



Research papers

Unravelling the sources contributing to the urban water supply: An isotope perspective from Ljubljana, Slovenia

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ARTICLE INFO

This manuscript was handled by Marco Borga, Editor-in-Chief, with the assistance of Daniele Penna, Associate Editor

Keywords:

Urban hydrology
Isotopes
Water sources
Groundwater
Water management
Slovenia

ABSTRACT

In cities experiencing rapid urbanization, we must continually update our understanding of the partitioning of drinking water sources concerning its supply if it is to be managed sustainably. This need is especially crucial given the pressure on water resources arising from evolving land use patterns and climate change. For this reason, a city-wide study of stable water isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) in precipitation, surface water and groundwater across Ljubljana, Slovenia, was undertaken. The goal was to characterise the temporal dynamics of urban water cycling and trace the various sources contributing to the city's drinking water supply. Monthly water sampling, combined with hydrogeochemical and *in-situ* data, permitted the identification of local precipitation and surface water contributions to its two groundwater supply aquifers. In addition, a re-examination of the mean residence times (MRT) of surface waters revealed an MRT of 3–4 years, which is much longer than previously reported. Also, changes in the contributions of surface water and precipitation to groundwater were observed compared to previous studies. These findings improve our understanding of local water partitioning and provide valuable insights for water managers addressing future urban water resource management.

1. Introduction

Freshwater is a vital resource for urban areas, yet achieving its sustainable management presents challenges in light of increasing urbanization (United Nations, 2019) and a changing climate (Caretta and Mukherji, 2022). While it has conventionally been assumed that distinct climate types adhere to foreseeable seasonal patterns, amounts of precipitation, and temperature variability, these assumptions are now being challenged due to climate variability caused by human activity (Abbass et al., 2022; Caretta and Mukherji, 2022). The impact of climate change on freshwater resources extends across many sectors, including agriculture, forestry, industry, and transportation (Dolinar, 2018; Wang et al., 2016).

In spite of such impacts, the consequences of extreme weather events on water sources and their long-term effects on water resources have not yet been thoroughly studied (Buras et al., 2020). This knowledge gap leaves urban areas vulnerable to the uncertainties of climate change and

raises concerns about the future supply of freshwater. In Slovenia, a country characterised by diverse climate zones and topography, climate projection indicates a substantial rise in the mean annual temperature by the end of the 21st century, ranging from 1.3 °C to even 4.1 °C, depending on the various scenarios (Dolinar, 2018). Although projected changes in precipitation for this region, positioned in a transition zone, are less reliable, various models predict increased precipitation throughout the year (Dolinar, 2018), with the most significant increase expected in winter.

Importantly, insufficient urban planning continues to pose a significant threat to the natural dynamics of the freshwater supply by altering the water cycle; for example, changes in infiltration are associated with increased runoff and decreased recharge (McGrane, 2016). Addressing these challenges is a complex undertaking, especially since it requires a deep understanding of how water demand changes in response to climatic variations (Miller and Belton, 2014), insight into the interactions between engineered and natural hydrological systems (McGrane, 2016),

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<https://doi.org/10.1016/j.jhydrol.2024.130892>

Received 24 January 2023; Received in revised form 24 January 2024; Accepted 30 January 2024

Available online 16 February 2024

0022-1694/© 2024 Published by Elsevier B.V.

and developing more integrated water management strategies (He et al., 2021).

Traditionally, water managers have relied on various technologies, such as hydrometric and hydrochemical measurements, to guarantee the quality and quantity of water delivered to the end user. However, this kind of analysis is often limited in urbanised areas (Pataki et al., 2011) and is difficult to verify due to a lack of field measurements (Waldrip et al., 2016). For this reason, knowledge of the sources contributing to the water supply system and their spatiotemporal distribution is necessary to understand how these systems respond to climate change (Sánchez-Murillo et al., 2020a), but sampling large and heterogeneous urban areas and their hinterlands remains a significant challenge.

Despite such limitations, research on the urban water cycle has advanced by utilising stable isotopes of H and O in water as environmental tracers. Together with physicochemical data, they provide insight into the spatiotemporal variations of water partitioning, water flow in catchments, and interactions between different water sources (Ortega et al., 2022). They also provide information on mixing and circulation within the hydrological cycle (Clark and Fritz, 1997; Clark, 2015). More recently, the application of isotope-based methods to urban areas has yielded promising results, such as the contribution of sources to municipal tap water at various spatiotemporal scales (Bowen et al., 2007; de Wet et al., 2020; Ehleringer et al., 2016; Tipple et al., 2017). Other studies have investigated the relationship between tap water isotope ratios and elemental geochemistry and their implications for water resource management practices (Nagode et al., 2021; Tipple et al., 2017). The aim here was to derive residence times of stream water (Kuhlemann et al., 2021) and create end-member mixing models (Nagode et al., 2021; Sánchez-Murillo et al., 2020b) to obtain quantitative information about sources and mixing in urban water systems.

As a case study, Ljubljana, a city with a population of approximately 300,000, exemplifies many of the challenges mentioned previously. Over the last three years, it has seen an annual increase in population of around 14,000 (SURs, 2022). The provision of water comes from two aquifers: the Ljubljansko polje aquifer (Lp aquifer) and the Ljubljansko barje aquifer (Lb aquifer), both of which are characterised by distinct recharge areas (Nagode et al., 2022; 2021; 2020 and references therein). In Ljubljana, water managers are interested in assessing temporal changes in each aquifer's contributions to the city's drinking water supply, precipitation regime, and increased urban land cover effects.

In the case of Ljubljana, isotope investigations have been conducted mainly in the Ljubljansko polje aquifer (Nagode et al., 2020; Vizintin et al., 2009; Vrzel et al., 2018), while only a few researchers have studied the connection between the Lp and Lb aquifers (Cerar and Urbanc, 2013; Nagode et al., 2020), or studied the Lb aquifer (Janža, 2022; Urbanc and Jamnik, 2002). However, using stable isotopes, it was confirmed that most groundwater is derived from a combination of locally infiltrated surface water and local precipitation (Urbanc and Jamnik, 1998; Vrzel et al., 2018); a detailed review of all isotope investigations in the area is given by Nagode et al. (2020).

The main focus of the present study was to verify end-members, re-evaluate the contribution of water sources to the drinking water supply, and assess the effects of changes to the water supply system. To address these objectives, environmental hydrochemical and isotope tracers were employed to investigate the system's origin, mixing processes, and water movement, which involved monthly precipitation, surface water, and groundwater sampling. Hydrometeorological and hydrochemical data were obtained from the Slovenian Environment Agency, Ljubljana ARSO (2022) and public utility VOKA SNAGA d.o.o.

Furthermore, an investigation of the short-term dynamics of precipitation, surface water, and groundwater using stable isotopes was performed, including re-evaluating source water contributions, assessing the MRT of surface water, and estimating the correlation between precipitation, surface water, and groundwater. The findings from this study underscore the importance of monitoring natural systems, particularly given that climate change impacts groundwater recharge

(Chaturvedi et al., 2021). The study also provides essential information for water managers, particularly those tasked with comprehending the present state of the Ljubljana water supply, its vulnerabilities, and its sustainable management, ultimately benefiting the entire population in the region.

2. Study site

2.1. Environmental context

The study area (Fig. 1) is situated in the lowland region of central Slovenia, which is part of the eastern Ljubljana basin. This basin includes the Lp aquifer to the north and the Lb aquifer to the south, covering an area of 109.1 km² and 129.3 km², respectively (ARSO, 2004). According to the Köppen classification system, it belongs to the temperate climate, i.e., Köppen–Geiger code Cfa (Beck et al., 2018). The basin has a mean annual temperature of 10.94 °C and receives an average annual precipitation of 1362 mm, based on the 1981–2010 Climate Normals (ARSO, 2022). Typically, the driest season is winter (Dec-Feb), with minimal rainfall, totalling 246 mm (snow precipitation being typical during winter). The wettest seasons are autumn (Sep-Nov) and summer (Jun-Aug), with 423 mm and 396 mm, respectively, followed to a lesser extent by spring (Mar-May), which receives 297 mm (1981–2010 Climate Normals).

2.1.1. Surface water hydrology

The main watercourses flowing through the study area are the Sava (Lp aquifer) and the Ljubljana Rivers (Fig. 1). The Sava River, located on the northern part of the Lp aquifer, forms part of the Sava River catchment. The main direction of the Sava River flow in the study area is from northwest to east, with discharge varying between 40 m³/s and 700 m³/s (Jamnik et al., 2003), and is strongly interconnected with the groundwater (Bračić Železnik and Jamnik, 2005). The other important river in the Lp aquifer is the Ljubljana, which flows over the Lb aquifer and enters the Lp aquifer through the narrow passage between the Grajski and Rožnik hills. However, due to the impermeability of its river bed, it does not contribute to groundwater recharge (Jamnik et al., 2003). The Ljubljana River is the right tributary of the Sava River at the Eastern border of the study area, whereas the Iška River (Fig. 1) is the right tributary of the Ljubljana River and flows in a northerly direction from the Krim-Mokrec karst mountains and discharges near Iška vas settlement at a rate of between 0 and 90 m³/s.

