ISOTOPIC FINGERPRINT OF WATER FROM SOURCE TO TAP

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Doctoral Dissertation
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MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA
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IZOTOPSKO SLEDENJE VODE OD VIRA DO PIPE

Doktorska disertacija

Supervisor: Dr. Polona Vreča

Ljubljana, Slovenia, August 2024

We never know the worth of water till the well is dry.

Thomas Fuller

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Abstract

Rapid population growth and increasing water demand places a serious strain on both quantity and quality of available local water resources. Climate change puts additional pressure by altering the water balance, affecting recharge conditions, and contributing to pollution and water degradation. Addressing these issues requires water management strategies that enhance both quality and availability of water sources. Understanding of the urban water cycle is necessary, including knowledge of water sources, distribution networks, and various components of the water supply system. The urban water cycle is complex and heterogeneous. It involves natural and engineered systems that vary spatially and temporally. One way to address these challenges effectively is by applying environmental tracers like stable water isotopes. This thesis uses stable water isotopes, along with hydrochemical and hydro-meteorological data, to evaluate the spatio-temporal patterns of water sources and flow paths, and to characterize the isotope signatures of different components within the urban water cycle. Sampling was conducted from 2018 to 2021 in Ljubljana's aquifers, covering the entire journey from source to tap.

Firstly, a review of previous isotope investigations had been performed to identify key knowledge gaps. A preliminary investigation was performed in 2018, collecting samples from source to tap. Following this, a two-year sampling of water sources (i.e. precipitation, surface water and groundwater) was conducted. Additionally, extensive tap water sampling was carried out across Ljubljana. It was complemented by a 24-hour sampling experiments to analyse temporal variations in tap water composition.

Key findings include the characterization of water sources, changes in source contributions and the influence of climate on water isotopes. The study revealed unique isotopic fingerprints of different sources, despite the isotopic signal range being narrow due to the limited size of the Ljubljana catchment. Isotopic and hydro-chemical analyses revealed dynamic interactions between precipitation, surface water and groundwater. Source contributions were shown to vary over time. Isotopic data correlated with climate variations, indicating that future climate projections could significantly impact the isotopic composition of water sources. Potential changes in groundwater recharge dynamics were implied by observation of longer mean residence times of surface water. The study also found that the isotopic composition of tap water reflected the mixed contributions from different wellfields, providing insights into the water supply system's structure and operation. Seasonal and hourly variations in tap water isotopes highlighted the dynamic nature of water distribution and the influence of management practices. The research identified the potential for using isotope data in combination with concentration of certain elements as proxies for water source mixing ratios.

The research provides valuable data for water managers by offering insights into water dynamics in urban areas and contributing to strategic planning of water infrastructure. The thesis also emphasizes the need for continuous, long-term monitoring of water sources and the publication of data to ensure transparency and reproducibility in scientific research.

Povzetek

Hitro naraščanje prebivalstva in povečano povpraševanje po vodi močno obremenjujeta količino in kakovost lokalnih vodnih virov. Podnebne spremembe dodatno obremenjujejo vodno bilanco, vplivajo na napajanje vodonosnikov in prispevajo k onesnaževanju ter degradaciji vodnih virov. Za reševanje teh izzivov so potrebne strategije upravljanja vodnih virov, ki izboljšujejo tako kakovost kot tudi razpoložljivost. Za razvoj takšnih strategij je potrebno razumevanje urbanega vodnega kroga. To vključuje poznavanje vodnih virov, vodovodnega omrežja in različnih komponent sistema oskrbe z vodo. Urbani vodni krog je kompleksen in raznolik. V njem se prepletajo tako naravni kot umetni sistemi, ki se spreminjajo v času in prostoru. Uporaba okoljskih sledilcev, kot so izotopi vode, je eden od načinov kako nasloviti te izzive.

V tej disertaciji so stabilni izotopi vode, skupaj s hidro-kemijskimi in hidro-meteorološkimi podatki, uporabljeni za analizo prostorsko-časovnih vzorcev vodnih virov in tokov ter za prepoznavanje izotopskih značilnosti različnih komponent urbanega vodnega kroga. Vzorčenje je potekalo med letoma 2018 in 2021 v ljubljanskih vodonosnikih in zajema celotno pot vode od izvora do pipe.

Najprej smo pregledali prejšnje izotopske raziskave, da bi identificirali ključne vrzeli v znanju. Leta 2018 smo izvedli predhodno raziskavo, pri kateri smo zbirali vzorce vode od izvora do pipe. V nadaljevanju smo dve leti vzorčili različne vodne vire (padavine, površinske in podzemne vode). Poleg tega smo po celotni Ljubljani izvedli obsežno vzorčenje pitne vode, ki smo ga dopolnili s 24-urnimi eksperimenti, da bi analizirali časovne spremembe v sestavi pitne vode.

Ključne ugotovitve vključujejo značilnosti vodnih virov, spremembe v deležih posameznih virov in vpliv podnebja na izotope vode. Študija je pokazala edinstvene izotopske značilnosti različnih virov, čeprav je bil razpon izotopskih signalov omejen zaradi majhne velikosti ljubljanskega vodnega zaledja. Izotopske in hidro-kemijske analize so razkrile dinamične interakcije med padavinami, površinskimi in podzemnimi vodami. Prispevki posameznih virov so se skozi čas spreminjali. Izotopski podatki so pokazali povezavo s podnebnimi spremembami, kar pomeni, da bi lahko prihodnje podnebne spremembe pomembno vplivale na izotopsko sestavo vodnih virov. Opazovanja daljših povprečnih časov zadrževanja površinske vode kažejo na možne spremembe v dinamiki napajanja podzemnih voda. Študija je tudi pokazala, da izotopska sestava pitne vode odraža mešanje vode iz različnih črpališč, kar ponuja vpogled v strukturo in delovanje sistema oskrbe z vodo. Sezonske in urne spremembe v izotopski sestavi pitne vode poudarjajo dinamično naravo distribucije vode in vpliv upravljavskih praks. Raziskava je prepoznala potencial za uporabo izotopskih podatkov v kombinaciji z določenimi kemijskimi elementi kot pokazatelji za razmerja mešanja vodnih virov.

Ta raziskava ponuja dragocene podatke za upravljavce vodnih virov, saj omogoča boljše razumevanje dinamike vode v urbanih območjih in prispeva k strateškemu načrtovanju vodne infrastrukture. Disertacija prav tako poudarja potrebo po stalnem, dolgoročnem spremljanju vodnih virov ter objavi podatkov za zagotavljanje preglednosti in ponovljivosti v znanstvenih raziskavah.

