4 ‰ and -12.05 and -11.14 ‰, respectively. The sampling test lasted from 05/06/15 to 01/07/15 (Vreča et al., 2015). In 2019, few additional 24-hour pumping tests were performed (Table 2).

To conclude, the data shows a broad range of $\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C_{DIC}$ values in groundwater in the LB. Historically, isotope investigations were rare. In the last years, the $\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C_{DIC}$ are used more often but still sporadic. Also, different wells in the wellfield Brest yield different isotope compositions. This variation is because the depths of the wells are not consistent, and the groundwater is captured from different aquifers. Therefore, careful consideration about how to implement isotope techniques in the future is needed for better water resource management of the wellfield Brest.

Ljubljansko polje

According to available data, isotope investigations of groundwater from the LP were not performed until 1997. The first samples were collected between October 1997 and September 1998 at 13 pumping wells in the wellfields Kleče, Hrastje, Jarški prod and Šentvid (Urbanc & Jamnik, 1998). Samples were collected only for $\delta^{18}O$ analysis. A more extensive set of observations (October 1997 to September 1999) is presented by Andjelov et al. (2005). From this data, the authors estimated the proportion of locally infiltrated precipitation and water from the Sava River, but only reported the mean values of all measurements obtained during the sampling period for selected wells. Reported $\delta^{18}O$ values in the groundwater were between -9.0 and -8.6 ‰ in Kleče (7 wells), -9.1 and -9.0 ‰ in Jarški prod (2 wells), and -8.9 and -8.8 ‰ in Hrastje (3 wells). In Šentvid, the mean value of several measurements from a single well was -8.8 ‰ (Urbanc & Jamnik, 1998). However, from the figures, it is possible to read the values for specific wells for the entire sampling period (Urbanc & Jamnik, 1998; Jamnik & Urbanc, 2003; Andjelov et al., 2005). At the same time, samples from the Sava River at Tacen were collected (Jamnik & Urbanc, 2003). The results, although only shown graphically, confirmed the influence of human activities on groundwater quality in

Table 2. $\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C_{DIC}$ results (minimum to maximum values) of the sampling performed in 2019 during 24-hour pumping tests. (TA = total alkalinity, EC = electrical conductivity)

Date of sampling	Name	Parameters identified	$\delta^{18}O$	$\delta^{2}H$	$\delta^{13}C_{DIC}$	Reference
09/04/19-10/4/19	PB–24b/19	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$ TA, EC, ^{3}H, $^{87}Sr/^{86}Sr$, $^{88}Sr/^{86}Sr$	-9.59 to -9.50 ‰ (N=10)	-63.9 to -63.1 ‰ (N=10)	-11.1 ‰ (N=2)	Vreča et al., 2019e
02/9/19-03/09/19	PB–24a/19	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$, TA, EC, ^{3}H, $^{87}Sr/^{86}Sr$, $^{88}Sr/^{86}Sr$	-9.49 to -9.42 ‰ (N=3)	-62.8 to -62.5 ‰ (N=3)	-11.4 to -11.1 ‰ (N=3)	Vreča et al., 2019f
03/10/19-04/10/19	PB–24c/19	$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$, TA, ^{3}H $^{87}Sr/^{86}Sr$, $^{88}Sr/^{86}Sr$ and EC	-9.50 to -9.48 ‰ (N=3)	-62.9 to -62.3 ‰ (N=3)	-11.2 to -10.9 ‰ (N=3)	Vreča et al., 2019f

those wells where the recharge zone extends under the city (Urbanc & Jamnik, 1998).

In July and October 2003, the Institute for Public Health in Maribor collected samples at following locations: Yulon, Hrastje 1a, Kleče 17, GeoZS, Kleče 11, Šentvid 2A, Kleče 8a, Hrastje 3, Navje, Petrol- Šmartinska cesta, L.P. Vodovodna, HMZ Hrastje, for the $\delta^{13}C_{DIC}$ and alkalinity measurements. The $\delta^{13}C_{DIC}$ values were ranged from -14.7 to -12.2 ‰. The $\delta^{13}C_{DIC}$ results from LP were graphically presented in Kanduč (2006), together with $\delta^{13}C_{DIC}$ values of samples from the Sava River to indicate possible biogeochemical processes in the groundwater-river water system.

From March 2010 to December 2011, monthly samples were collected for $\delta^{18}O$ and $\delta^{2}H$ analyses from seven wells at three wellfields: Kleče, Hrastje, and Jarški prod, and from the Sava River at Šentjakob (Vrzel et al., 2018). Based on $\delta^{18}O$ and $\delta^{2}H$ results, the authors determined the proportion of the Sava River in groundwater resulting from periods of low and high precipitation in 2010 and 2011. Numerical values are reported in the *Supplementary Data* and are presented here as a box plot (Fig. 3). The authors found that both sources directly influence the groundwater: infiltration of local precipitation and recharge from the Sava River. Based on average $\delta^{18}O$ and $\delta^{2}H$ values, it was apparent that groundwater from Kleče 11, Hrastje 3, and Hrastje 8 contained only a low amount of the Sava River water (up to 14 %) and was mostly composed of recently infiltrated local precipitation. For comparison, a higher percentage of the Sava River water (up to 86 %) is present in the groundwater in wells Jarški prod 1, Jarški prod 3, Kleče 8 and Kleče 12. Findings were similar to that reported by Urbanc & Jamnik (1998).

More detailed investigations (from 2000 to 2014) in LP were performed in the area of Union Brewery where groundwater in Pleistocene fluvial sediments and the lower gravel aquifer is exploited by the Brewery (Trček 2005; 2006; 2017). The Union Brewery's lysimeter was ideal for studying urban water infiltration and to make accurate measurements of water flow and water balance parameters. It consisted of 42 boreholes drilled into the right and left walls of the construction (Juren et al., 2003; Trček, 2005). As part of its sustainable groundwater management plan, extensive studies of groundwater flow and solute transport were performed from 2003 to 2014 to predict groundwater flow and contaminant transport through the unsaturated and saturated zone of the urban intergranular aquifer (Trček, 2017).