2.1.2. Geology

The Lp aquifer is hosted in rocks deposited in a tectonic depression formed in the early Pleistocene. The bedrock comprises Permian and Carboniferous slate claystone and sandstone that can also be found in the surrounding hills. The depression was filled in by the Sava River deposits comprising Pleistocene and Holocene silty-sandy gravels and sandy gravel with lenses of conglomerate transported from alpine glaciers (Žlebnik, 1971). The thickness of the fluvial deposit varies, i.e., in the area surrounding Kleče, it ranges between 70 and 105 m, whereas, in the vicinity of Hrastje, Jarški prod, and Šentvid, it ranges between 70 and 80 m in depth (Bračić Železnik et al., 2005; Bračić Železnik and Jamnik, 2005).

A large subsidence wetland area, intersected by numerous faults, lies in the southern part of the Ljubljana basin where the Lb aquifer is situated. The basement consists of Upper Triassic dolomite and Jurassic limestone on the south, west, and central parts, and Triassic and Permian–Carboniferous shaly mudstone and sandstone to the north and east (Placer, 2008). Rivers and creeks from Krim-Mokrec hills filled the area with Pleistocene and Holocene fluvial and lacustrine sediments (Mencej, 1988) up to 160 m in depth, while in the vicinity of Brest, the sediment depth reaches 110 m.

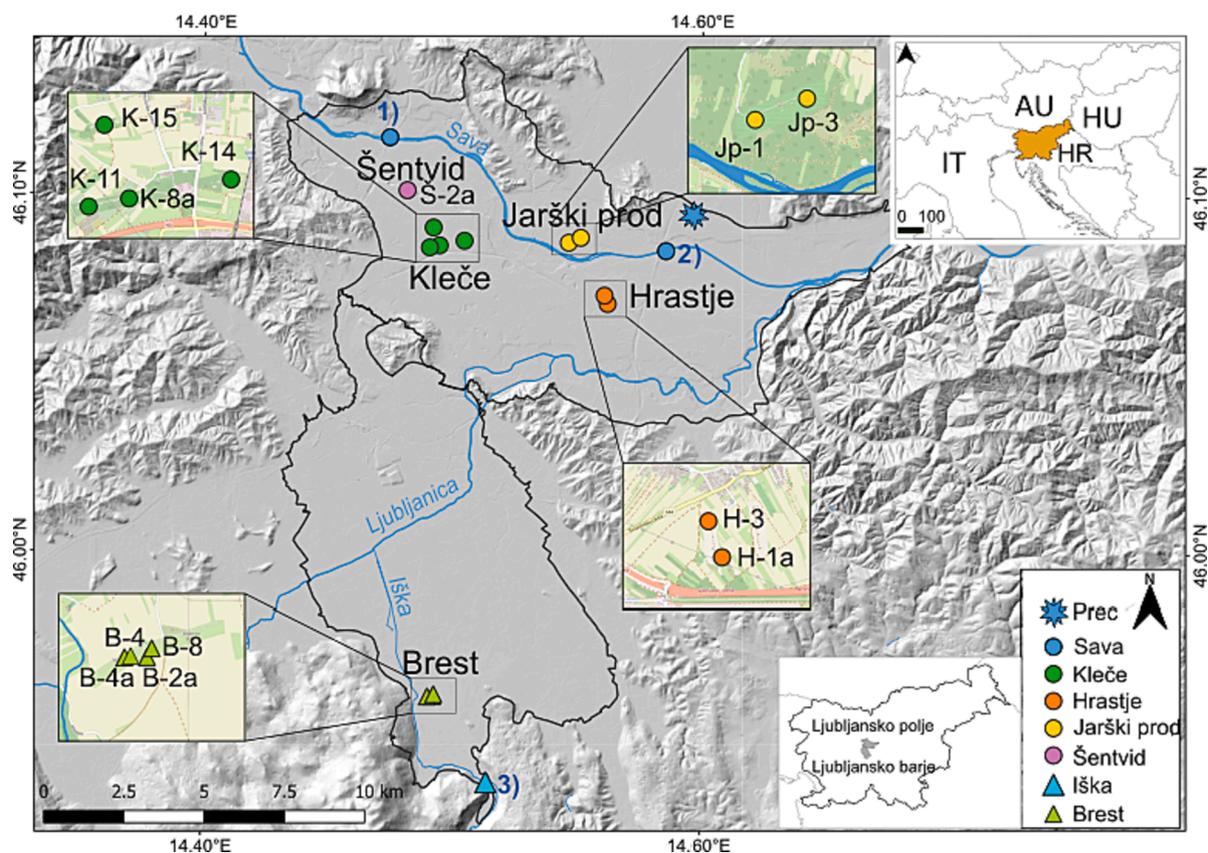


Fig. 1. a) Location of Slovenia in Europe; b) Sampling area in Slovenia with Ljubljansko polje and Ljubljansko barje aquifer; c) Sampling locations of precipitation (Prec), surface water at two rivers (Sava at Brod (1) and Šentjakob (2) and Iška River at Iška vas (3)) and sampling wells in Kleče (K), Brest (B), Hrastje (H), Jarški prod (Jp) and Šentvid (S) wellfields. More details about the wells are given by Nagode et al. (2022).

2.1.3. Hydrogeology

The Lp aquifer is unconfined in most areas, but in some places, layers of low hydraulic conductivity can form perched aquifers (Sram, 2012). Several studies have concluded that the Sava River on the northern edge of the Ljubljansko polje supplies the aquifer with water, while downstream from Šentjakob, groundwater drains into the river (Janža et al., 2015). A smaller amount of groundwater recharge is from lateral underground inflow from neighbouring aquifers such as the Kamniško–Bistriško polje and Lp aquifers (Jamnik et al., 2000). The groundwater responsiveness in the Lp aquifer reacts more quickly to river events than precipitation events due to its higher horizontal than vertical hydraulic conductivity (Vrzel et al., 2019). The hydraulic conductivity ranges from $3\text{--}7 \times 10^{-3}$ m/s on the borders to 10^{-2} m/s in the central part (Jamnik et al., 2003). The groundwater flow is generally directed towards the southeast, where four wellfields are situated: Kleče, Hrastje, Jarški prod and Šentvid (Fig. 1), comprising perforated screens varying from 200 to 290 m a.s.l. (Nagode et al., 2022). In 2020 and 2021, the daily extraction rates were $51974 \text{ m}^3/\text{day}$, $7139 \text{ m}^3/\text{day}$, $4385 \text{ m}^3/\text{day}$ and $7047 \text{ m}^3/\text{day}$, respectively (Jamnik and Žitnik, 2022).

Most groundwater flows through the gravel layers in the Lb aquifer and is under artesian or sub-artesian pressure. The presence of sediments with different hydraulic properties and lenses of fine-grained material has meant that separate multi-layered aquifers have developed. These include a Holocene gravel aquifer whose upper surface is a water table free to fluctuate, an Upper Pleistocene aquifer with the artesian groundwater level, a Lower Pleistocene aquifer with sub-artesian GW level, and a Karstic-fissure carbonate aquifer.

The upper alluvial fan of the Iška River, positioned in the south of the Lb aquifer, is directly recharged by precipitation and seepage from the Iška River, while the deeper parts of the aquifer are recharged by the percolation of water through carbonate rocks from the karstic aquifer

south and west of the Ljubljansko barje (Janža, 2022; Mencej, 1988). The upper part of the aquifer reacts rapidly to increases in the flow of the Iška River and is sensitive to drought and low river water levels (Janža, 2022; Breznik, 1975). The hydraulic conductivity is estimated to be between 1×10^{-3} m/s and 2×10^{-5} m/s (Pregl and Narat, 2016, 2015a, 2015b), while the direction of flow is from south to north (Janža, 2022). Groundwater in this area is extracted from the Brest wellfield, providing approximately 10 % of Ljubljana's drinking water (Jamnik et al., 2003) at a daily rate of $9514 \text{ m}^3/\text{day}$ (2020–2021). Perforated screens are positioned at 290 m and 270 m a.s.l. for shallow wells and 270 to 195 m a.s.l. for the deeper wells (Nagode et al., 2022).

2.2. Data sources and methods

The surface water and groundwater isotope datasets ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) and the in-situ parameters used in this work are published in Žagar et al., (2022a,2022b), and the geochemistry obtained from VOKA SNAGA d.o.o. database are provided in the supplementary material (Table S1).

2.2.1. Water sampling and analysis

The sampling strategy was to observe the common water types in the study area monthly over two years (2020 to 2021) using precipitation ($N=24$), surface water ($N=56$), and groundwater ($N=248$) measurements. In Ljubljana (Fig. 1), at the IJS-Reaktor station (46.094612 14.597046, SLONIP, 2022, <https://slonip.ijs.si>), monthly isotope composition samples were collected ($N=24$) and the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values determined. The samples were collected using the precipitation collector described in Vreča and Malenšek (2016). Long-term isotopic data (1981–2010) for precipitation were also included (Vreča et al., 2022, 2014, 2008), while the daily air temperature (T_{air}) and precipitation (P) data were obtained from the Slovenian Environment Agency

for the station at Ljubljana–Bežigrad (meteo.si, 2022).

Surface water and groundwater sampling began in January 2020 with the monthly sampling of the Sava River at Brod and Šentjakob (Fig. 1). The sampling of the Iška River at Iška vas (Fig. 1) began in March 2021. Grab samples were collected using a polypropylene Burklee TM angular beaker attached to a BurkleeTM telescopic rod (Burklee GmbH, Bad Bellingen, DE). In-situ temperature measurements and electrical conductivity were recorded using a calibrated UltrameterTM II 6PFCE (MYRON L Company, Carlsbad, CA, USA), with an accuracy of ± 0.15 °C and ± 1 $\mu\text{S}/\text{cm}$. Fifty-six surface water samples were collected over two years.