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Abbreviations

A ... Kleče water supply area until 2020
A1 ... Kleče water supply area after 2020
ARSO ... Slovenian Environment Agency
B ... Hrastje water supply area until 2020
B1 ... Hrastje water supply area after 2020
C ... Brest water supply area until 2020
C1 ... Brest water supply area after 2020
CRP ... Coordinated Research Project
D ... Jarški prod water supply area until 2020
D1 ... Jarški prod water supply area after 2020
DA ... Kleče/Jarški prod water supply area after 2020
DI-IRMS ... Dual Inlet Isotope Ratio Mass Spectrometer
δ ... Delta, relative isotopic composition, given in parts per thousand or "per mille" (‰)
E ... Šentvid water supply area until 2020
E1 ... Šentvid water supply area after 2020
EC ... Electrical Conductivity
F ... Hrastje/Jarški prod water supply area until 2020
F1 ... Hrastje/Kleče water supply area after 2020
G ... Kleče/Brest water supply area until 2020
G1 ... Kleče/Brest water supply area after 2020
GMWL ... Global Meteoric Water Line
H ... Kleče/Hrastje/Jarški prod water supply area until 2020
H1 ... Kleče/Hrastje water supply area after 2020
IAEA ... International Atomic Energy Agency
IRMS ... Isotope Ratio Mass Spectrometry
δ^{2}H ... Isotopic Composition of Hydrogen
δ^{18}O ... Isotopic Composition of Oxygen
$\delta^{13}C_{DIC}$ ... Isotopic Composition of Carbon in the Dissolve Inorganic Carbon
I2 ... Kleče/Hrastje/Brest water supply area until 2020
I3 ... Kleče/Brest/Hrastje water supply area after 2020
JSI ... Jožef Stefan Institute
LMWL ... Local Meteoric Water Line
LEL ... Evaporation Line
LRM ... Laboratory Reference Material

MOL ... City Municipality of Ljubljana
MRT ... Mean Residence Time
MWL ... Meteoric Water Line
N ... Normalisation
PCA ... Principal Component Analysis
QC ... Independent Quality Control
$^{2}H/^{1}H$ ... Ratio of ^{2}H to ^{1}H
$^{18}O/^{16}O$ ... Ratio of ^{18}O to ^{16}O
$^{87}Sr/^{86}Sr$ ... Strontium Isotope Ratio
SDG ... Sustainable Development Goals
SLAP ... Standard Light Antarctic Precipitation
T ... Temperature
TSS ... Type of the Sampling Site
UHI ... Urban Heat Island
VSMOW ... Vienna Standard Mean Ocean Water
WMO ... World Meteorological Organisation
WSA ... Water Supply Area
WSS ... Water Supply System

Chapter 1

Introduction

1.1 Background and Motivation

The Doctoral thesis investigates the partitioning and flow dynamics of water within the urban water supply systems. The subsequent chapters provide a comprehensive summary explaining the changes of water signal from its source to the tap as well as examine the impact of urbanization and climate change on water availability.

1.1.1 Water cycle in the urban areas and its impact

One of the fundamental concepts in nature is the hydrological cycle, known as the water cycle. Water is stored and circulates between different parts of the Earth including atmosphere, lithosphere, biosphere and hydrosphere. Water can be stored in the oceans, snow, glaciers, streams, lakes, vegetation, soils, and groundwater. The main processes that drive the hydrological cycle are (Figure 1.1a):

- Atmospheric processes: evaporation, condensation and precipitation;
- Cryospheric processes: snowmelt;
- Vegetation processes: transpiration;
- Surface and soil processes: infiltration, percolation and runoff;
- Groundwater processes: groundwater flow, and rock-water interactions.

Due to the population growth, industrialization and urbanization, the hydrological cycle is affected and greatly modify. The effects of urbanization are well-documented and widely studied (Oudin, Salavati, Furusho-Percot, Ribstein, & Saadi, 2018; Sheetal, 2017; Trudeau & Richardson, 2016). Key impacts of urbanization on the hydrological cycle include increased runoff and flood risk, decreased groundwater recharge, water quality degradation and microclimate change due to urban heat islands effect (UHI) (Figure 1.1b) (Salvadore, Bronders, & Batelaan, 2015). Managing these impacts in cities remains a significant challenge.

Cities around the word are rapidly expanding and are now home to 4.2 billion people, which accounts for over 50 % of the world's population (Pörtner & Roberts, 2022). This number is expected to grow to 85 % by the end of the twenty-first century (OECD, 2015), presenting a significant challenge for urban water provision. Over the past 60 years, domestic water consumption has nearly quadrupled (Flörke et al., 2013) and is showing no signs of slowing down, with future projections anticipating an increase of up to 80 % by 2050 (Flörke, Schneider, & McDonald, 2018; United Nations, Department of Economic and Social Affairs, & Population Division, 2019). As a consequence, health and water security issues have emerged, that in turn have an impact on the local water cycle by decreasing

water quantity and quality and leading to a growing lack of access to safe water. Moreover, the direct impact of human activities (i.e. expansion of cities both inland and along coastlines, intensive pumping, overexploitation, leakages, extraction of water for agricultural, industrial and domestic use and poor sanitation) presents a significant component of regional water cycle and will only intensify over time (Allan et al., 2020; McGrane, 2016).

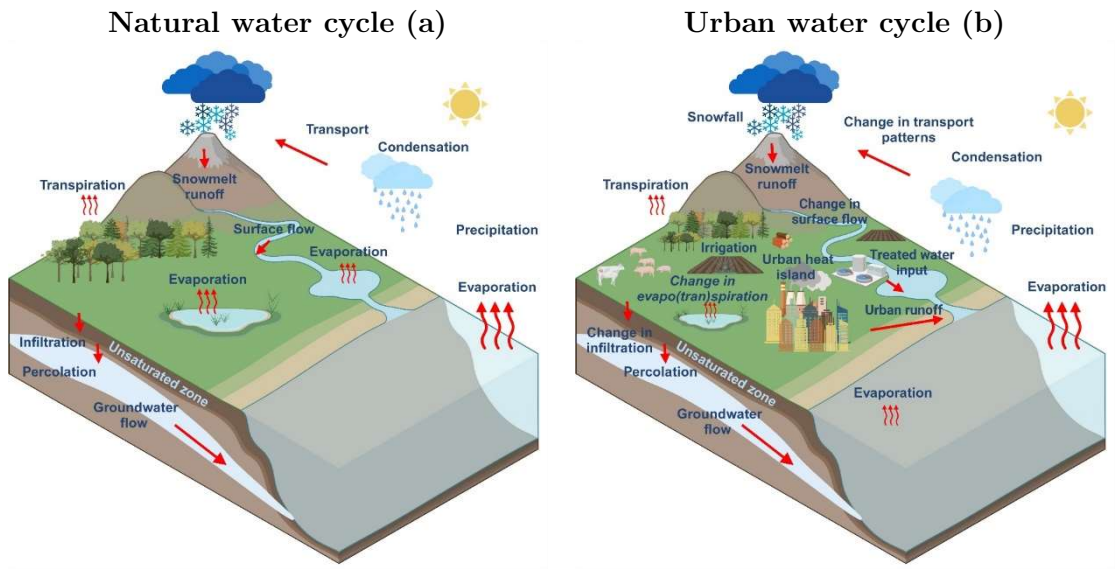

Figure 1.1: Natural (a) and urban (b) water cycle.

Historically, cities have usually relied on groundwater from springs and shallow wells as their primary source of clean drinking water, as it is usually more protected from pollution and seasonal changes compared to surface water (Dao et al., 2024; Taylor et al., 2013). In recent years, water extraction increased significantly in many cities around the world, sometimes reaching its limits. Due to this heavy usage, the groundwater levels under these cities have significantly declined. In densely populated urban centres, water scarcity becomes a more pressing issue, especially where the demand for water exceeds what local sources can supply (Howard & Israfilov, 2002; Jenkins, Lund, & Howitt, 2003; Padowski & Gorelick, 2014). Many cities, therefore, have turned to importing water from distant location, relying on complex systems that transport water over mountain ranges, extensive extraction from groundwater or surface water, or the transfer of water from distant river basins or reservoirs (Gleick, 2003; Kellner & Brunner, 2021; Tipple et al., 2017). To meet the demands of growing urban populations, these water sources are often overexploited, leading to negative consequences such as land subsidence due to groundwater extraction in thick unconsolidated areas, or saltwater intrusion in coastal aquifers (Howard & Israfilov, 2002).