Actual stable isotope monitoring began in July 2003 (Trček, 2005) with the aim to obtain information about mixing processes and groundwater residence times in the unsaturated zone and to determine the risk of contamination of drinking water. From July 2003 to August 2004, monthly groundwater samples were collected, and $\delta^{18}O$ and $\delta^{2}H$ values determined. Trček (2005) reported $\delta^{18}O$ groundwater values between -14.7 ‰ and -4.5 ‰. All other $\delta^{18}O$ values were presented as boxplots, and no values for $\delta^{2}H$ are reported. A synthesis of one-years' worth of data revealed two types of flow: lateral flow, which has an essential role in the protection of groundwater of

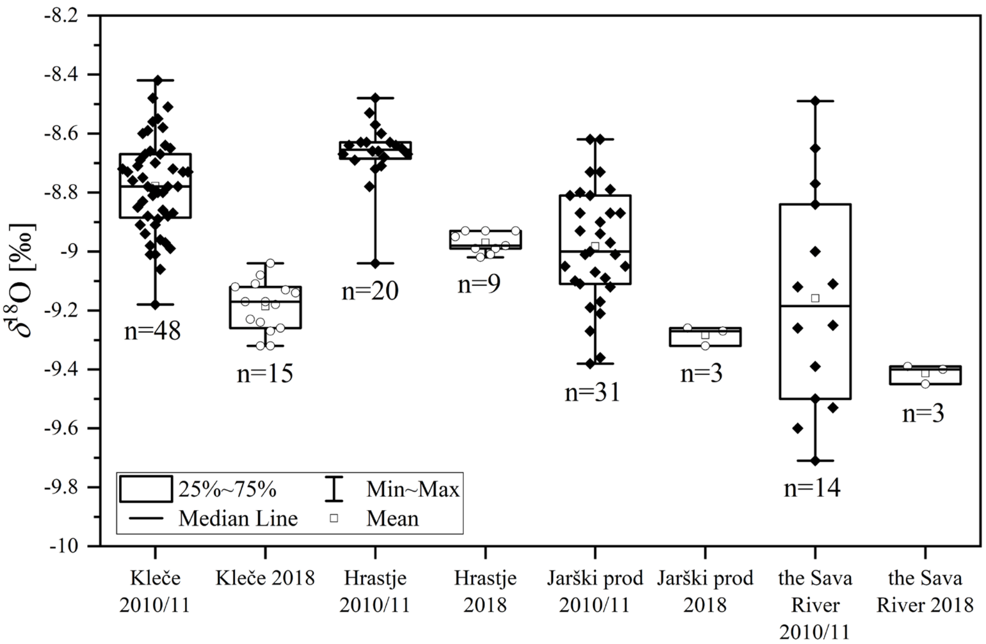

Fig. 3. Box plots of $\delta^{18}O$ values taken from Vrzel et al., 2018 (period 2010/2011) and from research performed in autumn 2018 for wells in Kleče, Hrastje, Jarški prod and the Sava River (Vreča et al., 2019a; 2019b).

the Pleistocene alluvial gravel aquifer, and vertical flow, which is the main factor controlling contaminant transport towards the saturated zone (Trček, 2005).

From July 2003 to June 2004 and from July 2004 to June 2005, $\delta^{18}O$ and $\delta^{2}H$ values in 16 observation wells (piezometers) were measured next to the Union Brewery. The mean values from a single sampling site for $\delta^{18}O$ varied between -9.21 and -8.70 ‰ (Trček, 2006). During the same period (from July 2003 to June 2005) monthly oxygen isotope measurements of groundwater (lysimeter) ranged from -14.7 to -4.4 ‰, while the means of single sampling points were between -10.7 and -8 ‰ (Trček, 2005). In 2017, Trček published the results of the 2004 to 2014 investigation (Trček, 2017). Water samples were collected daily, weekly or at monthly intervals, although only seasonal monitoring was performed after 2010. Samples were collected from 18 observation points on the right side of the Union Brewery lysimeter, while precipitation was collected near the entrance to the lysimeter. The $\delta^{18}O$ values in groundwater from 2004 to 2010 ranged from -16 to -6 ‰. In precipitation, $\delta^{18}O$ values ranged from -18 to -3 ‰. Trček studied the weighted averages of the lysimeter water $\delta^{18}O$ values for the period 2005-2009 to get a better insight into the lysimeter drainage system. Reported values varied between -9.82 and -7.62 ‰. Again, Trček emphasised the importance of lateral flow and that the goal for future investigations should be directed towards vertical transport studies of contaminant loads (Trček, 2017).

The Union Brewery also produces bottled water, both still and flavoured water, which is sold under the Zala brand. In September 2004, extensive research of the general chemistry, $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ of bottled waters available on the Slovene Market was undertaken (Brenčič & Vreča, 2005; 2006; 2007; 2010). The authors reported that $\delta^{2}H$, $\delta^{18}O$ and $\delta^{13}C_{DIC}$ values of still water were between -61 and -60 ‰, -8.90 and -8.95 ‰ and -12.7 and -12.3 ‰, respectively. For flavoured waters, values for $\delta^{2}H$, $\delta^{18}O$ and $\delta^{13}C_{DIC}$ ranged between -61 and -59 ‰, -8.95 and -8.80 ‰, and -13.5 and -12.5 ‰ (Brenčič & Vreča, 2006; 2007).

Isotope investigations of groundwater were also performed at the pumping station LMV-1 (located near the Kleče wellfield) from 2009 to 2011 (Mezga, 2014). The three-year sampling campaign covered three annual season cycles: groundwater at each sampling location was sampled twice, in spring (March-July) and autumn (August-November). The samples were collected as part of an extensive survey looking at the origin of groundwater in Slovenia. For the LMV-1, the authors reported mean values of $\delta^{18}O$ of -8.59 ± 0.33 ‰, $\delta^{2}H$ of -60.4 ± 0.6 ‰ and $\delta^{13}C_{DIC}$ of -12.7 ± 1.3 ‰ (Mezga et al., 2014).