Groundwater sampling included 13 wells (Fig. 1, Table 2) pre-selected by water managers: Kleče 8a (K-8a), Kleče 11 (K-11), Kleče 14 (K-14), Kleče 15 (K-15), Hrastje 1a (H-1a), Hrastje 3 (H-3), Brest 4 (B-4), Brest 2a (B-2a), Brest 4a (B-4a), Brest 8 (B-8), Jarški prod 1 (Jp-1), Jarški prod 3 (Jp-3) and Sentvid 2a (Š-2a). Samples were collected monthly by the technical staff of the water distribution company on the same day. On the following day, surface water samples were collected. If the pre-selected well was not operating, the closest well was sampled instead (those results are not discussed in this article). The number of groundwater samples was 248. In-situ measurements were performed using a Superfast Thermapen 4 digital thermometer (Electronic Temperature Instruments Ltd). All surface water and groundwater samples were collected in airtight 60 ml HDPE bottles and stored at 5 °C until analysis.

The oxygen and hydrogen isotopic compositions ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) were determined on all 328 water samples using the $\text{H}_2\text{-H}_2\text{O}$ (Coplen et al., 1991) and $\text{CO}_2\text{-H}_2\text{O}$ (Epstein and Mayeda, 1953; Avak and Brand, 1995) equilibration technique at the Jožef Stefan Institute. Isotope analyses were conducted using a dual inlet isotope ratio mass spectrometer (DI IRMS, Finnigan MAT DELTA plus, Finnigan MAT GmbH, Bremen, Germany) with an automated $\text{H}_2\text{-H}_2\text{O}$ and $\text{CO}_2\text{-H}_2\text{O}$ equilibrator HDOeq48 Equilibration Unit (custom built by M. Jaklitsch). All samples were measured in duplicate and together with laboratory reference materials (LRM). The LRMs were calibrated periodically against primary IAEA calibration standards VSMOW2 and SLAP2 to the VSMOW/SLAP scale. The results were normalized to the VSMOW/SLAP scale using the LIMS (Laboratory Information Management System for Light Stable Isotopes) programme and are expressed in the δ notation (in ‰) as a mean value and standard deviation. Two LRMs, namely W-3869 and W-3871, with defined isotope values, were used to normalise results. The measurement uncertainty was estimated using the Kragten method (Carter and Barwick, 2011) and was 0.9 ‰ for $\delta^2\text{H}$ and 0.04 ‰ for $\delta^{18}\text{O}$. The internal LRM W-45 and commercial reference materials, USGS 45 or USGS 47, with defined isotopic values and estimated measurement uncertainty, were added to each measurement sequence for independent quality control. The average sample repeatability was 0.3 ‰ for $\delta^2\text{H}$ and 0.02 ‰ for $\delta^{18}\text{O}$. The deuterium excess (d-excess) was calculated as d-excess [‰] = $\delta^2\text{H} - 8 \times \delta^{18}\text{O}$ (Dansgaard, 1964).

The major cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) and anions (Cl^- , SO_4^{2-} , HCO_3^-) components and Br^- as a minor component, were regularly monitored in the groundwater at selected sites (K-8a, K-11, K-14, K-15, H-1a, H-3, B-4, B-2a, B-4a, B-8, Jp-1, Jp-3, Š-2a). Sampling was conducted between January 2020 and December 2021 during four to six campaigns, depending on the sampling location. Groundwater samples from the Sentvid wellfield were collected to determine the concentrations of only Ca^{2+} and Mg^{2+} cations. Thirty-nine samples were collected by the technical staff of the water distribution company from 13 wells and analysed by ion chromatography Metrohm MIC-3, Switzerland measurement (coverage factor $K=2$, reliability 95 %) at the accredited laboratory of Water Supply Company VOKA SNAGA d.o.o. The accuracy of the chemical analyses was checked by calculating their ionic balance error (ϵ); all the analyses had $\epsilon \leq 5$ %.

2.2.2. Calculations

Data analysis – All basic descriptive statistics were performed using Microsoft® Office Excel 2019 and OriginPro 2021 for plotting. Weighted

means for precipitation and surface water data were calculated using cumulative mean monthly precipitation amounts and monthly discharge, respectively. A classical Piper diagram was used to deduce the groundwater chemical types.

Local Meteoric Water Lines – A Local Meteoric Water Line (LMWL) from January 2020–December 2021 ($N=24$) was constructed using the precipitation-weighted reduced major axis method (LMWL_{PWRMA}) using Python script (Pavšek and Vreča, 2022). The obtained equation was compared with the Global Meteoric Water Line (GMWL): $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$ (Craig, 1961).

Isotope mass balance – A simple isotope-mass balance was employed due to the statistical difference between the $\delta^{18}\text{O}$ value of local precipitation and in the Sava and Iška Rivers ($p=0.05$). The fraction of the groundwater was defined as:

$$\delta_{\text{GW}}(t) = p\delta_{\text{R}}(t) + (1 - p)\delta_{\text{P}}(t) \quad (1)$$

where p is the fraction of the river water and subscripts GW, R, and P stay for groundwater in wells, river and local precipitation, respectively. The value p can be calculated by rearranging Eq. (1) and using the mean isotopic composition of the components:

$$p = (\bar{\delta}_{\text{GW}} - \bar{\delta}_{\text{P}}) / (\bar{\delta}_{\text{R}} - \bar{\delta}_{\text{P}}) \quad (2)$$

A weighted mean isotopic composition of -8.47 ‰ for precipitation was used, while -9.19 ‰ and -9.15 ‰ were used for the Sava and Iška Rivers, based on the study data. The isotope composition of the surface water of the Sava and the Iška Rivers varies slightly compared with the isotopic composition of the precipitation (δ_{P}). Consequently, the travel time from the river water to the groundwater can be estimated by fitting Eq (3), whereas the fraction of the surface water is obtained from Eq (2).

$$\delta_{\text{GW}}(t) = p \int_0^{\infty} \delta_{\text{R}}(t - t')g(t')dt' + (1 - p) \quad (3)$$

Mean residence time – Seasonal trends in $\delta^{18}\text{O}$ in precipitation and surface water of the Sava River at Brod and Šentjakob were modelled using the same approach described by Ogrinc et al. (2018) to compare results. Periodic regression analysis was used to fit seasonal sine wave curves to annual $\delta^{18}\text{O}$ variations in precipitation and surface water and is defined as:

$$\delta^{18}\text{O} = X + A[\cos(ct - \theta)] \quad (4)$$

where $\delta^{18}\text{O}$ is modelled $\delta^{18}\text{O}$ (‰), X is the weighted mean annual amplitude, c is the radial frequency of annual fluctuation (0.017214 rad/d), t is the time in days after the start of the sampling, and θ is the phase lag. The MRT was defined by using the exponential model, where the precipitation is assumed to mix rapidly with the surface water using the following equation:

$$T = c^{-1}[(A_{z_2}/A_{z_1})^{-2} - 1]^{0.5} \quad (5)$$

where A_{z_1} is the amplitude of precipitation $\delta^{18}\text{O}$ (‰), A_{z_2} is the amplitude of the surface water $\delta^{18}\text{O}$ (‰), and c is the radial frequency of annual fluctuations as defined in the Eq (4).

3. Results

The hydrochemical and isotopic ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) characterisation of precipitation, surface water and groundwater presents an updated contribution to previous investigations (Cerar and Urbanc, 2013; Nagode et al., 2020; Vrzel et al., 2018) of the water sources in the Ljubljana basin. All data is plotted on the $\delta^2\text{H}$ – $\delta^{18}\text{O}$. Mean air temperature (°C), amount of precipitation (mm), and mean isotope composition of $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) for precipitation for periods during sampling and long-term averages are presented in Table 1. Table 2 displays the mean, standard deviation, minimum, and maximum values for precipitation, the Sava and Iška Rivers, and groundwater.

Table 1

Mean air temperature (°C), precipitation amount (mm), and mean weighted isotope composition of $\delta^{18}\text{O}$ (‰) and $\delta^2\text{H}$ (‰) for precipitation collected at the Station Ljubljana (Reaktor) for the periods 2020, 2021, 2020–2021 and 1981–2010, respectively.

	Mean T (°C)	Mean P (mm)	Mean weighted $\delta^{18}\text{O}$ (‰)	Mean weighted $\delta^2\text{H}$ (‰)
2020	12.1	1262	−8.04	−53.2
2021	11.5	1442	−8.85	−58.8
2020–2021	11.8	1352	−8.47	−56.2
1981–2010	10.9	1362	−8.65	−59.2

3.1. Climatic and isotope dynamic of precipitation

In the Ljubljana area, 2020 and 2021 experienced temperatures more than 0.8 °C higher than the long-term (1981–2010) annual mean air temperature of 10.9 °C. Additionally, there was a precipitation deficit of 7.3 % in 2020 and a surplus of 5.9 % in 2021 compared to the long-term mean annual precipitation of 1362 mm (Table 1) (ARSO, 2022).