In natural systems (Figure 1.1a), the recharge of aquifers mainly depends on precipitation, evapotranspiration, and surface runoff. In an urbanized catchment, the water cycle is modified by anthropogenic activity, leading to new pathways, and reduced or changed natural pathways (Figure 1.1b). Land cover in urbanized catchment is extremely heterogeneous and multiple interactions occur within physical phenomena (Salvadore et al., 2015). While urban areas typically do not alter incident precipitation, it increases surface runoff and reduces direct recharge by half, due to impermeable covers like roads, parking spaces and buildings proliferate. Usually, the rainfall-runoff response of urban

streams is faster and more pronounced than in natural environments (Fletcher, Andrieu, & Hamel, 2013; McGrane, 2016). In addition, the urbanization can significantly affect evapo(transpi)ration due to the phenomenon of UHI or the increase in temperature of urban centres as compared to their surroundings (Salvadore et al., 2015).

Despite these changes, urban areas can introduce new sources of recharge. For instance, water from leaking pipes, septic systems, and heavily irrigated parks often compensates for the reduced natural recharge. The impact of urbanization on groundwater can be substantial, leading to elevated water tables that can cause flooding and damage infrastructure. Thus, understanding and managing urban water balances is crucial to mitigate these effects (Oudin et al., 2018).

For efficient management of water sources in urban areas, detailed information on flow patterns and interactions between different water bodies is needed. Urban areas are strongly affected by changes in land use (Gessner et al., 2014) and anthropogenic activities that impact the whole recharge area of aquifer. This can affect the water budget, reduce aquifer recharge, and alter the properties of groundwater quality, flow and the availability and renewability of water resources (Schirmer, Leschik, & Musolff, 2013), making adaptation through management a significant challenge and a priority worldwide (Wang et al., 2016).

1.1.2 Climate change and urban water availability

Climate change has profoundly affected many of Earth's systems, and introduce a layer of unpredictability and complexity to the hydrological cycle, especially in urban settings. One of the most notable effects of climate change is the uncertainty of water partitioning and cycling in urban areas, that, for example leads to more variable and extreme precipitation events. Studies indicate a trend towards less frequent but more extreme precipitation events increasing the likelihood of both droughts and flash floods (Allan et al., 2020; Bertalanič et al., 2019; Caretta & Mukherji, 2022; Dolinar, 2018). Increased temperature increases evaporation rates and alters the balance of water inputs and outputs in urban areas. Changes in streamflow patterns and snow cover reduction have an impact on water availably, particularly in regions dependent on snowmelt for their water supply (Caretta & Mukherji, 2022; Markonis et al., 2021). In Europe, 2020 was the warmest year on record (WMO, 2021). The year 2021 was cooler due to moderate La Niña events, making it the seventh warmest year between 2015 and 2021 (WMO, 2022). The adverse impacts of climate change are already affecting the Sustainable Development goals (SDG) adopted by world leaders who recognized water as one of the most fundamental and indispensable of all-natural resources. Consequently, one of the SDGs (SDG No.6) is to ensure the availability and sustainable management of water and sanitation for all. Furthermore, water is critical component for achieving many other aspects of sustainable development, influencing health, food security and economic development (UN DESA, 2022). Despite the growing risks and challenges associated with urban water provision, the water resources of most cities remain poorly investigated and evaluated. This sets back the efforts to assess the distribution and causes of urban water stress.

Slovenia is known for its wide range of climate conditions, as it encompasses three very distinct climate types alternate or intertwine in a very small area: sub-mediterranean, mountain and temperate-continental climate types (Ogrin, Repe, Štaut, Svetlin, & Ogrin, 2023). Due to climate diversity, determined by factors such as geographical location, rugged landscape and proximity to the sea, each climate region's response to global warming is unique and the local changes are expected to be more pronounced than the regional ones. Climate models project a significant increase in the mean annual temperature in Slovenia

by the end of the 21st century, ranging from 1.3 °C to even 4.1 °C across all seasons, depending on the type of scenarios (Dolinar, 2018). This will impact the frequency and duration of the heatwaves, while precipitation patterns are predicted to change in winter, with uncertain changes expected in summer (Bertalanič et al., 2019). Interestingly, the average annual recharge of groundwater is expected to increase by up to 30 % by the end of the century compared to period 1981-2010. All this climate change will ultimately impact the provision of tap water in the urban areas.

1.2 Application of Stable Isotopes of Water to Study Water Cycle

The global water cycle, or hydrological cycle, is a complex system, involving different processes (i.e. evaporation, precipitation, transpiration). The isotopes of hydrogen and oxygen, making up the water molecule, are natural tracers of water that can provide an understanding of origin, age and partitioning through different phases of the water cycle. The following subchapters introduce the basic principles of stable isotopes and the challenges of its application in the urban areas.

1.2.1 Basic principles of isotope hydrology

An isotope is an atom of element with a specific number of neutrons but the same number of protons. Isotopes can be stable, radioactive (decay to another element) or radiogenic (product of decay), or both radioactive and radiogenic, if they are part of a decay chain. To study the water cycle, isotopic composition of hydrogen and oxygen have been used as a tracer for many years. Hydrogen naturally exist in three isotopic forms: protium (^{1}H), deuterium (^{2}H) and tritium (^{3}H), with tritium being radioactive with half-life of 12.32 years (Lucas & Unterweger, 2000). Oxygen has three naturally occurring stable isotopes (^{16}O, ^{17}O and ^{18}O). In environment, these isotopes act as conservative tracers, meaning their abundances remain largely unaffected by chemical processes or interaction with catchment materials (except in geothermal environments) or when interacting with gases like H_2S or CO_2. Instead, the isotopic composition of water varies primarily due phase changes of matter, driven by measurable differences in isotope mass (Aggarwal, Gat, & Froehlich, 2005; I. Clark & Fritz, 1997; Jasechko, 2019). Isotopic fractionation refers to the processes that resulted in the differential partitioning of stable isotopes during physical or chemical transformation. It is defined as the partitioning of heavy versus light isotopes in exchange reactions. The extent of isotopic fractionation is especially pronounced in hydrogen isotopes, up to 1000 ‰, because the mass difference is twofold or 100 percent, for $^{2}H/^{1}H$. Isotopic fractionation is primarily driven by two mechanisms i) equilibrium isotopic exchange and ii) kinetic effects (Clark & Fritz, 1997; Kendall & McDonnell, 1998).

Equilibrium isotopic fractionation occurs during isotopic exchange between coexisting phases that are in thermodynamic equilibrium. It is generally associated with reversible reactions (e.g., liquid-vapour molecular exchange where the air overlying the water is saturated) where isotopes redistribute themselves along various species of compounds in a closed well mixed system. Kinetic isotopic fractionation in contrast, is controlled by rate at which reactions occur. These processes include evaporation, diffusion and dissociation reactions. They are usually associated with unidirectional and relatively rapid transformation. The basis of the fractionation is due to differences in velocities between isotopic molecules; lighter isotopes typically move or react faster than heavier isotopes, leading to their preferential participation in the system (Clark, 2015; Sharp, 2007).

1.2.1.1 Isotope ratios and notation

Isotopic variations in nature are slight and are not easily measured in an absolute sense. Therefore, the delta notation (δ) is used for conveniently and accurately expressing such small differences in parts per thousand (denoted as ‰ or permil). This notation is defined as the difference between the isotopes in a given material to a standard of know composition. δ values are calculated as (Brand & Coplen, 2012; McKinney, McCrea, Epstein, Allen, & Urey, 1950):

$$\delta\ (‰) = \frac{Rsample}{Rstandard} - 1 \times 1000 \tag{1.1}$$

where R_{sample} and $R_{standard}$ are ratios of heavy isotope to light isotope (e.g. $^{2}H/^{1}H$ and $^{18}O/^{16}O$) in a sample or in an international standard, respectively. The delta notation scale is between -1000 to ∞. A positive δ values means that the isotopic ratio of the sample is higher than that of a standard, while negative δ values ratios are lower than of the standard (Kendall & Doctor, 2003).