Ljubljansko polje and Ljubljansko barje simultaneous investigations

Simultaneous isotope investigations of both aquifers are rare. Cerar & Urbanc (2013) studied their interactions during two sampling campaigns in autumn 2010 and spring 2011. They aimed to obtain a better understanding of how the aquifers interact in order to improve a hydrogeological conceptual model of the aquifers. In total, they collected 138 samples at 69 locations from 28 wells from the five main wellfields, five industry wells, two private wells, 29 boreholes, and five samples of surface water. Based on the hydrogeological and the geographical position of the aquifers they divided LB into three areas: the northern part, middle part and southern part, including the area of Brest and Iški vršaj (Cerar & Urbanc, 2013). The $\delta^{18}O$ in the groundwater of the northern part of LB varied between -9.0 and -8.6 ‰. Groundwater from this part of the aquifer is enriched in ^{18}O isotope compared to the other parts of the aquifers. This enrichment is due to the higher influence of local precipitation on the open aquifer. $\delta^{18}O$ values in the middle part of the aquifer were from -10.0 to -9.1 ‰, while $\delta^{18}O$ values in the southern part (including Brest and Iški vršaj) were -9.6 to -9.2 ‰. In their final report, Urbanc et al. (2012) report the range of $\delta^{18}O$ values for groundwater from Brest to vary between -9.6 and -9.4 ‰ (tabulated values not given). For LP, $\delta^{18}O$ values in Kleče wells varied from -9.1 to -8.7 ‰, -8.9 to -8.8 ‰ in Šentvid, -8.9 to -8.8 ‰ in Hrastje, and from -9.3 to -9.0 ‰ in Jarški prod.

Jamnik & Urbanc (2000) were the first to study the connections between LB and LP. They found that LP is partially recharged with groundwater from LB. However, Cerar & Urbanc, (2013) also showed that based on the hydrochemical composition (Ca/Mg molar ratio and HCO_3^- concentration) of water, the contribution of groundwater from LB is of minor importance. The minimal contribution was detected near the boundary between the two aquifers. By measuring tritium activity, they classified groundwater in LP as “modern waters” with a residence time of up to 10 years, at the interface between the aquifers as “submodern waters” with a residence time of more than 50 years and in LB as “older waters” with residence time between 10 and 50 years.

However, increased tritium activities also indicated "bomb tritium" from nuclear experiments in the 1960s (Cerar & Urbanc 2013). Vrzel et al. (2018) confirmed "modern" water was mainly present in LP and also estimated, using the $^{3}H/He$ method, that 10 % of groundwater in Kleče is very old, but additional analyses are needed for precise determinations.

In the period from March 2010 to October 2010 $\delta^{13}C_{DIC}$ was measured monthly along with alkalinity and pH at LP in the following wells: Hrastje 3, 8 (average -12.6 ‰, n = 12), Kleče 8, 11, 12 (average -12.1 ‰, n = 22), Jarški prod 1, 3 (average -11.3 ‰, n = 13), and the Sava River at Dolsko (average -10.6 ‰, n = 7) (Kanduč, unpublished data). At LB sampling was performed only in June 2010 at wells Brest 1a, Brest 2a and Brest 4a with $\delta^{13}C_{DIC}$ values ranging from -11.3 ‰ to -10.8 ‰ (Kanduč, unpublished data). To our best knowledge, this was for the first time $\delta^{13}C_{DIC}$ was measured at LB.

Vreča et al., (2019c) were the first to perform a stable isotope survey (June and July 2014) of tap water covering Slovenia according to our best knowledge. The authors determined $\delta^{18}O$ and $\delta^{2}H$ values in nine tap water samples collected in Ljubljana and its vicinity. The $\delta^{18}O$ and $\delta^{2}H$ values varied between -9.74 and -9.06 ‰, and between -65.2 and -60.1 ‰, respectively. The most negative values were in tap water from wellfield Brest and the most positive from Kleče.

A more detailed investigation within the Ljubljana water supply system started in 2018. The $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ values of all objects in the system (wells, joint exits from water pumping station, water reservoirs, water treatment locations, fountains and taps) ranged from -9.53 and -8.68 ‰, -63.6 and -57.8 ‰ and -15.3 and -9.38 ‰, respectively. Also, $\delta^{2}H$ and $\delta^{18}O$ values in samples from Šentvid were less negative, while samples from Brest had on average lower $\delta^{13}C_{DIC}$ values (Vreča et al., 2019a; 2019b). The results for wells Kleče, Hrastje, Jarški prod and the Sava River are presented in Fig. 3 together with data from Vrzel et al., (2018). The values for 2018 are lower and less spread, which is a result of a shorter sampling period (September to November).

The first 24-hour analysis of tap water was performed from 9:00 on 24/04/19 until 9:00 on 25/04/19, with an emphasis on the hourly variability (Vreča et al., 2019d). The tap water was sampled in the basement of the main building of the JSI where water from two wellfields (Kleče and Brest) is mixed. The diurnal variations of $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$ were small. However, 24-hour differences in isotope and major and trace elemental composition suggest that the proportion of groundwater from Kleče and Brest water fields changed over 24 hours.

Based on the past investigations of LP and LB, especially 2018 - 2019, the authors selected a systematic multi-analytical approach that started in 2020. Monthly monitoring of $\delta^{18}O$ and $\delta^{2}H$ and multi-element composition in groundwater in five wellfields (Kleče (4 wells), Brest (4 wells), Hrastje (2 wells), Jarški prod (2 wells), and Šentvid (1 well)) was established. Also, samples from the Sava River (Brod and Šentjakob) are collected on the same day and additional tap water investigations are planned.

The Sava River

Numerous isotope investigations have been performed along the Sava River basin (e.g., Kanduč, 2006; Ogrinc et al., 2008; Brenčič & Vreča, 2016; Torkar et al., 2016; Vrzel et al., 2018; Ogrinc et al., 2018). However, only sampling locations close to Ljubljana (Tacen, Brod, Dolsko, Šentjakob and Črnuče) are relevant for this review (Table 1 and 2). Among these studies, ten reported $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$ values (Table 2).

Table 3. Values for $\delta^{18}O$ (‰), $\delta^{2}H$ (‰) and $\delta^{13}C_{DIC}$ (‰) for the Sava River at Tacen, Brod, Črnuče, Šentjakob and Dolsko performed in different investigations (locations are downstream).