Monthly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in precipitation followed a seasonal pattern: more negative values in winter and more positive values in summer (Fig. 2). A precipitation-weighted mean for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ was -8.47 ± 0.22 ‰ and -56.2 ± 1.5 ‰ (N=24) (Table 1), with an overall variability of 9.55 ‰ and 74.9 ‰ over the two years, respectively. D-excess values ranged from 2.7 to 16.0 ‰. On a monthly scale, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in precipitation correlated well with the mean air temperature (Spearman coefficient $r > 0.6$, $p < 0.05$, N=24) but not with the monthly precipitation amount ($r = -0.24$, $p < 0.05$). The LMWL_{PWRMA} was $\delta^2\text{H} = (7.23 \pm 0.16) \delta^{18}\text{O} + (5.06 \pm 1.44) R^2 = 0.99$, N=24 (Fig. 3).

3.2. Hydrometric and isotope dynamic in surface water

The Sava River exhibited fluctuations in its flow regime, with the lowest mean discharge of 286.5 m³/s occurring in January–February 2020, followed by a steady increase throughout the year, culminating in the winter months (2020/2021) with a total of 361.7 m³/s. The discharge then decreased to 293.2 m³/s in autumn 2021. The discharge showed no seasonal variation, with daily means ranging from 31.6 to 385.7 m³/s. The discharge of the Sava River at Šentjakob in 2020 was 13.2 % lower, while in 2021, it was 6.1 % higher compared to characteristic discharges over the long-term, i.e., 82.0 m³/s between 1981 and 2010. Additional variability is evident in the measured water physiochemical parameters (Fig. 2), e.g., the EC was low and ranged from

Table 2

Sampling locations with the number of samples (N), descriptive parameters (GKY, GKX, elevation, type of sampling water, type of well and depth of perforated screens) with basic descriptive statistics (mean, standard deviation, minimum and maximum) for $\delta^{18}\text{O}$ (‰), $\delta^2\text{H}$ (‰) and mean d-excess for the period 2020–2021 (Žagar et al., 2022a, 2022b).

Sampling location	N	GKY	GKX	Elevation (m)	Type	Type of well	Depth (m)	$\delta^{18}\text{O}$ (‰)				$\delta^2\text{H}$ (‰)				d – excess (‰)
								Mean	SD	Min	Max	Mean	SD	Min	Max	
Ljubljana – Reaktor	24	468841	106168	282.2	P	/	/	−8.15	2.6	−13.44	−3.89	−54.1	19.3	−99.2	−24.3	11.1
Sava River Brod	23	459354	108611	293.4	SW	/	/	−9.26	0.11	−9.58	−9.04	−60.9	1.0	−63.2	−59.1	13.2
Sava River Šentjakob	23	468013	105074	269.7	SW	/	/	−9.23	0.14	−9.62	−9.01	−60.6	0.8	−62.4	−59.2	13.2
Iška River	10	462362	88597	324.5	SW	/	/	−9.17	0.23	−8.68	−9.51	−60.3	2.0	−56.9	−63.7	13.1
Kleče 8a (K-8a)	19	461311	104771	307.1	GW	Shallow	278–241	−9.15	0.05	−9.22	−9.05	−60.9	0.7	−62.6	−60.0	12.3
Kleče 11 (K-11)	20	461006	104703	307.9	GW	Shallow	274.7–249.7	−8.85	0.03	−8.90	−8.79	−59.3	0.8	−61.0	−57.8	11.5
Kleče 14 (K-14)	14	462081	104914	304.1	GW	Shallow	274.7–246.7	−9.00	0.08	−9.11	−8.84	−59.8	0.9	−61.8	−58.8	12.2
Kleče 15 (K-15)	22	461113	105323	306.5	GW	Shallow	277.5–249.5	−9.01	0.10	−9.17	−8.84	−60.2	1.0	−61.6	−58.3	11.9
Brest 4 (B-4)	12	460926	90791	299.8	GW	Shallow	289.2–273.2	−8.91	0.26	−9.36	−8.40	−58.5	1.5	−60.5	−55.5	12.8
Brest 2a (B-2a)	22	461079	90789	299.5	GW	Deep	204.5–198.5	−9.50	0.02	−9.54	−9.47	−63.6	0.5	−64.2	−62.2	12.4
Brest 4a (B-4a)	22	460913	90783	300.2	GW	Deep	269.9–195.9	−9.51	0.02	−9.55	−9.48	−63.3	0.6	−64.1	−61.9	12.8
Brest 8 (B-8)	19	461112	90853	300.4	GW	Shallow	288.8–272.8	−8.75	0.21	−9.03	−8.36	−58.2	1.5	−59.7	−54.5	11.8
Sentvid 2a (Š-2a)	21	460308	106494	309.2	GW	Shallow	267.6–264.6	−8.84	0.25	−8.98	−8.73	−59.1	1.1	−61.1	−57.2	11.6
Hrastje 1a (H-1a)	21	466549	102944	286.8	GW	Shallow	274.8–239.4	−8.85	0.03	−8.89	−8.80	−59.5	0.6	−60.9	−58.4	11.3
Hrastje 3 (H-3)	11	466448	103203	287.3	GW	Shallow	275.4–243.4	−8.92	0.04	−8.96	−8.85	−60.0	0.5	−61.0	−59.1	11.4
Jarški prod 1 (Jp-1)	23	465335	104849	283.1	GW	Shallow	261.1–235.1	−9.20	0.05	−9.34	−9.14	−60.6	0.9	−61.9	−58.1	13.0
Jarški prod 3 (Jp-3)	22	465711	105005	281.4	GW	Shallow	257–221.6	−8.93	0.11	−9.13	−8.72	−59.3	1.2	−61.4	−56.7	12.1

225 to 372 $\mu\text{S}/\text{cm}^{-1}$, with the lowest value observed during the highest discharge (May 2020). The river water temperature showed the expected seasonality, with the highest values observed in the summers of 2020 and 2021. Altogether, the temperature ranged from 3.9 to 16.8 °C. In comparison to $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in precipitation, the monthly surface water isotope patterns were significantly dampened with no pronounced seasonality and with an overall variability of 3.2 ‰ for $\delta^2\text{H}$ and 0.61 ‰ for $\delta^{18}\text{O}$ during the 2-year sampling period (Fig. 2). The lowest $\delta^{18}\text{O}$ occurred in June 2021, with a value of −9.62 ‰. The mean seasonal signal for $\delta^{18}\text{O}$ does not vary significantly across all four seasons, with mean values of −9.24 ‰ for winter, spring, and summer and −9.20 ‰ for autumn.

The monitoring of the Iška River only began in March 2021 (Fig. 2). However, discharge and temperature data for the sampling period are available. The discharge observed is lower than the Sava River (0.09 to 11.83 m³/s), with a much smaller recharge area. The highest discharge can be observed for autumn 2020, winter 2020/2021 and spring 2021, followed by a gradual decrease in autumn 2021 (Fig. 2). The EC was higher than in the Sava River, ranging from 358 to 423 $\mu\text{S}/\text{cm}^{-1}$. The change of the EC does not follow the same pattern as observed in the Sava River. This difference can be attributed to the unique characteristics of the Iška River recharge area, which originates in a karstic region. In such geological formations, water–rock interactions have a pronounced influence on the overall conductivity of the water (Appelo and Postma, 2005). The temperature followed the expected seasonality, ranging from 0.0 °C to 22.3 °C, with the highest in the summer of 2021 (Fig. 2). The temperature generally remained lower than the Sava River, except in June 2021. The isotope signal was strongly dampened (between −9.51 and −8.68 ‰) with the most positive value of −9.03 ‰ in summer. The discharge weighted mean was for $\delta^{18}\text{O}$ −9.15 ‰ and −59.9 ‰ for $\delta^2\text{H}$. The Iška River had higher seasonal variations than the Sava River.

3.3. Groundwater level and isotope composition

The available groundwater level data between 2015 and 2021 in the Lp aquifer shows a similar seasonal pattern to groundwater level oscillation in the Lb aquifer, where the lowest water table usually occurs at the end of the summer or at the beginning of autumn, with a minimum in August, while the highest level is significant for the winter months with a peak in December (ARSO database archive). At the beginning of 2020, the groundwater levels in the Lp aquifer were high, while in subsequent months, the groundwater level gradually decreased until June 2020.