Hydrogen and oxygen isotopic ratios are normally calibrated using the international standards V-SMOW (Vienna Standard Mean Ocean Water) and SLAP (Standard Light Antarctic Precipitation) (Coplen, 1988; Craig, 1961). Stable isotopes are typically measured with an isotope ratio mass spectrometer (IRMS), or a cavity ringdown laser spectrometer (LS). The IRMS is based on detecting characteristic peaks with different intensities that correspond to the ratios of stable isotopes in a sample. The LS is based on absorption properties of an absorbent (water) (Leonard Wassenaar, Terzer-Wassmuth, & Douence, 2021). Increasingly, scientists are using LS due to lower capital cost and consumable demands, ease of use, and ongoing improvements in analytical precision (Wassenaar et al., 2018).

1.2.1.2 Water lines

Meteoric water, including all forms of precipitation (rain, fog, hail, snow, sleet) primarily falls over the oceans (around 90 %), with only small fraction transported over continents by winds where it picks up additional water vapour from inland sources. Based on the precipitation data from locations around the globe, linear relation between $\delta^{2}H$ and $\delta^{18}O$ was observed (Epstein & Mayeda, 1953; Friedman, 1953) called the meteoric water line (MWL). It was later defined by Craig (1961) as the “global meteoric water line” (GMWL) (Figure 1.2) as:

$$\delta^{2}H\ (‰) = 8 \times \delta^{18}O + 10 \tag{1.2}$$

The GMWL is very useful in hydrology as it provides the information of the origin of modern and ancient groundwater and its interactions with surface waters (Hatvani et al., 2023). It is an average of many local meteoric water lines (LMWL), that are affected based on climatic and geographical parameters (Araguás-Araguás, Froehlich, & Rozanski, 2000). More precise LMWLs differ from the GMWL and can be used in addition to groundwater and or surface water data, to investigate processes such as water-rock interaction, evaporation, recharge and mixing (Jasechko, 2019). Most LMWLs have slopes between 4.8 to 10.9 (Putman, Fiorella, Bowen, & Cai, 2019) and limited range of $\delta^{2}H$ and $\delta^{18}O$ compared to GMWL. The intercept of the LMWLs varies across the globe between -24 ‰ to +27 ‰ (Putman et al., 2019). The LMWLs for higher altitude regions tent to plot lower on a $\delta^{2}H$-

$\delta^{18}O$ diagram, while lower latitude and more arid regions tend to plot higher on the diagram (Carol Kendall & McDonnell, 1998) (Figure 1.2).

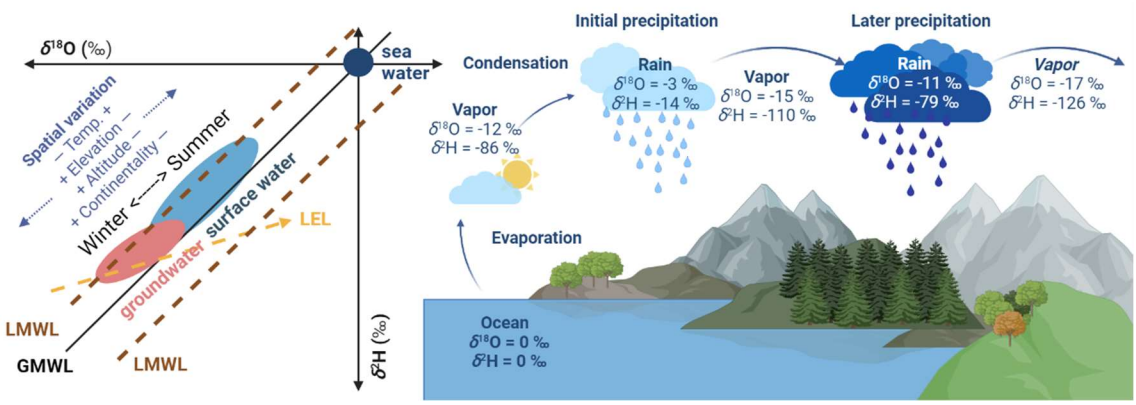

Figure 1.2: Water isotope variations in dual-isotope space showing typical composition of different water bodies and water lines (GMWL, LMWL, LEL) (left part) and progressive rainout (right part). Modified by (Sharp, 2007).

The spread of δ^2H and $\delta^{18}O$ along the GMWL is influenced by various factors and can occur over long time periods, between seasons and even within a single storm (Sharp, 2007). Under equilibrium conditions, water samples, such as precipitation, usually align along the GMWL. However, short-term investigations can exhibit a bias due to anomalous climatic events (Hatvani et al., 2023; Vreča et al., 2024). Samples under equilibrium condition show seasonal variation, with winter samples being more depleted and summer samples more enriched in heavy isotopes (Figure 1.2) (Carol Kendall & McDonnell, 1998). The environmental factors affecting water isotopes include temperature, latitude, distance inland, altitude and the amount of precipitation (Dansgaard, 1964). Isotope variations are also due to environmental conditions at the source of the vapor (Araguás-Araguás et al., 2000), and the mixing of air masses during atmospheric transport. During water evaporation, fractionation causes the remaining liquid water to become more enriched in the heavy isotopes because the departing vapor contains more light isotopes. This fractionation causes water isotopes to deviate from the MWL (Figure 1.2), following a local evaporation line (LEL) with a lower slope than that of the MWL. As moisture moves over continents, its isotope values further change due to temperature-driven rainout (Gat, 1996) and the recycling of water vapour from land surfaces (Figure 1.2).

Non-equilibrium evaporative fractionation from a limited amount of water can impact the slope of the linear relationship of δ^2H and $\delta^{18}O$ and move a water sample upwards along the LEL with a slope < 8 (Dansgaard, 1964). Such deviations from the GMWL can be described by the deuterium excess (d-excess), an indicator of non-equilibrium conditions and rate of evaporation, described as:

$$d - excess\ (‰) = \delta^2H - 8 \times \delta^{18}O \tag{1.3}$$

Traditionally, the d-excess is mainly used to constrain the moisture sources of precipitation, as it mainly depends on the relative humidity and surface sea temperature at the evaporative sources. If the evaporation increases, the residual water will get more enriched in heavy isotopes (Clark, 2015; Kendall & McDonnell, 1998) and the d-excess will decrease (Dansgaard, 1964). On the other hand, high d-excess in water vapour over continents may also arise from the evaporation of land surfaces (i.e. lakes and soil waters) (Putman et al., 2019).

1.2.1.3 From precipitation to surface water and groundwater

Precipitation represents the starting for the studies of surface water and groundwater. Precipitation is intercepted by a large drainage basin that recharge the surface waters. The surface waters can also be recharged by groundwater, meaning the δ^2H and δ^{18}O of surface water reflect the mix of precipitation and groundwater. Streams mainly fed by precipitation show larger seasonal changes, while groundwater-dominated streams show smaller changes. Larger basins experience more evaporation effects. The contribution of these sources differs based on the physical setting of the drainage basin, climatic parameters and human activities (Kendall & Doctor, 2003). Surface water can also have different isotopic composition as can be derived from precipitation at a higher altitude (Figure 1.2).