Location		$\delta^{18}O$	$\delta^{2}H$	$\delta^{13}C_{DIC}$	Reference
Sava Tacen	Min	-10.1	-67.0	/	Urbanc & Jamnik, 1998; Andjelov et al., 2005; Ogrinc et al., 2008; Urbanc et al., 2012; Cerar & Urbanc, 2013
	Max	-8.51	-57.9	/	
Sava Brod	Min	-10.1	-67.0	-10.7	Kanduč, 2006; Vreča et al., 2019a; 2019b
	Max	-9.2	-60.4	-8.5	
Sava Črnuče		-9.39	-62.4	-9.2	Vreča et al., 2019a; 2019b
Sava Šentjakob	Min	-9.7	-66.4		Vrzel et al., 2018; Vreča et al., 2019a; 2019b
	Max	-8.5	-57.6		
Sava Dolsko	Min	-9.9	-68.0	-12.7	Kanduč, 2006; Ogrinc et al., 2008; 2018
	Max	-8.2	-55.0	-9.9	

Isotope investigations of the Sava River near Ljubljana began in October 1997, when the first sampling in Tacen was performed (Urbanc & Jamnik, 1998). In 2004, Kanduč, (2006) undertook a more systematic monitoring programme of O, H and C isotopes from April 2004, September 2004 and January 2005 at Brod and Dolsko. Ogrinc et al. (2008) also determined δ^{18}O and δ^{2}H in the Sava River watershed at Tacen and Dolsko in April, September, and December of 2004 and monthly from January 2005 to August 2006. The authors used data to provide information on hydrological flow paths and to estimate the water residence times. The data (Ogrinc et al., 2008) also forms part of the long-term the Global Network of Isotopes in Rivers database (GNIR; IAEA, 2020), managed by IAEA. The mean residence times at Tacen and Dolsko of 1.54 and 1.09 years, respectively, were estimated by using an exponential model in which precipitation inputs are assumed to mix rapidly with resident water. It was also observed that the Sava River responds quickly to precipitation, which is reflected in the isotope composition of the Sava River water (Ogrinc et al., 2008). Vrzel et al. (2018) report similar δ^{18}O values in river water at Šentjakob from March 2010 to December 2011. Monthly isotope sampling data at Dolsko during 2007 to 2010 revealed a mean residence time of 1.20 years, which is higher than previously estimated (1.09 years) in 2004-2006 period (Ogrinc et al., 2018).

Precipitation

Isotope composition of precipitation was monitored at six different locations in Ljubljana, as reported in 13 records (Table 1). Continuous and systematic monitoring of the isotope composition of monthly composite samples has been carried out in Ljubljana by the JSI since 1981 (Pezdič, 1999; 2003; Vreča et al., 2008; 2014; Vreča & Malenšek, 2016). Published data are also included in the Global Network of Isotopes in Precipitation (GNIP) and in the Slovenian Network of Isotopes in Precipitation (SLONIP) from 1981 to 2010. In 1981-2018, the δ^{18}O and δ^{2}H values varied between -19.40 and -1.65 ‰ (mean -8.65 ‰, n=428) and between -147.8 and -7.3 ‰ (mean -59.4 ‰, n=425). The data is an important input into GNIP, which has been evaluated many times (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; 2020; Pezdič, 1999; 2003; Brenčič & Vreča, 2006; Vreča et al., 2006; Ogrinc et al., 2008; 2018; 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; Vrzel et al., 2018). The isotope composition of precipitation was also monitored at other locations around Ljubljana in the frame of several short-term investigations. For example, the precipitation was collected in the wellfield Kleče from October 1997 to September 1998 (Urbanc & Jamnik, 1998). The reported δ^{18}O ranged from -12.0 to -5.5 ‰. Trček (2005; 2017) monitored δ^{18}O values in precipitation from January 2003 to August 2004 and again from 2004 to 2014 at the Union Brewery. δ^{18}O values were from -15.2 to -4.1 ‰ (mean -8.9 ‰) during 2003-2004 and -18 to -3 ‰ during the extended observation period (2004 to 2014). Cerar & Urbanc (2013) have also reported the monthly composition of precipitation at the GeoZS in Ljubljana monitored since 2010; however, the exact sampling period is not reported. The average monthly δ^{18}O value was -8.51 ‰ (Cerar & Urbanc, 2013).

Conclusions

The use of isotopes to characterize water resources and to track the movement of water in the LP and LB over the past 40 years has significantly improved our understanding of groundwater quality and hydrological processes affecting its recharge and the distribution. Despite this, most isotope data are a result of intermittent short-term studies, and only a few represent long-term monitoring programmes. From all of the analysed articles and reports, it is evident that limited sampling and coverage of monitoring of well networks presents a high risk of, e.g., not detecting contamination events (Jamnik et al., 2012).

The first δ^{18}O and δ^{2}H investigations of groundwater in the LB began in 1976, and only later in 1997 in LP. Also, in 1997 investigations at the Sava River in Tacen started. The first time $\delta^{13}C_{DIC}$ was systematically measured at LP was in 2003, while at LB it was only in 2010. Historically, isotope studies were performed in the LP; however, since 2011, isotope data are used more frequently, but still sporadically in the LB. These investigations mainly involve sampling from wells – sampling was most often performed in Kleče, while other objects in the water supply system were not well sampled. Five locations on the Sava River near Ljubljana were identified. Also, precipitation was monitored for δ^{18}O and δ^{2}H at six different locations.

To our knowledge, 102 relevant records were found and analysed; however, only 41 records published O, H and C isotope data and underwent a detailed review. The highest number of publications contained $\delta^{18}O$ data (40 records), followed by $\delta^{2}H$ (32 records), while $\delta^{13}C_{DIC}$ investigations were rarely implemented (13 records). Also, long-term systemic approach with more frequent (e.g., seasonal) monitoring of relevant environmental isotope tracers is missing. In the scope of this review, we would also like to point out that many investigations contain an insufficient description of sampling times and exact locations (missing coordinates), analytical methods, and reporting of raw data. In this regards, better use of supplementary material, which should include all appropriate metadata would be beneficial and necessary for proper comparison in time and space and would enable tracing isotope changes in water resources.

The first stable water isotope survey of tap water in the City of Ljubljana was performed in 2014. In order to assess the usefulness of environmental isotopes more systematically, monitoring has been performed on the drinking water supply system of Ljubljana since 2018.

Based on all of the results from previous investigations of LP and LB, monthly monitoring of $\delta^{18}O$ and $\delta^{2}H$ in groundwater in five water supply facilities was established in January 2020. Besides, also the Sava River is sampled at two locations monthly and additional more detail sampling of tap water is planned. The results will be used to prepare guidelines for future isotope monitoring that will provide a better overall understanding of water interactions of domestic supply important for water managers.

Acknowledgements

This review paper was prepared in the frame of the programme P1-0143, Young research program (PR-09780) and IAEA CRP contract No. 22843 - Use of Isotope Techniques for the Evaluation of Water Sources for Domestic Supply in Urban Areas (F33024). We thank also the reviewers for all valuable comments and D. Heath for linguistic corrections.

References

Aggarwal, P. K., Gat, J. R. & Froehlich, K. F. 2005: Isotopes in the water cycle. Springer, Dordrecht: 381 p.