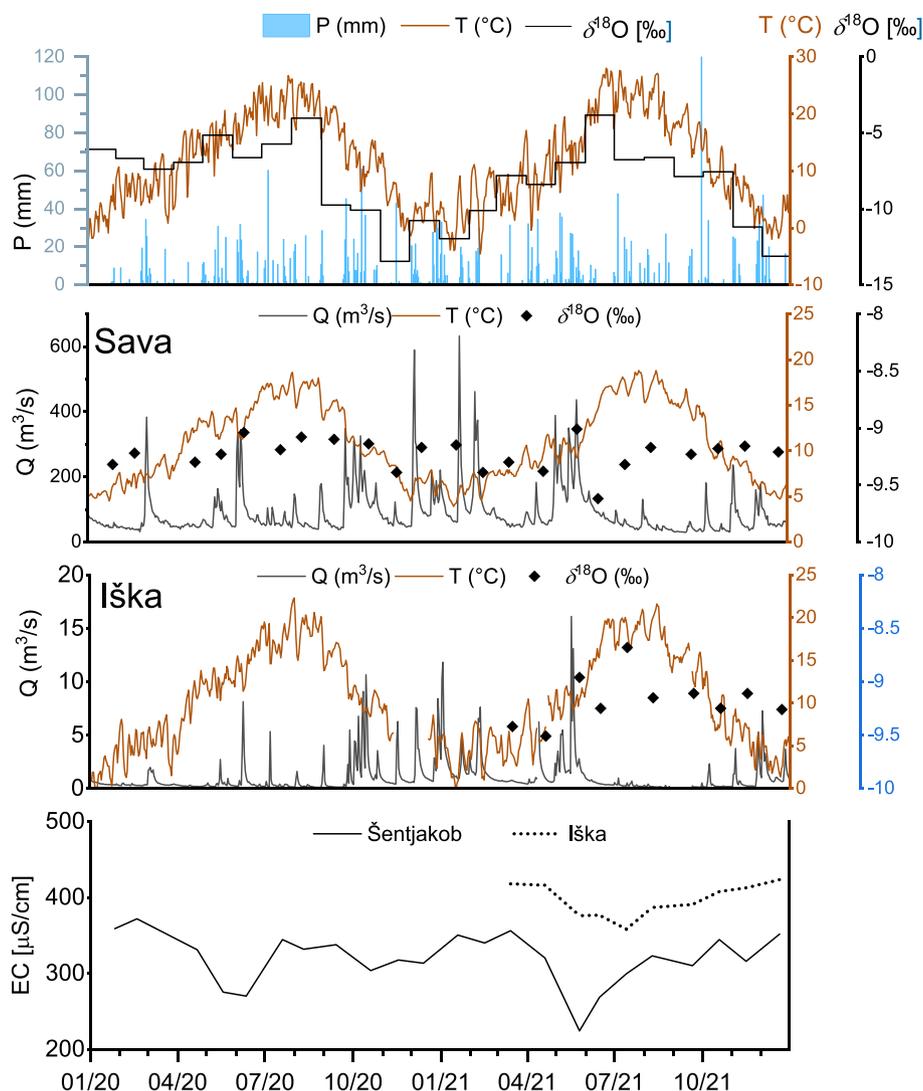


Fig. 2. Time series of the daily amount of precipitation, air temperature, surface water discharge (ARSO, 2021) and surface water temperature for the Sava and Iška River, $\delta^{18}\text{O}$ in precipitation and surface water and electrical conductivity in the Sava and Iška River over the 2-year study period. For a comparison with long-term values, please refer to paragraphs 3.1 and 3.2.

This trend reversed in the second half of the year and reached its peak at most measuring stations in December 2020. The highest groundwater levels were recorded in June 2021, followed by a gradual reduction until November 2021. In the area of the Lp aquifer, groundwater temperature ranged from 9.9 to 13.6 °C measured at B-4 and H-1a. Generally, the highest temperature was observed at the Hrastje wellfield.

The groundwater level measurements in the Pleistocene aquifer of Lb at the national groundwater monitoring stations between 2015 and 2021 revealed seasonal patterns, with the lowest values typically occurring from August to October and the highest from December to March. In 2020 and 2021, the mean monthly groundwater levels were the highest in January 2020, then gradually decreased until September of the same year. Subsequently, two higher peaks in groundwater level were observed, the first between January and February and a second between May and June 2021, followed by a decrease until October 2021. The end of 2022 was favourable regarding quantitative groundwater status, but groundwater levels have not reached the water levels from January 2020. Groundwater temperature oscillated between 10 and 16 °C in 2020 and 2021 (ARSO database archive).

In the Lp aquifer, groundwater samples show minor variations in their isotope composition (Table 2 and Figs. 3 and 4). The $\delta^{18}\text{O}$ values in groundwater varied between -9.34 ‰ and -8.72 ‰, with the lowest

variability for K-11 (0.11 ‰) and H-1a (0.09 ‰) and the highest for Jp-3 (0.41 ‰). The overall increase in $\delta^{18}\text{O}$ values with time can be observed in K-8a, K-11, K-15 and Š-2a. Interestingly, samples collected in colder months were more positive for Jp-3 and H-1a.

In the area of the Lb aquifer, both shallow and deep aquifers contribute to the extracted water. The mean $\delta^{18}\text{O}$ values in the Iška River were more negative than those in the shallower wells, while the values in the deeper wells were even more negative than those found in surface water. The $\delta^{18}\text{O}$ in groundwater varied from -9.55 to -8.26 ‰, with a range of 1.29 ‰ (Table 2 and Figs. 3 and 4). It is worth noting that the overall range of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values observed in groundwater was relatively small compared to the broader variability seen in precipitation and the Iška River. Additionally, there was no evidence of evaporative water loss in the shallow groundwater, as indicated by the data points (Fig. 3, green dots) aligning closely with the local meteoric water line (Clark and Fritz, 1997). The $\delta^{18}\text{O}$ values isotopes in deep groundwater also showed a more negative signal than precipitation and the Iška River, underscoring the homogeneity of the river's water composition (Figs. 2 and 3).

In most wellfields of Lp and Lb aquifers, the d-excess increased during the observation period, while in Kleče, no trend was observable. The d-excess of all groundwater samples ranged from 9.7 to 15.2 ‰

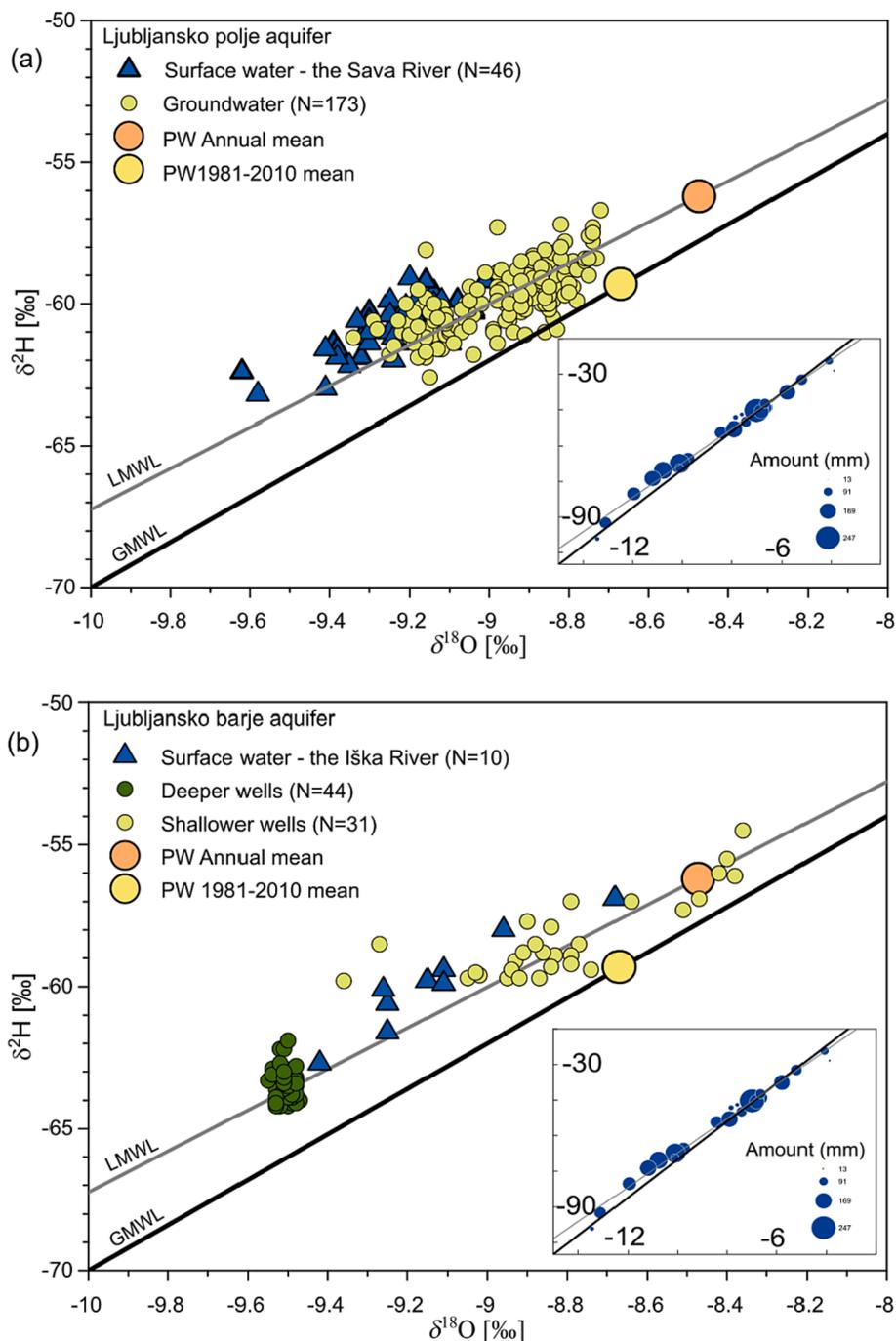


Fig. 3. Dual isotope plot showing the isotope composition of i) precipitation (blue circular dots), precipitation weighted (PW) mean for the period 1981–2010 (yellow circle) and 2020–2021 (orange circle), ii) surface water and iii) groundwater regarding the seasons for a) Lp aquifer and b) Lb aquifer (Žagar et al., 2022a, 2022b). Lines representing GMWL and LMWL_{PWRMA} correspond to global and local meteoric lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Fig. 4). The absence of apparent evaporative loss during shallow subsurface infiltration is supported by the work of Vrzel et al. (2018).