When precipitation infiltrate the ground its isotopic composition can be altered before reaching the saturated zone (Penna et al., 2018). Factors that can alter the isotopic composition include temperature, partial evaporation and selective recharge (Kendall & Doctor, 2003). After water becomes part of the groundwater system, the isotope rations can be changed only by mixing with other sources. The variability is in the deep groundwater uniform, reflecting the past climatic conditions under which the recharge took place (Cheng et al., 2016).

1.2.2 Application of water isotopes in urban areas

Traditionally, water managers have used a range of technologies, including hydrometric and hydrochemical measurements, to ensure the quality and quantity of water provided to consumers. However, in urban areas, this type of analysis is often constrained (Pataki et al., 2011) and can be difficult to validate due to insufficient field measurements (Waldrip, Niven, Abel, & Schlegel, 2016). Consequently, understanding the sources contributing to the water supply system and their spatiotemporal distribution it is important to understand how these systems adapt to climate change (Sánchez-Murillo et al., 2020). Yet, sampling across vast and varied urban environments and their surrounding areas remains a considerable challenge. In recent years, the application of stable isotopes of water in urban water supply system present a major new research frontier in isotope hydrology (Ehleringer, Barnette, Jameel, Tipple, & Bowen, 2016; Jameel et al., 2018), however urban areas are still under-represented in the literature (Kuhlemann, Tetzlaff, & Soulsby, 2021).

The application of isotopes in investigating drinking water has been conducted on both national and local scales. National-level studies conducted in the USA, South Africa, Canada and China (Bhuiyan et al., 2023; Bowen, Ehleringer, Chesson, Stange, & Cerling, 2007; Landwehr, Coplen, & Stewart, 2014; West, February, & Bowen, 2014; Zhao et al., 2017) have provided valuable insights into the regional and temporal variability, reliability and origins of water sources. More recently regional and local scale investigations have focused on the specific management practices, sources and quality of water supplies, offering detailed information critical for local water resource management (Meng, Liu, Xiang, & Liu, 2024; Sánchez-Murillo et al., 2020; Shakya et al., 2022; Tipple et al., 2017).

Tap water isotopes are used for different purposes. In hydrological studies, isotopic analysis of tap water is essential for understanding processes such as the mixing of water from different sources (Jameel et al., 2016; Kuhlemann, Tetzlaff, & Soulsby, 2020; Tipple et al., 2017; West et al., 2014), to investigate the relationship between tap water isotopes and their implications for water resource management practices (de Wet, West, & Harris, 2020; Tipple et al., 2017) and to derive residence times of stream water (Kuhlemann et al., 2021) and end-member mixing models (Sánchez-Murillo et al., 2020) for obtaining quantitative information about sources and mixing in urban water systems (Leslie, Welch, & Lyons, 2014). Moreover, δ^2H and δ^{18}O were in the past also used to trace and identify

groundwater intrusions into the municipal tap water network, helping to pinpoint contamination sources and leakage areas in the distribution system (Kracht, Gresch, & Gujer, 2007; Shakya et al., 2022). One important application is also the geolocation of water sources; the isotopic composition of tap water can identify the geographic origin of the water, which is particularly useful in forensic science for tracing the movement of individuals or materials based on the water they have consumed (Bowen et al., 2007; Ehleringer et al., 2008; Landwehr et al., 2014). Additionally, tap water isotopes are valuable in climate studies as they reflect the climatic conditions at the time the water was sourced, providing essential data for climate models (Bowen et al., 2007). Tap water isotopes can also be used as a proxy for river water isotopes (Meng et al., 2024).

In Slovenia, one-time national wide tap water sampling was performed, including eight samples from Ljubljana's water supply areas (Vreča, Nagode, Žigon, & Vaupotič, 2019). No additional isotope sampling was performed in the urban water supply system.

These applications demonstrate the versatility of isotopic analysis in various fields, highlighting its importance in understanding and managing water resources, studying environmental processes, and conducting forensic investigations (Landwehr et al., 2014). However, there is still a need for development of new technologies and more testing of isotope approaches for better understanding of processes in urban water supply system, especially in the context of climate change and urban growth.

1.3 Study Site

1.3.1 Study site Ljubljana

The study area (Figure 1.3) is situated in the lowland region of central Slovenia, which is part of the eastern Ljubljana basin. This basin includes the Ljubljansko polje aquifer to the north and the Ljubljansko barje aquifer to the south.

The Ljubljansko polje tectonic depression was formed by tectonic subsidence in the early Pleistocene composed of Permian and Carboniferous slate claystone and sandstone that can also be found in the surrounding hills (Žlebnik, 1971). During the Pleistocene and Holocene periods, the Sava River filled the depression comprising silty-sandy gravels and sandy gravel with lenses of conglomerate transported from alpine glaciers. The thickness of the fluvial deposit varies with the deepest point to the pre-Quaternary bedrock of 105 meters (Bračič Železnik, Pintar, & Urbanc, 2005). The thickness of these fluvial sediments increases towards the center of the Ljubljansko polje, where it even exceeds 100 m (Bračič Železnik et al., 2005). The aquifer system has an intergranular porosity, and an unconfined groundwater table, located on 20–25 m below the surface (Vrzel, Solomon, Blažeka, & Ogrinc, 2018) and can fluctuate up to 10 m (source archive JP VOKA SNAGA d.o.o.). It is an unconfined aquifer, but locally, on the SW part, layers with low hydraulic conductivity appear and on those areas perched aquifers are formed. (Šram, Brenčič, Lapanje, & Janža, 2012).

The primary watercourses flowing through the study area are the Sava, the Ljubljanica and the Iška Rivers (Figure 1.3). The Sava River, part of the Sava River catchment, flows from northwest to east, with discharge varying between 40 m^3/s and 700 m^3/s (Jamnik, Železnik, & Urbanc, 2003). It is closely interconnected with the groundwater (Bračič Železnik & Jamnik, 2005; Bračič Železnik et al., 2005).

Studies suggest that the Sava River, located on the northern part of the Ljubljansko polje, serves as a significant water source for the aquifer. Conversely, groundwater tends to drain into the river downstream from Šentjakob (Janža, 2015). Additionally, a smaller portion of groundwater recharge is from lateral underground inflow from adjacent aquifers

like the Kamniško−Bistriško polje and Ljubljansko barje aquifers (Jamnik et al., 2000). With higher horizontal than vertical hydraulic conductivity, the aquifer responds more rapidly to river events (Vrzel et al., 2019). Hydraulic conductivity ranges from 3−7x10^{-3} m/s at the borders to 10^{-2} m/s in the central area (Jamnik et al., 2003). Hydrological conditions are marked by intensive interactions between Sava River and groundwater, which has strong influence on groundwater dynamics. Estimated groundwater flow rates and pollutant transport range from few m/day to up to 20 m/day (Janža, Prestor, Urbanc, & Jamnik, 2005). Groundwater generally flows southeast and is exploited at Ljubljansko polje from four wellfields: Kleče, Hrastje, Jarški prod and Šentvid where drinking water is pumped from 16, 10, 3 and 3 wells, respectively. Well depths typically range from 30 to 105 m below the surface, with perforated screens varying from 200 to 290 m a.s.l.