Andjelov, M., Rejec Brancelj, I., Smrekar, A., Kladnik, D. & Perko, D. 2005: Podtalnica Ljubljanskega polja. Geografija Slovenije, 10. Založba ZRC, Ljubljana: 251 p.

ARSO, 2012: Agency of Republic of Slovenia for Environment. Archive of hydrological data. Internet: http://vode.arso.gov.si/hidarhiv/pov_arhiv_tab.php (23. 6. 2020)

Avak, H. & Brand, W. A. 1995: The Finning MAT HDO-Equilibration - A fully automated H2O/gas phase equilibration system for hydrogen and oxygen isotope analyses. Thermo Electronic Corporation, Application News, 11: 1–13.

Bowen, G. J., Wassenaar, L. I. & Hobson, K. A. 2005: Global application of stable hydrogen and oxygen isotopes to wildlife forensics. Oecologia, 143: 337–348. https://doi.org/10.1007/s00442-004-1813-y

Bowen, G. J., Cai, Z., Fiorella, R. P. & Putman, A. L. 2019: Isotopes in the Water Cycle: Regional- to Global-Scale Patterns and Applications. Annu. Rev. Earth Planet. Sci., 47: 453–479. https://doi.org/10.1146/annurev-earth-053018-060220

Bračič Železnik, B. & Globevnik, L. 2014: Measurement, modelling and analysis of hydrological and hydrogeological processes and trends in a marsh area. In: Daniell, T. (eds.): Hydrology in a Changing World: Environmental and Human Dimensions. IAHS Publication 363, Montpellier: 413–418.

Bračič Železnik, B. 2016: Dinamika podzemne vode sistemov vodonosnikov Iškega vršaja. M.Sc. thesis. University of Ljubljana, Faculty of civil and geodetic engineering, Ljubljana: 57 p.

Bračič Železnik, B., Čenčur Curk, B., Žvab Rožič, P., Torkar, A., Vreča, P. & Brenčič., M. 2017: Deep karstified dolomite aquifer as a source of drinking water – isotopic measurements. In: EGU General Assembly 2017. https://doi.org/10.13140/RG.2.2.27772.44166

Brenčič, M. & Vreča, P. 2005: General Chemistry of bottled waters on the Slovene market = Splošne kemijske karakteristike ustekleničenih vod na slovenskem tržišču. RMZ, 52: 549–560.

Brenčič, M. & Vreča, P. 2006: Identification of sources and production processes of bottled waters by stable hydrogen and oxygen isotope ratios. Rapid Commun. Mass Spectrom., 20/21: 3205–3212. https://doi.org/10.1002/rcm.2726

Brenčič, M. & Vreča, P. 2007: Isotopic composition of dissolved inorganic carbon in bottled waters on the Slovene market. Food chem., 101/4: 1533–1542. https://doi.org/10.1016/j.foodchem.2006.04.003

Brenčič, M. & Vreča, P. 2010: The use of a finite mixture distribution model in bottled water characterisation and authentication with stable hydrogen, oxygen and carbon isotopes – Case study from Slovenia. J. Geochem. Explor., 107/3: 391–399. https://doi.org/10.1016/j.gexplo.2010.08.006

Brenčič, M. 2011: Izotopske analize sedimenta in vode iz piezometra P-23 in vodnjaka VD-Brest-3a. Katedra za aplikativno geologijo – Oddelek za geologijo, Ljubljana: 41 p.

Brenčič, M. & Vreča, P. 2016: Hydrogeological and isotope mapping of the karstic River Savica in NW Slovenia. Environ. Earth Sci., 75:651. https://doi.org/10.1007/s12665-016-5479-7

Breznik, M. 1984: Zmogljivost črpališča Brest v sušni dobi. Univerza Edvarda Kardelja v Ljubljani, Ljubljana.

Brilly, M., Jamnik, B. & Drobne, D. 2003: Chromium contamination of the Ljubljansko Polje aquifer. RMZ, 50/1: 71–74.

Cerar, S. & Urbanc, J. 2013: Carbonate chemistry and isotope characteristics of groundwater of Ljubljansko Polje and Ljubljansko Barje aquifers in Slovenia. Sci. World J., 2013: 948394. https://doi.org/10.1155/2013/948394

Clark, I. & Fritz, P. 1997: Environmental isotopes in hydrogeology. Taylor & Francis: Boca Raton, New York: 328 p.

Clark, I. 2015: Groundwater Geochemistry and Isotopes, 1st Edition, 456 p.

Craig, H. 1961: Isotope variations in meteoric waters. Science, 133: 1702–1703. https://doi.org/10.1126/science.133.3465.1702

Dansgaard, W. 1954: The O^{18}-abundance in fresh water. Geochim. Cosmochim. Acta, 6/5–6: 241–260. https://doi.org/10.1016/0016-7037(54)90003-4

de Groot, P. A. 2004: Handbook of stable isotope analytical techniques. Elsevier, Amsterdam: 1258 p.

Du, M., Zhang, M., Wang, S., Chen, F., Zhao, P., Zhou, S. & Zhang, Y. 2019: Stable Isotope Ratios in Tap Water of a Riverside City in a Semi-Arid Climate: An Application to Water Source Determination. Water, 11: 1441. https://doi.org/10.3390/w11071441

Ehleringer, R. J., Cerling, T., West, B. J. Podlesak, W. D., Chesson, L. & Bowen, G. J. 2008: Spatial considerations of stable isotope analyses in environmental forensics. In: Hester, R. E. & Harrison, R. M. (eds.): Environmental Forensics. The Royal Society of Chemistry, University of York, UK: 36–53.