The chemical characteristics of the samples are representative of the different aquifers and the main physicochemical processes controlling them (Fig. 5). The groundwater from the Lp aquifer is characterised as a Ca–HCO₃ facies and the Lb aquifer as a Ca–Mg–HCO₃ facies. The Lp aquifer has higher SO₄²⁻, Cl⁻, Na⁺ and K⁺ levels, while high levels of K⁺ were recorded in the Lb aquifer (B-3). The highest concentration of Cl⁻ was observed for the Hrastje wellfield in addition to higher EC, T and NO₃⁻ values compared to other Lp aquifer wells. Likewise, higher NO₃⁻, EC values and Cl⁻ concentration are notable at K-11 and K-14 compared

to other wells in the Kleče wellfield. Higher NO₃⁻ content can be attributed to fertilisers used in the area, while the concentration of Ca²⁺, Mg²⁺, Na⁺, HCO₃⁻, EC and NO₃⁻ in Kleče, Hrastje and Jarški prod increases with distance from the Sava River. Furthermore, the chemical analysis results indicate that the Lp aquifer is more affected by anthropogenic activities than the Lb aquifer.

At the Lb aquifer, the two wells that tap deep into the Pleistocene aquifer are characterised by their lower Na⁺, K⁺, Cl⁻ and SO₄²⁻ levels. However, higher NO₃⁻ concentrations can also be observed compared to other wells in the Brest wellfield. The EC of the shallow wells is higher compared to the deeper wells. In addition, the levels of Ca²⁺ and Mg²⁺

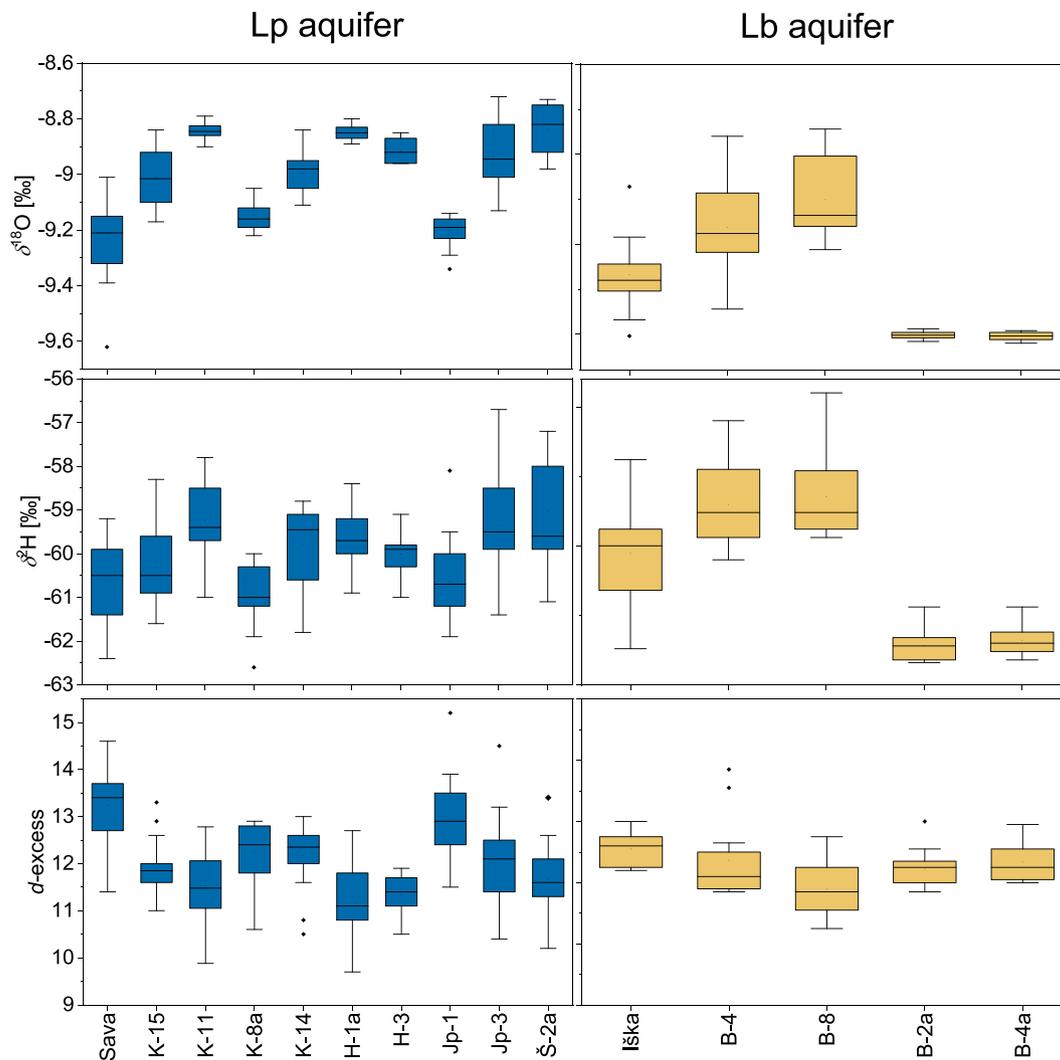


Fig. 4. Boxplots comparing the isotopic composition of surface water and groundwater at the Lp aquifer (left) and Lb aquifer (right) during 2020–2021 monthly sampling. For abbreviations, see Table 2.

are lower in the deeper wells than in the shallower ones due to the smaller amount of dissolved CO_2 in precipitation as it begins to recharge the carbonate hinterland at higher altitudes. The levels of nitrates (mg/L) increase from Iška to the outer shallower wells due to the increased ground permeability and higher water levels in the shallow wells. The Cl^- levels were generally low but still lower in the deeper wells than the shallower ones. The SO_4^{2-} and Cl^- levels show a positive correlation in each wellfield, suggesting that both components derive from the same source.

4. Discussion

4.1. Climate conditions and isotopic characteristics of precipitation

Compared to the long-term mean, elevated temperatures during 2020–2021 aligned with climate projections for the Ljubljana basin (Dolinar, 2018). This finding provided a unique opportunity to discern the influence of climate change on the urban area. Analysing the climatic data for these years revealed that the mean annual temperature exceeded that of 2020/21 by 0.9 °C and 0.6 °C, respectively, with the meteorological source meteo (2022) corroborating these differences. Moreover, this warming trend was especially pronounced during the winter months. Furthermore, alterations in precipitation patterns were noted, including reduced rainfall during summer and autumn, coupled

with an increase during spring.

The precipitation isotope data plotted along the LMWL close to GMWL (Fig. 3). The more negative $\delta^{18}\text{O}$ values recorded in Dec 2020 and Jan, Feb and Dec 2021 can be attributed to the lower mean monthly temperature, precipitation in the form of snowfall, and minimal evaporation. In contrast, the initial stages of the 2020 sampling campaign were characterised by relatively positive $\delta^{18}\text{O}$ values. These more positive values were likely due to the absence of snow precipitation in winter 2019/20 and minimal precipitation in Jan and Feb (meteo.si, 2022). The precipitation-weighted $\delta^{18}\text{O}$ and $\delta^2\text{H}$ means over the study period were -8.47 and -56.2 ‰, respectively. These values (Fig. 3) are more positive compared to the long-term means (-8.65 ± 0.02 ‰ vs -59.2 ± 0.1 ‰; SLONIP, 2022). This finding could be attributed to higher air temperatures during the sampling period.

The LMWL_{PWRMA} $\delta^2\text{H} = (7.23 \pm 0.16) \delta^{18}\text{O} + (5.06 \pm 1.44)$ for the study periods deviates from the long-term LMWL_{PWRMA} $\delta^2\text{H} = (8.09 \pm 0.07) \delta^{18}\text{O} + (10.62 \pm 0.6)$ $R^2=0.99$ (N=334, SLONIP, 2022) and GMWL (Craig, 1961) by having a lower intercept and slope. In addition, differences in the line intercepts can be attributed to warmer summer and winter months compared to the long-term mean. Previous investigation indicated that the LMWL for Ljubljana for 2007–2010 (Vreča et al., 2014) was close to the GMWL; however, compared to this study, a significant difference can be observed for the intercept and slope. Precipitation is of mixed Atlantic-Mediterranean origin, which is also