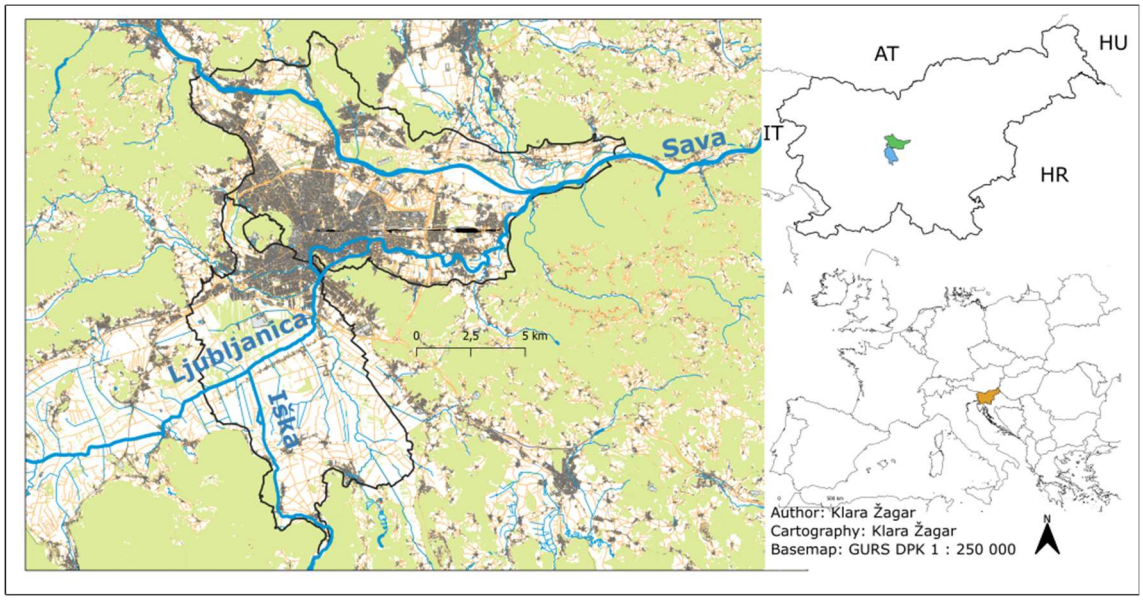

Figure 1.3: Location of the study area: a) postion of Ljubljansko polje and Ljubljansko barje.

The catchment area of Ljubljansko polje is urbanized, with high pressures on groundwater quality arising from urbanization, industry, traffic, agriculture and long-standing environmental burdens. Unknown pollution sources represent an important part of these pressures (Janža, 2015). The good chemical status of the groundwater is threatened despite the implementation of basic measures and the existence of strict environmental legislation (Jamnik, Janža, & Prestor, 2012; Jamnik et al., 2012). Prompt action must be taken to avoid serious impacts on the water supply in the case of a spill of hazardous substances (Janža, 2015) or additional environmental interventions (i.e. building new sewage system).

The Ljubljansko barje aquifer extends from the southern part of Ljubljana to the Krimsko-Mokrško hills. During the Pleistocene and Holocene periods, the lowlands of Ljubljansko barje was filled up with alluvial, marshy and lacustrine sediments (Mencej, 1988), and the area sank due to faults. In southern, westerns and central part of the Ljubljansko barje is the basement composed of Upper Triassic dolomite and Jurassic limestone, while in northern and eastern parts is the basement made of Triassic and Permo-Carbnoniferous shaly mudstone, quartz sandstone and conglomerate characterized by very low hydraulic conductivity (Cerar & Urbanc, 2013; Mencej, 1988). The ground is deeper in the east compared to the west. At the southern edge, it drops steeply from a few tens

of meters to 100 meters deep. In the north, it's over 150 meters deep. Due to the heterogeneity of sediments, hydrogeology conditions on Ljubljansko barje is more complicated than on Ljubljansko polje (Cerar & Urbanc, 2013; Mencej, 1988), forming a multi-layer aquifer system. At the southern and western edge of the basin there are many karst springs and some surface flow. The general hydraulics of Ljubljana barje is driven by the Ljubljanica River flow, which enters the Ljubljansko polje aquifer through the narrow passage between the Grajski and Rožnik hills but does not contribute to groundwater recharge due to its impermeable river bed (Jamnik et al., 2003). The Iška River, a right tributary of the Ljubljanica River, flows northward from the Krim-Mokrc karst mountains, discharging near Iška vas settlement at rates ranging from 0 to 90 m^3/s. In addition to precipitation infiltration, the upper portion of the Brest wellfield area receives recharge from seepage from the Iška River. Deeper parts of the aquifer system experience indirect recharge by deep percolation of water infiltrated in the southern hinterland (Krim-Mokrc karst mountains). This water is then conducted through fissures and conduits in carbonate rocks (Mencej, 1988) and affect the dynamics of groundwater. Groundwater is exploited from 13 wells at the Brest wellfield. Wells penetrate shallow and deep aquifers, with screens located between 290 m and 270 m a.s.l. for shallow wells and 270 to 195 m a.s.l. for deeper wells.

The pumping rate at the wellfield Brest is dependent on the hydrological conditions; during the dry periods, only 40 L/s can be pumped from all shallow wells (Železnik, 2016). The hydrochemical characteristics of the drinking water in the wellfield Brest are dependent of the river Iška and are changing according to the distance from it (Cerar & Urbanc, 2013; Urbanc & Jamnik, 2002). A strong connection between surface water and groundwater is very important as the aquifer is very shallow and relatively poorly protected. Due to karst hinterland, surface water seeps directly to the shallow groundwater through channels and conduits.

The Ljubljansko barje's water resources are under significant pressure as the agricultural land and less commercially productive areas are being changed to urban areas. Environmental problems include water pollution, rising water demand for water, flood and drought risk and decline of water retention capacities, decreasing groundwater levels and terrain subsidence (Bracic Zeleznik & Globevnik, 2014).

Climatically, Ljubljana is located in an area of temperate continental climate, i.e., Köppen–Geiger code Cfb (Ogrin et al., 2023), characterized by large precipitation amounts. Long term mean annual air temperature is 11.4 °C with long-term mean annual precipitation of 1368 mm, based on the 1991–2020 Climate Normals ('Meteo.Si - Ljubljana Bežigrad', 2024) (Table 1.1 and 1.2). Ljubljana is showing quite distinctive air warming trends, most notable in summer months (0.4 °C/10 years). The precipitation maximum is observed for autumn months with average of 448 mm for 30-year period. (Bertalanič et al., 2019). In Ljubljana, 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, while no annual trends in amount of precipitation is observed. Although projected changes in precipitation for this region, positioned in a transition zone, are less reliable, various models predict increased precipitation throughout the year with the most significant increase expected in winter (Bertalanič et al., 2019; Dolinar, 2018). Flow regimes of rivers also change based on the past observations. There is a noticeable decrease in the spring flood peak and an increase in the autumn peak. In recent years this has led to droughts conditions during the spring and summer months and high-water levels in the autumn (Kobold, 2007).

Table 1.1: Average monthly air temperature (°C) for the long-term periods of 1981-2010 and 1991-2020, as well as for the years 2018, 2019, 2020, 2021 ("Meteo.si", 2024).

Year / Month	01	02	03	04	05	06	07	08	09	10	11	12	**Yearly**
1981-2010	0.2	1.9	6.4	10.8	15.8	19.1	21.3	20.5	15.9	11.2	5.5	1.2	**10.8**
1991-2020	1.0	2.6	7.1	11.6	16.1	20.0	21.8	21.3	16.1	11.4	6.4	1.5	**11.4**
2018	4.8	–0.1	4.6	15.2	18.0	20.9	22.3	22.8	17.5	13.2	8.2	2.2	**12.5**
2019	0.7	4.9	9.0	11.6	12.9	23.5	22.9	22.6	16.8	13.2	8.8	3.6	**12.6**
2020	1.9	6.8	7.2	13.0	15.3	19.6	21.8	22.2	17.5	11.9	5.3	2.9	**12.2**
2021	1.2	5.9	6.7	9.1	13.5	23.1	23.3	21.0	17.5	9.8	5.9	1.3	**11.5**

Table 1.2: Amount of precipitation (in mm) for the long-term periods of 1981-2010 and 1991-2020 ("Meteo.Si", 2024), as well as for the years 2018, 2019, 2020, 2021 (Cegnar, 2019, 2020).