Ehleringer, J. R., Barnette, J. E., Jameel, Y., Tipple, B. J. & Bowen, G. J. 2016: Urban water – a new frontier in isotope hydrology. Isot. Environ. Healt. S., 52/4–5: 477–486. https://doi.org/10.1080/10256016.2016.1171217

Epstein, S. & Mayeda, T. 1953: Variation of ^{18}O content of waters from natural sources. Geochim. Cosmochim. Acta, 4/5: 213–224. https://doi.org/10.1016/0016-7037(53)90051-9

Gat, J. R. 1996: Oxygen and hydrogen isotopes in the hydrologic cycle. Annu. Rev. Earth Planet. Sci., 24/1: 225–262. https://doi.org/10.1146/annurev.earth.24.1.225

Gehre, M., Hoefling, R., Kowski, P. & Strauch, G. 1996: Sample preparation device for quantitative hydrogen isotope analysis using chromium metal. Anal. Chem., 68/24: 4414–4417. https://doi.org/10.1021/ac9606766

Horita, J., Ueda, A., Mizukami, K. & Takatori, I. 1989: Automatic δD and $\delta^{18}O$ analyses of multi-water samples using H_2^- and CO_2^- water equilibration methods with a common equilibration set-up. Appl. Radiat. Isot., 40/9: 801–805. https://doi.org/10.1016/0883-2889(89)90100-7

Horvantinčić, N., Barešić, J., Krajcar Bronić, I., Obelić, B., Karman, K. & Forisz, I. 2011: Study of the bank filtered groundwater system of the Sava River at Zagreb (Croatia) using isotope analyses. Central European Geology, 54/1-2: 121–127. https://doi.org/10.1556/CEuGeol.54.2011.1-2.12

Hughes, C. E. & Crawford, J. 2012: A new precipitation weighted method for determining the meteoric water line for hydrological applications demonstrated using Australian and global GNIP data. J. Hydrol., 464–465: 344–351. https://doi.org/10.1016/j.jhydrol.2012.07.029

IAEA, 2020: Global Network of Isotopes in Rivers. The GNIR Internet: https://nucleus.iaea.org/wiser (23. 6. 2020)

Ichiyanagi, K. 2007: Review: Studies and Applications of Stable Isotopes in Precipitation. J. Jpn. Assoc. Hydrolog. Sci., 37: 165–185.

Jameel, Y., Brewer, S., Good, S. P., Tipple, B. J., Ehleringer, J. R. & Bowen, G. J. 2016: Tap water isotope ratios reflect urban water system structure and dynamics across a semiarid metropolitan area. Water Resour. Res., 52: 5891–5910. https://doi.org/10.1002/2016WR019104

Jamnik, B. & Urbanc, J. 2000: Izvor in kakovost podzemne vode Ljubljanskega polja = Origin and quality of groundwater from Ljubljansko polje. RMZ, 47: 167–178.

Jamnik, B., Kristensen, M., Anderson, U, Sorensen, H. R., Refsgaard, A. & Gustavsson, L. 2000: Water resources management model for Ljubljansko polje and Ljubljansko Barje, Final Report Project No. 98-50228, DHI

Water & Environment, Denmark, in association with Geological Survey of Slovenia, Hydro – Engineering and Hydro-Consulting, Slovenia.

Jamnik, B. & Urbanc, J. 2003: Isotope investigations as a tool for water resource management in Ljubljana City (Slovenia) (IAEA-CN--104). International Atomic Energy Agency (IAEA), 189–190.

Jamnik, B., Bračič Železnik, B. & Urbanc, J. 2003: Diffuse pollution of water protection zones in Ljubljana, Slovenia. In: Proceedings of the 7th International Specialized Conference on Diffuse Pollution and Basin Management, Dublin: 7/1–5.

Jamnik, B., Auersperger, P., Urbanc, J., Lah, K. & Prestor, J. 2009: Pharmaceuticals as indicators of anthropogenic influence on the groundwater of Ljubljansko polje and Ljubljansko barje aquifers. Geologija, 52/2: 241–248. https://doi.org/10.5474/geologija.2009.024

Jamnik, B., Janža, M. & Prestor, J. 2012: Project INCOME: developing a comprehensive approach for Slovenian aquifer management. Water 21 Magazine of the International Water Association, 49 p.

Jamnik, B. & Žitnik, M. 2020: Letno poročilo o skladnosti pitne vode na oskrbovalnih območjih v upravljanju JP VOKA SNAGA v letu 2019. JP VOKA SNAGA, Ljubljana: 27 p.

Janža, M., Prestor, J., Urbanc, J. & Jamnik, B. 2005: TCE contamination plume spreading in highly productive aquifer of Ljubljansko polje. In: EGU General Assembly, Vienna.

Janža, M. 2015: A decision support system for emergency response to groundwater resource pollution in an urban area (Ljubljana, Slovenia). Environ. Earth Sci., 73/7: 3763–3774. https://doi.org/10.1007/s12665-014-3662-2

Juren, A., Pregl, M. & Veselič, M. 2003: Project of an urban lysimeter at the Union brewery, Ljubljana, Slovenia. RMZ, 50/3: 153–156.

Kanduč. T. 2006: Hidrogeokemične značilnosti in kroženje ogljika v porečju reke Save v Sloveniji. Ph.D. Thesis. University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology, Ljubljana: 141 p.

Kanduč, T., Mori, N., Kocman, D., Stibilj, V. & Grassa, F. 2012: Hydrogeochemistry of Alpine springs from North Slovenia: Insights from stable isotopes. Chem. Geol., 300/301: 40–54. https://doi.org/10.1016/j.chemgeo.2012.01.012

Karahodžič, M. 2005: Dinamika izotopov dušika v nitratih v naravnem zaledju Ljubljanskega polja. Master thesis. University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology, Ljubljana: 92 p.

Kendall, C. & Doctor, D. 2003: Stable Isotope Applications in Hydrologic Studies. Treatise on Geochemistry, 5: 319–364. https://doi.org/10.1016/b0-08-043751-6/05081-7

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

Krajcar Bronić, I., Barešić, J., Borković, D., Sironić, A., Lovrenčić Mikelić, I. & Vreča, P. 2020: Long-Term Isotope Records of Precipitation in Zagreb, Croatia. Water, 12/226: 1–28. https://doi.org/10.3390/w12010226

Marković, T., Brkić, Ž. & Larva, O. 2013: Using hydrochemical data and modelling to enhance the knowledge of groundwater flow and quality in an alluvial aquifer of Zagreb, Croatia. Sci. Total Environ., 458–460: 508–516. https://doi.org/10.1016/j.scitotenv.2013.04.013

Meier-Augenstein, W. & Schimmelmann, A. 2019: A guide for proper utilisation of stable isotope reference materials. Isot. Environ. Healt. S., 55/2: 113–128. https://doi.org/10.1080/10256016.2018.1538137

Mencej, Z. 1988/1989: Prodni zasipi pod jezerskimi sedimenti Ljubljanskega barja. Geologija, 31/32: 517–553.

Mezga, K. 2014: Natural hydrochemical background and dynamics of groundwater in Slovenia. Doctoral dissertation. University of Nova Gorica, Nova Gorica: 226 p.