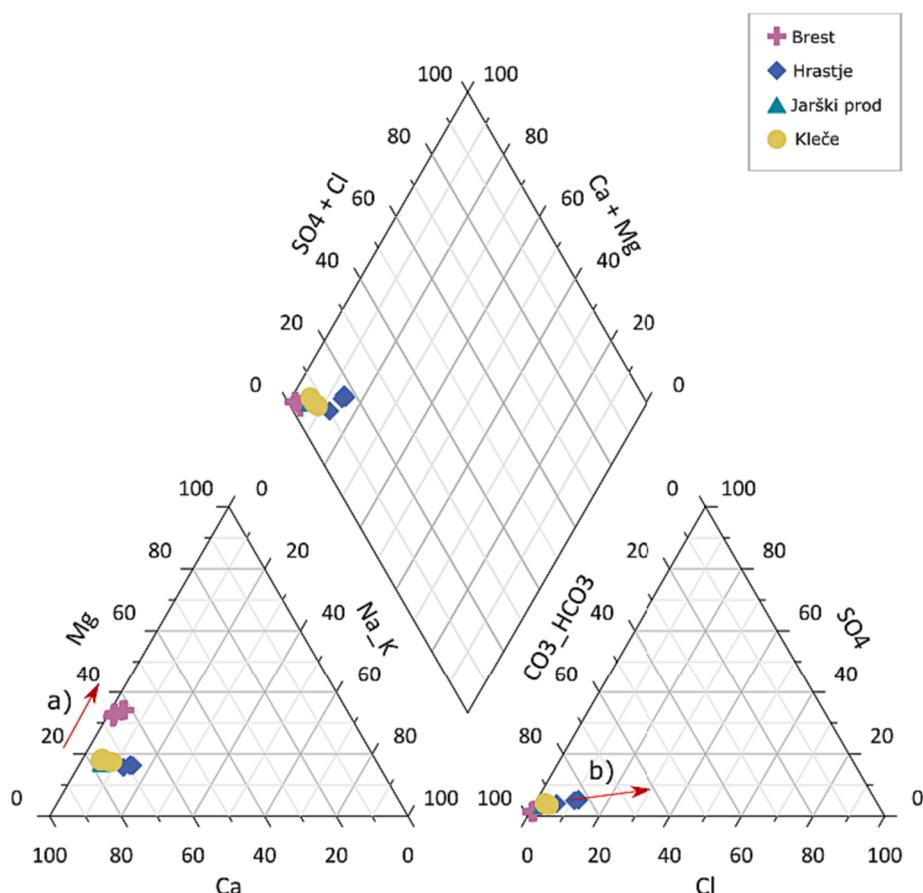


Fig. 5. Piper diagram of samples that represent different hydrogeological units. The letters refer to the main processes inducing: (a) dissolution of limestones ($\text{Ca} > 50\%$) or dolostones ($\text{Ca} = \text{Mg} > 50\%$ and $\text{Mg} > 50\%$) and (b) ionic exchange.

reflected in the fluctuations of the d-excess, i.e., from 2.7 ‰ and 16.0 ‰. The d-excess weighted mean for the study area during 2020–21 was higher (11.6 ‰) than the Atlantic air mass values where d-excess = 10 ‰ (Gat and Dansgaard, 1972). Moreover, almost all winter months are presented by a d-excess higher than 10 ‰, suggesting different origins of the air masses, i.e., the influence of Mediterranean air masses (Gat et al., 1996; Kern et al., 2020; Vreča et al., 2006). Also, storm events during warmer months can result in lower d-excess and indicate the secondary evaporation of the raindrops in the warm and dry atmosphere. From March–August 2020–2021, the lower relative humidity (50–76 %, meteo.si, 2022) likely facilitated the partial evaporation of raindrops below the cloud base, resulting in lower d-excess values.

4.2. Surface water characteristics

The sampling period from January to April 2020 also coincided with an approximately 10 % lower river flow at Sava Šentjakob compared to the reference period (1981–2010). Additionally, a small temporal variability in the isotopic composition was observed in the Sava River, with surface water values varying with flow conditions (Fig. 2). The difference between the $\delta^{18}\text{O}$ of precipitation and those observed in the Sava River, along with the temporal fluctuation in $\delta^{18}\text{O}$ values, can be attributed to the extensive catchment area of the Sava River at the isotope sampling sites. Notably, a significant portion of this catchment extends to higher Alpine altitudes. This finding helps answer questions related to the factors influencing isotopic values in the Sava River, particularly during specific periods when precipitation from higher altitudes plays a significant role in the river's discharge, as observed in previous studies (Ogrinc et al., 2008; Vrzel et al., 2018). Based on the projected changes, the Alpine region will experience above-average

warming. Moreover, in a changing climate, shorter periods with reduced snow cover, increasing precipitation in winter, and higher intensity and frequency of exceptional events (i.e. floods and droughts) are expected, affecting future recharge rates (Dolinar, 2018). Minor temporal variations in the surface water isotopic signature that also occur after the heavy rain events indicate well-mixed surface water of a groundwater-dominated catchment and point to their being a permeable subsurface and large storage capacity (Scheliga et al., 2017).

The lack of variability in the surface water is also reflected in the estimations of residence times. The model was first used to calculate the amplitude in $\delta^{18}\text{O}$ values (Eq. (4) for the precipitation data, yielding an amplitude of 2.86 ‰. This outcome aligns with findings from previous investigations (Ogrinc et al., 2008). Although precipitation data are relatively well described ($R^2=0.58$), the modelled $\delta^{18}\text{O}$ values of surface water oversimplify temporal variations. The estimated amplitudes in $\delta^{18}\text{O}$ values for the Sava River at Brod and Šentjakob were notably reduced, resulting in an amplitude of 0.11 and 0.13 ‰. Correspondingly, the MRT was estimated at 4.1 and 3.5 years, respectively.

These findings suggest that the Sava River exhibits limited influence from young water from precipitation. In comparison to previous investigations (Ogrinc et al., 2018; 2008), the authors' more recent MRS estimations exceed three years, whereas some other studies indicate similar extended MRT estimations for small catchments, such as the Erpe catchment (Kuhleman et al., 2021). A poor Spearman correlation coefficient ($R^2 < 0.4$; $p < 0.05$) between $\delta^{18}\text{O}$ and temperature, water flow and precipitation were also observed, suggesting that other processes are influencing the $\delta^{18}\text{O}$ composition of surface water, namely the influence of the upstream precipitation events and possible seepage of groundwater into the river (Scheliga et al., 2017).

The observed longer MRT could also result from sampling during low

and semi-low flow conditions in the study area; however, similar conditions will likely become more common. Longer MRT of surface water results in uncertain age estimates as it is derived from older groundwater reservoirs with longer ages (>4 years), which is the limit to discern ages using stable isotopes (McGuire and McDonnell, 2006).

While the Sava River primarily recharges the Lp aquifer, the considerably smaller Iška River contributes to Lb aquifer recharge. Its smaller size renders it susceptible to the influence of warm and dry climatic conditions, as observed during the study period. These conditions were characterised by positive $\delta^{18}\text{O}$ value (Fig. 2) and lower d-excess in July 2021, indicative of surface evaporation. Alternatively, the increased EC in Mar-Apr 2021 and Oct-Dec 2021 (Fig. 2) suggest the possible higher rate of groundwater in the stream and the introduction of diffuse nutrients, probably from domestic gardens or agriculture (Gücker and Pusch, 2006).

4.3. Estimation of the rate of surface water and precipitation in groundwater sources

Minor differences in the isotope composition of groundwater are noticeable between the Lp and Lb aquifers. Specifically, shallower wells in the Lb aquifer exhibit a more positive isotope signal, while the deeper wells are presented with a lower isotope signal than the Lp aquifer. However, it is worth noting that these differences do not span a wide range. This limited variability reflects the relatively small scale of the Ljubljana water supply system, which predominantly relies on local

precipitation and surface water as its primary sources. The limited temporal variability in the Sava River (Fig. 2) is reflected in the temporal dynamics of the groundwater, where the clear distinction between isotope values in different wells is not readily apparent (Table 2). For both aquifers, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ plot close to the long-term weighted mean value of the local precipitation infiltrating the soil (Fig. 3) that eventually becomes groundwater, suggesting recharge by modern precipitation (Clark and Fritz, 1997; Rozanski, 1985; Urbanc and Jamnik, 2002) with a mean value similar to surface water. In the past, the Sava River and precipitation's contribution to the groundwater have been estimated, for example, by Urbanc and Jamnik (1998) and Vrzel et al. (2018), whose results have been reevaluated during this study.

In Kleče, the contribution of the Sava River increased compared to precipitation, with the largest difference observed in the wells K-8a (38 %) and K-11 (33 %), both in the centre of the wellfield. In H-1a, the contribution of surface water increased only slightly, while in well H-3, it increased by 47 %. In contrast, the contribution of surface water decreased in Š-2a (−10 %) and Jp-3 (−18 %). In Jp-1, there was no change (Fig. 6). This observation agrees with the literature since the Sava River in the north-western part supplies and drains the Lp aquifer in the eastern part (Janža, 2015).