Year / Month	01	02	03	04	05	06	07	08	09	10	11	12	**Yearly**
1981-2010	69	70	88	99	109	144	115	137	147	147	129	107	**1362**
1991-2020	67	84	83	97	114	125	122	124	160	150	138	104	**1368**
2018	73	132	122	102	131	83	138	223	126	125	109	12	**1376**
2019	66	98	48	89	239	46	142	112	145	76	188	130	**1379**
2020	14	42	105	25	115	147	160	87	133	203	48	183	**1262**
2021	141	85	57	129	247	25	150	105	167	47	165	122	**1442**

1.3.2 Water supply system in Ljubljana

Public utility VOKA SNAGA d.o.o. oversees the distribution of drinking water to inhabitants of the city of Ljubljana and its surroundings through a comprehensive water supply system (WSS). The central WSS comprises five water supply facilities (Figure 1.4) as well as ten smaller local pumping stations (Figure 1.5) (JP VOKA SNAGA, 2013). Figure 1.5 shows the two wellfields, Jarški prod and Šentvid, from both the outside and the inside, respectively.

The central WSS extracts water from five water supply facilities: Kleče (A), Hrastje (B), Brest (C), Jarški prod (D) and Šentvid (E) wellfields (Figure 1.5). Except Hrastje wellfield, all other wellfields represent its own water supply area (WSA). Initially, the WSS was divided into nine water supply areas (Figure 1.5), namely Kleče (A), Hrastje (B), Brest (C), Jarški prod (D), Šentvid (E), Hrastje/Jarški prod (F), Kleče/Brest (G), Kleče/Hrastje/Jarški prod (H), Kleče/Hrastje/Brest (I2). Later, in 2020 this division changed resulting in one additional water supply area and changes in the existing water supply areas (i.e. different area sizes). Newly established areas include ten water supply areas (Figure 1.5): Kleče (A1), Hrastje (B1), Brest (C1), Jarški prod (D1), Šentvid (E1), Hrastje/Kleče (F1), Kleče/Brest (G1), Kleče/Hrastje (H1), Kleče/Brest/Hrastje (I3) and Kleče/Jarški prod (DA).

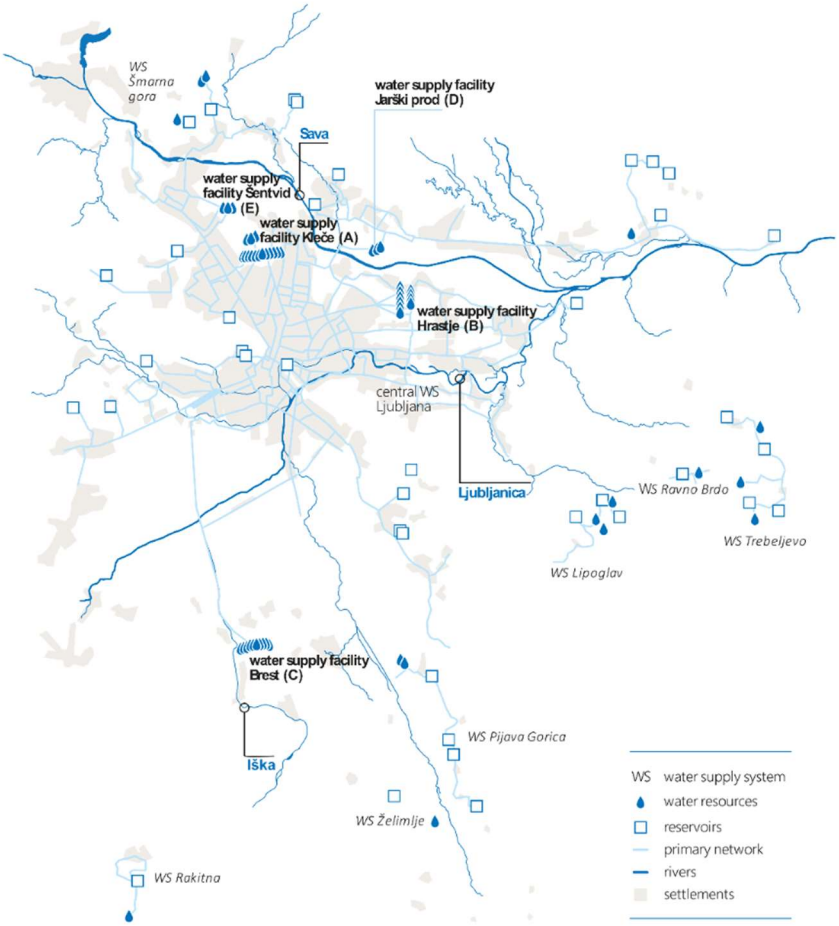

Figure 1.4: Locations and diversification of drinking water supply system in Ljubljana. Modified by JP VOKA SNAGA (2013).

The central WSS extracts water from five water supply facilities: Kleče (A), Hrastje (B), Brest (C), Jarški prod (D) and Šentvid (E) wellfields (Figure 1.5). Except Hrastje wellfield, all other wellfields represent its own water supply area (WSA). Initially, the WSS was divided into nine water supply areas (Figure 1.5), namely Kleče (A), Hrastje (B), Brest (C), Jarški prod (D), Šentvid (E), Hrastje/Jarški prod (F), Kleče/Brest (G), Kleče/Hrastje/Jarški prod (H), Kleče/Hrastje/Brest (I2). Later, in 2020 this division changed resulting in one additional water supply area and changes in the existing water supply areas (i.e. different area sizes). Newly established areas include ten water supply areas (Figure 1.5): Kleče (A1), Hrastje (B1), Brest (C1), Jarški prod (D1), Šentvid (E1), Hrastje/Kleče (F1), Kleče/Brest (G1), Kleče/Hrastje (H1), Kleče/Brest/Hrastje (I3) and Kleče/Jarški prod (DA).

Wellfields Kleče, Hrastje, Jarški prod and Šentvid are situated at the Ljubljansko polje aquifer, while the Brest wellfield is located in the Ljubljansko barje aquifer (Figures 1.3 and 1.5). Positioned south of the city of Ljubljana, the Brest wellfield, has been part of the water supply system since 1987, contributing approximately 10 % of the city´s drinking water. Primary water supply network consists of reservoirs, re-pumping stations and water pipelines of large diameters that run from water supply facilities. Further on, small diameters pipeline lead from the primary network in the direction of the consumers. Drinking water goes to the network without any technical water preparation, however it

is only occasionally chlorinated. Water is in the central WSS distributed to the consumers via 1,100 km long water supply network, with distribution of 115-150 L of drinking water per day/person. Altogether is the water distributed to 330,000 users through 42,000 connections. Some water supply areas are continuously supplied with water from a single water supply facility, while some with two or more water supply facilities, depending on water consumption and pressure condition in the system. Wellfields are strategically located within protected zones, restricting direct access to a pumping station to authorized personnel only. Once the water enters the system, it is kept in the networks no more than a few hours. In the water supply system, eleven re-pumping stations pumps are included into the network that pump water into reservoirs. From there water is released into the system using also pressure regulators, when needed (JP VOKA SNAGA, 2013).