Mezga, K., Urbanc, J. & Cerar, S. 2014: The isotope altitude effect reflected in groundwater: a case study from Slovenia. Isot. Environ. Health. Stud, 50/1: 33–51. https://doi.org/10.1080/10256016.2013.826213

Mook, W. G. 2001: Environmental isotopes in the hydrological cycle: principles and applications, Volumes I. Technical documents in Hydrology No. 39. IAEA-UNESCO: Paris, France.

Morrison, J., Brockwell, T., Merren, T., Fourel, F. & Phillips A. M. 2001: On-line high-precision stable hydrogen isotopic analyses on nanoliter water samples. Anal. Chem., 73/15: 3570–3575. https://doi.org/10.1021/ac001447t

Official Gazette RS, Nos. 19/04, 35/04, 26/06, 92/06, 25/09, 74/15 and 51/17. Rules on drinking water. Internet: http://www.pisrs.si/Pis.web/pregledPredpisa?id=PRAV3713 (25.9.2020)

Ogrinc, N., Kanduč, T., Stichler, W. & Vreča, P. 2008: Spatial and seasonal variations in $\delta^{18}O$ and δD values in the Sava River in Slovenia. J. Hydrol., 359/3-4: 303-312. https://doi.org/10.1016/j.jhydrol.2008.07.010

Ogrinc, N., Kocman, D., Milijević, N., Vreča, P., Vrzel, J. & Povinec, P. 2018: Distribution of H and O stable isotopes in the surface waters of the Sava River, the major tributary of the Danube River. J. Hydrol., 565: 365–373. https://doi.org/10.1016/j.jhydrol.2018.08.024

Pezdič, J. 1998: Stable isotopes as natural tracers of the karst recharge to the tertiary clastic aquifers: a case study of the southern part of Ljubljana marsh (Ljubljansko barje, Slovenia) = Stabilni izotopi kot naravna sledila pri napajanju terciarnega klastičnega vodonosnika iz krasa: študija južnega dela Ljubljanskega barja, Slovenija. Acta carsologica, 27/1: 349–360

Pezdič, J. 1999: Izotopi in geokemijski procesi. Naravoslovnothniška fakulteta, Oddelek za geologijo, Ljubljana: 269 p.

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

Prestor, J., Pestotnik, S., Meglič, P. & Janža, M. 2011: Model of environmental pressures and impacts. A.3.3 final report of INCOME project (LIFE+ programme). Geological Survey of Slovenia: Ljubljana.

Prestor, J., Jamnik, B., Pestotnik, S., Meglič, P., Cerar, S., Janža, M., Auersperger, P. & Bračič-Železnik, B. 2017: Upravljanje onesnaženj podzemne vode na ravni funkcionalnega mestnega območja. In: 23. Simpozij z mednarodno udeležbo, Vodni dnevi 2017, Portorož, 5.-6.10.

Rozanski, K., Araguas-Araguas, L. & Gonfiantini, R. 1993: Isotopic patterns in modern global precipitation. Geophys. Monogr., 78: 1–36. https://doi.org/10.1029/GM078p0001

SLONIP. Slovenian Network of Isotopes in Precipitation. The SLONIP Database. Internet: https://slonip.ijs.si/ (01. 07. 2020)

Tipple, B. J., Jameel, Y., Chau, T. H., Mancuso, C. J., Bowen, G. J., Dufour, A., Chesson, L. A. & Ehleringer, J. R. 2017: Stable hydrogen and oxygen isotopes of tap water reveal structure of the San Francisco Bay Areas water system and adjustments during a major drought. Water Res., 119: 212–224. https://doi.org/10.1016/j.watres.2017.04.022

Torkar, A., Brenčič, M. & Vreča, P. 2016: Chemical and isotopic characteristics of groundwater-dominated Radovna River (NW Slovenia). Environ. Earth Sci., 75/18: 1-18. https://doi.org/10.1007/s12665-016-6104-5

Trček, B. 2005: Investigations of flow system and solute transport at an urban lysimeter at Union Brewery, Ljubljana, Slovenia = Proučevanje tokovnega sistema in prenosa snovi v urbanem lizimetru Pivovarne Union, Ljubljana, Slovenija. RMZ, 52/4: 685–696.

Trček, B. 2006: Izotopske raziskave na območju vodnega telesa Pivovarne Union = Isotopic investigations in the area of the Union Brewery water body. Geologija, 49/1: 103–112. https://doi.org/10.5474/geologija.2006.008

Trček, B. 2017: Application of environmental tracers to study the drainage system of the unsaturated zone of the Ljubljansko polje aquifer = Uporaba naravnih sledil za študij drenažnega sistema nezasičene cone vodonosnika Ljubljanskega polja. Geologija, 60/2: 267–277. https://doi.org/10.5474/geologija.2017.019

Uhan, J. & Kranjc, M. 2003: Podzemne vode. In: Uhan, J. & Bat, M. (eds.): Vodno bogastvo Slovenije. Ministrstvo za okolje in prostor, Agencija Republike Slovenije za okolje, Ljubljana: 55–67.

Urbanc, J. & Jamnik, B. 1998: Izotopske raziskave podzemne vode Ljubljanskega polja = Isotope investigations of groundwater from Ljubljansko polje (Slovenia). Geologija, 41: 355–364. https://doi.org/10.5474/geologija.1998.018

Urbanc, J. & Jamnik, B. 2002: Izotopske raziskave vodnih virov Ljubljanskega barja = Isotopic investigations of the Ljubljansko barje water resources. Geologija, 45/2: 589–594. https://doi.org/10.5474/geologija.2002.070

Urbanc, J., Jamnik, B., Cerar, S. & Mali, N. 2012: Hydrogeological investigations for improvement of conceptual model. Final report. Geological Survey of Slovenia, Project: INCOME (LIFE07ENV/SLO/000725), Ljubljana: 48 p.