Important new insights can also be observed at the Lb aquifer. For example, the similar isotopic composition found between the Brest wellfield and the Iška River suggests that the riverbed surface infiltration must be an important recharge component for the shallower aquifer (Pezdič, 1998; Urbanc and Jamnik, 2002). However, from the data, we

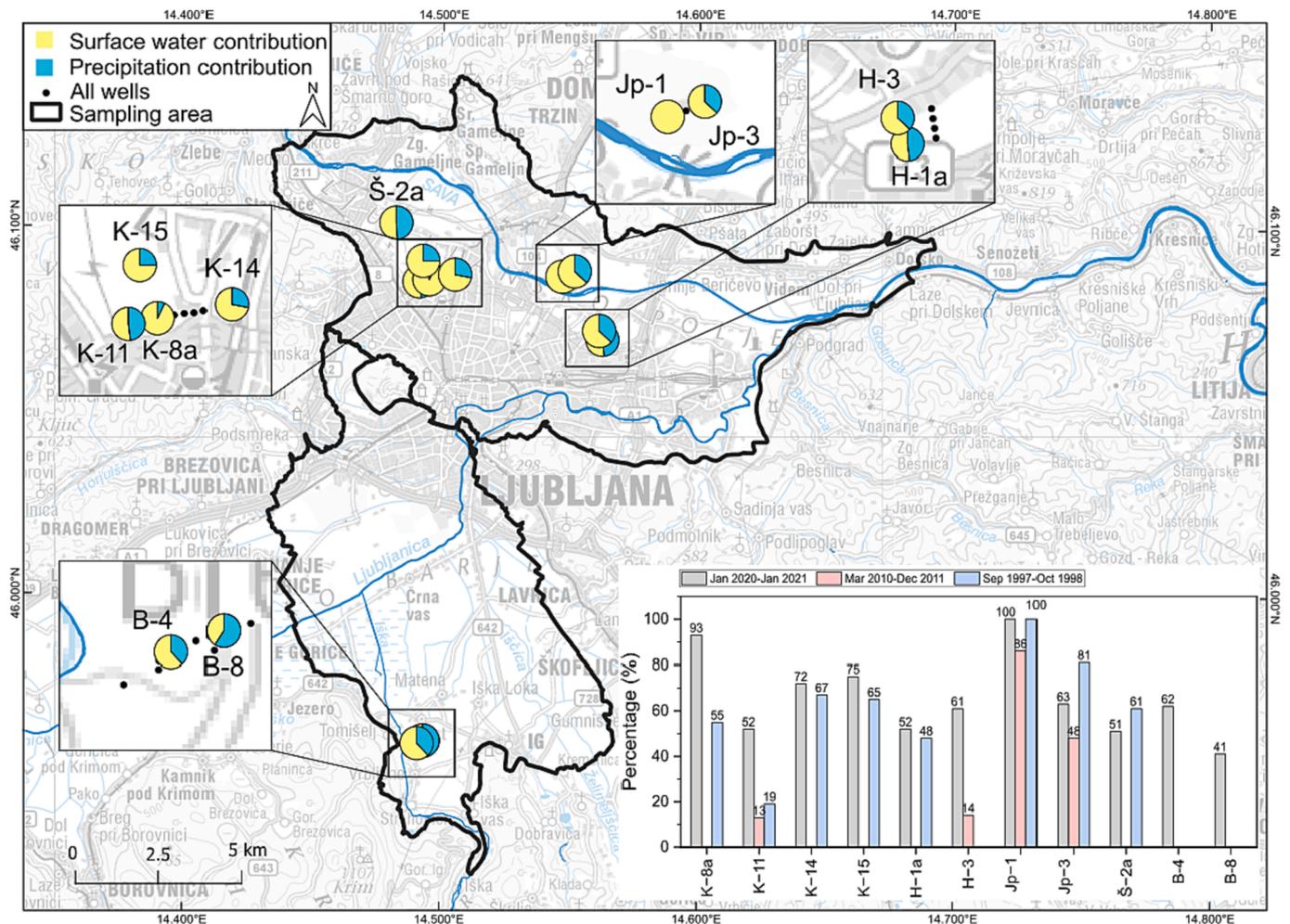


Fig. 6. Spatial distribution of estimated contributions of identified groundwater end-members: precipitation (blue) and surface water (yellow) between 2020 and 2021. On the right side, the inserted graph represents the percentage of surface water contribution to the respective well compared to the investigations (Urbanc and Jamnik, 1998; Vrzel et al., 2018). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

can observe a more positive isotope signal for groundwater from shallow wells than the Iška River, suggesting that precipitation contributes more to groundwater recharge than surface water. Also, the most positive values of stable water isotopes were observed during the winter months in well B-8 and can be related to the impact of the more positive isotope signal of surface water and precipitation during warmer months. The most negative delta values were observed in deeper wells (B-2a and B-4a), with little temporal variability (Fig. 4). Unfortunately, no comparison can be made as previous studies did not investigate deep wells, and there are no long-term observations of the isotopic composition of precipitation in the Lb aquifer recharge area.

4.4. Water management implications and future research

The short investigation in the Ljubljana basin showed significant temperature deviations during 2020–2021, in line with climate projections. These findings, consistent with earlier research (Urbanc and Jamnik, 1998; Vrzal et al., 2018), revealed precipitation pattern variations impacting isotope composition. Surface water characteristics reflected responses to flow conditions, highlighting upper catchment recharge influences. Our findings suggested that the Sava River and precipitation contribute to groundwater sources at Lp aquifer, but their impact varies across wells. Notably, in the Lb aquifer, precipitation appeared to play a significant role in groundwater recharge, with potential implications for water resource management in the region. These insights shed light on the complex interplay between climate, surface water, and groundwater dynamics in the Ljubljana basin.

Understanding these dynamics is crucial for sustainable water resource management, especially in urban areas where land use changes and human activities impact aquifer recharge, potentially altering groundwater quality and quantity (Schirmer et al., 2013). Changes in aquifer recharge can also affect the dynamics of pollutants due to surface-water interaction (Janža, 2015). Some pollutants in the study area, e.g., nitrates, atrazine, desethylatrazine, and hexavalent chromium, are already present in the soil, unsaturated, and saturated zones of the Lp and Lb aquifers (Janža, 2022; Urbanc et al., 2010). In addition, elevated Cl⁻ and Cl/Br ratios in the Lp aquifer signal agricultural and domestic contamination (Janža, 2015).

These findings have implications for national strategic planning, such as the construction of water resource infrastructure (i.e., dams and wellfields), particularly in light of increasing temperature and shifting precipitation patterns faster than the global average (Cegnar et al., 2021; Papadimitriou et al., 2016). Future urban development and population growth will also place additional pressure on water sources.

Diversifying future sources of supply and storage is a priority to meet increasing urban water requirements more sustainably. Recharged water may be sourced from various sources. For example, managed aquifer recharge (MAR) allows the recycling of urban stormwater and treated wastewater in urban areas, maximising urban water storage capacity to address runoff variability due to climate change (Page et al., 2018). Additionally, as surface water contribution rises, surface water management must adapt to drier conditions and potential increases in pollutant concentrations in drinking water sources due to reduced dilution from local precipitation (Abily et al., 2021).

While water isotopes can assess spatiotemporal variations in urban areas (Tippie et al., 2017), their interpretation can be challenging due to the similar isotopic composition of the water resources, which limits the isotopic variability observed in estimating water age. Similarly, monthly sampling can obscure temporal variability; thus, higher-resolution sampling over more extended periods (Kuhlemann et al., 2021) would likely reveal more complex dynamics.

5. Conclusion

The study on the hydrological dynamics of the Ljubljana basin during 2020–2021 has provided insights into the region's water resources, their

responses to climate change and their interactions between precipitation, surface water and groundwater. Elevated temperatures and shifting precipitation patterns impact the isotopic composition of precipitation and surface water. Stable isotopes in groundwater indicated minimal seasonal variability and attenuated the effects of variations in precipitation. This study's findings revealed that while the Sava River and precipitation contribute to groundwater sources at the Lp aquifer, their impact varies across wells. In most places, the contribution of the Sava River to the groundwater increased, while in two locations (Jp-3 and Š-2a), it decreased compared to previous investigations. Notably, in the Lb aquifer, precipitation appeared to play a significant role in groundwater recharge, with potential implications for water management in the region. Additionally, chemical analysis highlighted differences between aquifers, with the Lp aquifer being more affected by anthropogenic activities.

Water managers can harness these findings to make informed decisions in changing climate conditions. Diversifying future sources of supply and storage, such as managed aquifer recharge (MAR) for recycling urban stormwater and treated wastewater, could help meet increasing urban water requirements more sustainably. Additionally, as surface water's contribution to the groundwater increases, surface water management will need to adapt to drier conditions and potential increases in pollutant concentrations in drinking water sources due to reduced dilution from local precipitation. The Lb aquifer, tapping into the deeper Pleistocene aquifer, appears less vulnerable to contamination, making it a valuable resource.

As demonstrated in this study, stable isotopes play a crucial role in assessing spatiotemporal variations, providing valuable insights into water age estimation and the intricate dynamics of urban water systems. They serve as a unique tool for water managers, complementing other hydrological monitoring methods. The fresh stable isotope data complements prior investigations, sheds light on groundwater dynamics, and highlights changes in recharge patterns over time. Despite the challenges posed by researching heterogeneous urban areas, such as limited spatiotemporal groundwater monitoring and data constraints, this study contributes to a broader understanding of how climate change influences groundwater resources. Future research endeavours should continue to explore these complexities to ensure sustainable water management practices in the face of environmental change.

CRediT authorship contribution statement

Klara Žagar: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. **Lucia Ortega:** Project administration, Supervision, Writing – original draft, Writing – review & editing. **Urška Pavlič:** Data curation, Writing – review & editing. **Brigita Jamnik:** Conceptualization, Data curation, Resources, Writing – review & editing. **Branka Bračič Železnik:** Conceptualization, Resources, Writing – review & editing. **Polona Vreča:** Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data was submitted to Pangea database and the link for the reviewers is provided in Cover letter..

Acknowledgement

The data was gathered as part of various projects: the Slovenian Research Agency-ARRS Programme (P1-0143), the Young Research Program (PR-09780), the IAEA: CRP (F33024, No. 22843) and RER-7013, and COST Action CA19120: WATer isotopeS in the critical zONe: from groundwater recharge to plant transpiration (WATSON) STSM grant No. (CA19120-28497843). Special thanks are due to S. Žigon for his valuable help with H and O isotope analysis, M. Žitnik for sampling and L. Araguás-Araguás and S. Terzer-Wasmuth for the discussion of the results.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jhydrol.2024.130892>.

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