Vižintin, G., Souvent, P., Veselič, M. & Čenčur Curk, B. 2009: Determination of urban groundwater pollution in alluvial aquifer using linked process models considering urban water cycle. J. Hydrol., 377/3–4: 261–273. https://doi.org/10.1016/j.jhydrol.2009.08.025

Vodila, G., Palcsu, L., Futó, I. & Szántó, Zs. 2011: A 9-year record of stable isotope ratios of precipitation in Eastern Hungary: Implications on isotope hydrology and regional palaeoclimatology. J. Hydrol. 400: 144–153. https://doi.org/10.1016/j.jhydrol.2011.01.030

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

Vreča, P., Krajcar Bronić, I., Horvatinčić, N. & Barešić, J. 2006: Isotopic characteristics of precipitation in Slovenia and Croatia: Comparison of continental and maritime stations. J. Hydrol., 330/3–4: 457–469. https://doi.org/10.1016/j.jhydrol.2006.04.005

Vreča, P., Krajcar Bronić, I., Leis, A. & Brenčič, M. 2008: Isotopic composition of precipitation in Ljubljana (Slovenia). Geologija, 51/2: 169–180. https://doi.org/10.5474/geologija.2008.018

Vreča, P., Žigon, S., Zavadlav, S. & Šturm, M. 2011: Analizno poročilo št. GEO 009/2011, Institut "Jožef Stefan", Odsek za znanosti o okolju, Ljubljana: 6 p.

Vreča, P., Stibilj, V., Žigon, S. & Svetek, B. 2013: Analizno poročilo št. GEO 007/2013, Institut "Jožef Stefan", Odsek za znanosti o okolju, Ljubljana: 5 p.

Vreča, P., Krajcar Bronić, I., Leis, A. & Demšar, M. 2014: Isotopic composition of precipitation at the station Ljubljana (Reaktor), Slovenia – period 2007–2010. Geologija, 57/2: 217–230. https://doi:10.5474/geologija.2014.019

Vreča, P., Štrok, M., Žigon, S. & Svetek, B. 2015: Analizno poročilo št. GEO 005/2015, Institut "Jožef Stefan", Odsek za znanosti o okolju, Ljubljana: 4 p.

Vreča, P. & Malenšek, N. 2016: Slovenian Network of Isotopes in Precipitation (SLONIP) – a review of activities in the period 1981–2015. Geologija, 59/1: 67–84. https://doi.org/10.5474/geologija.2016.004

Vreča, P., Štrok, M., Žigon, S. & Svetek, B. 2017: Isotope composition of precipitation at stations Ljubljana-Portorož airport: period 2011-2015, IJS working report 12383, Jožef Stefan Institute, Department of Environmental Sciences, Ljubljana: 32 p.

Vreča, P., Nagode, K., Kanduč, T., Lojen, S., Šlejkovec, Z., Žigon, S., Močnik, N., Novak, R., Bračič-Železnik, B., Jamnik, B. & Žitnik, M. 2019a: First working report on multi-isotope characterization of water resources for domestic supply in Ljubljana, Slovenia, IJS working report 12759, Jožef Stefan Institute, Department of Environmental Sciences, Ljubljana: 26 p.

Vreča, P., Kanduč, T., Šlejkovec, Z., Žigon, S., Nagode, K., Močnik, N., Bračič-Železnik, B., Jamnik, B. & Žitnik, M. 2019b: Karakterizacija vodnih virov za javno oskrbo s pitno vodo v Ljubljani s pomočjo različnih geokemičnih analiz. In: Kuhar, M. (eds.): Raziskave s področja geodezije in geofizike 2018: zbornik del, 24. srečanje Slovenskega združenja za geodezijo in geofiziko. Fakulteta za gradbeništvo in geodezijo, Ljubljana: 111–119.

Vreča, P., Nagode, K., Žigon, S. & Vaupotič, J. 2019c: Working report on hydrogen and oxygen isotope composition of tap water in Slovenia, IJS working report 12950, Jožef Stefan Institute, Department of Environmental Sciences, Ljubljana: 40 p.

Vreča, P., Nagode, K., Kanduč, T., Zuliani, T. & Žigon, S. 2019d: Third Working report on Multi-isotope characterization of water resources for domestic supply in Ljubljana, Slovenia - 24 hours experiment of the tap water, IJS working report, 12905, Jožef Stefan Institute, Department of Environmental Sciences, Ljubljana: 38 p.

Vreča, P., Kanduč, T., Žigon, S., Nagode, K., Zuliani, T., Štrok, M. & Svetek, B. 2019e: Poročilo o določitvi izotopske sestave vode, črpalni poskus Brest, IJS delovno poročilo 12857, Institut "Jožef Stefan", Odsek za znanosti o okolju, Ljubljana: 3 p.

Vreča, P., Kanduč, T., Žigon, S., Nagode, K., Zuliani, T., Štrok, M. & Svetek, B. 2019f: Poročilo o določitvi izotopske sestave vode, črpalni poskus Brest (piezometra PB-24a/19 in PB-24c/19), IJS delovno poročilo 12985, Institut "Jožef Stefan", Odsek za znanosti o okolju, Ljubljana: 4 p.

Vrzel, J., Solomon, D. K., Blažeka, Ž. & Ogrinc, N. 2018: The study of the interactions between groundwater and Sava River water in the Ljubljansko polje aquifer system (Slovenia). J. Hydrol., 556: 384-396. https://doi.org/10.1016/j.jhydrol.2017.11.022

Wassenaar, L. I., Coplen, T. B. & Aggarwal, P. K. 2014: Approaches for Achieving Long-Term Accuracy and Precision of 18O and 2H for Waters Analyzed using Laser Absorption Spectrometers. Environ. Sci. Technol., 48: 1123–1131. https://doi.org/10.1021/es403354n

Wassenaar, L. I., Terzer-Wassmuth, S., Douence, C., Araguas-Araguas, L., Aggarwal, P. & Coplen, T. 2018: Seeking excellence: An evaluation of 235 international laboratories conducting water isotope analyses by isotope-ratio and laser-absorption spectrometry. Rapid Commun. Mass Spectrom., 32/5: 393–406. https://doi.org/10.1002/rcm.8052

Zavadlav, S., Mazej, D., Zavašnik, J., Rečnik, A., Dominguez-Víllar, D., Cukrov, N. & Lojen, S. 2012: C and O stable isotopic signatures of fast growing dripstones on alkaline substrates: reflection of growth mechanism, carbonate sources and environmental conditions. Isot. Environ. Health S., 48/2: 354–371. https://doi.org/10.1080/10256016.2012.645540

Zhao, S., Hu, H., Tian, F., Tie, Q., Wang, L., Liu, Y. & Shi, C. 2017: Divergence of stable isotopes in tap water across China. Sci. Rep., 7: 43653. https://doi.org/10.1038/srep43653

Žlebnik, L. 1971: Pleistocene Deposits of the Kranj, Sora and Ljubljana Fields. Geologija, 14: 5–51.