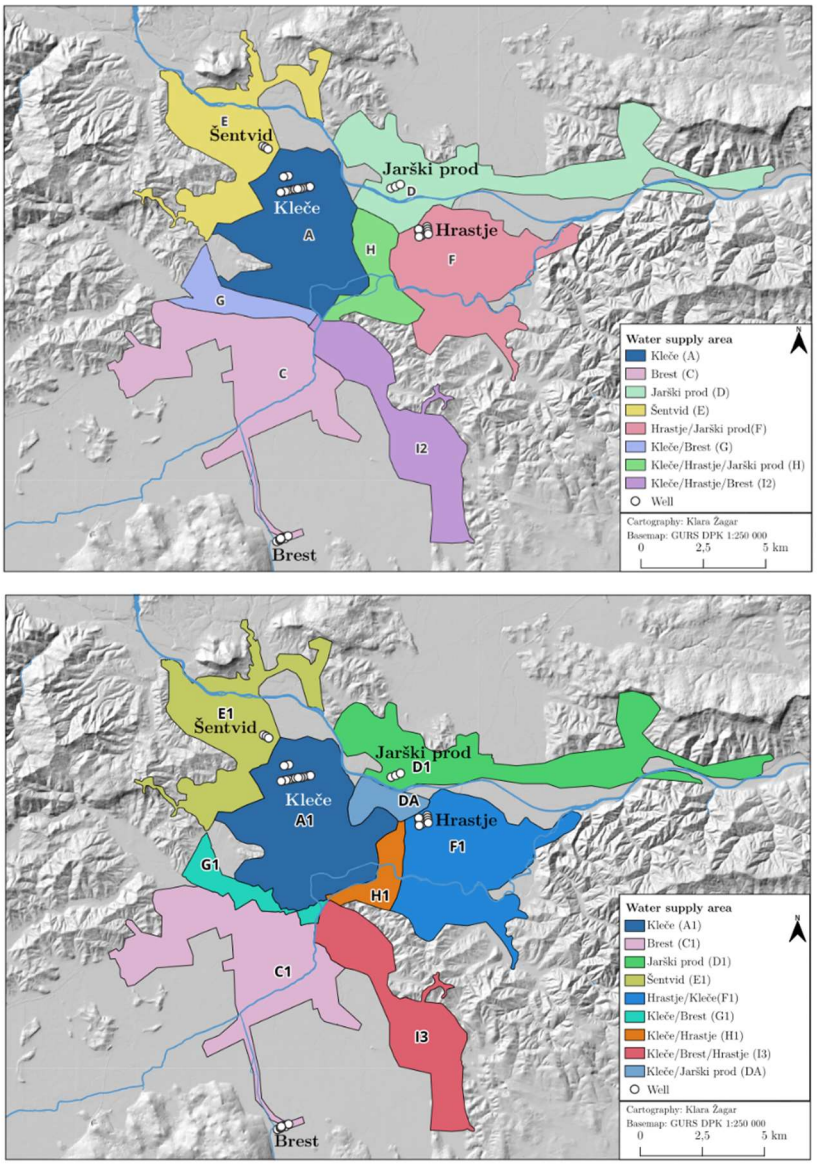

Figure 1.5: Water supply areas within Ljubljana's distribution system. The upper figure shows the nine WSA areas before 2020, while the lower figure shows the ten WSA areas after 2020. The wellfields are named Kleče, Brest, Hrastje, Jarški prod, and Šentvid.

1.3.3 Meteorological and hydrological conditions during the study period

The study, conducted between 2018 and 2021, reveals a noticeable increasing trend in temperatures. These years coincided with global records, as the years 2018-2021 ranked four warmest years on record (WMO, 2021a).

In Ljubljana, temperatures during this period were consistently above the long-term average (1981-2010), with anomalies of 1.7 °C, 1.8 °C, 1.4 °C and 0.7 °C, respectively (Table 1.1) (ARSO METEO, 2024). However, the temperature anomaly for the period 1991-2020 was comparatively lower (Figure 1.6). Rarely did the average monthly temperature fall below the long-term average, with May standing out as the month with the most pronounced deviation from the norm. Notably, the most significant temperature differences occurred during the first six months, with a less pronounced variance observed in the latter half of the year (Figure 1.6). Projections indicate that Slovenia will experience significant temperature changes across all seasons, with winter experiencing slightly enhanced warming. Warming will be the least pronounced in spring (Bertalanič et al., 2019). Additionally, Ljubljana is expected to experience even more significant temperature increases due to the UHI effect, where urban areas temperature increase more compared to the surrounding rural land (Liu et al., 2022).

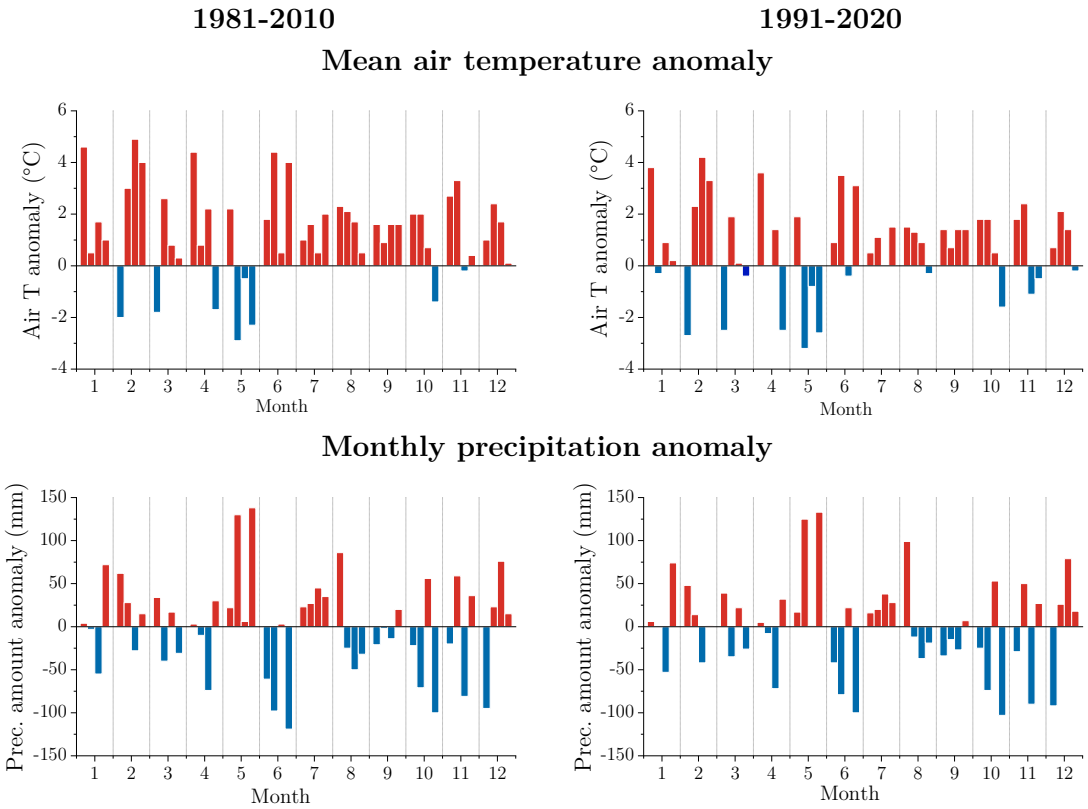

Figure 1.6: Mean air temperature and precipitation amount anomaly for period 2018, 2019, 2020 and 2021 based on long term averages 1981-2010 (left figures) and 1991-2020 (right figures).

Annual precipitation generally remained within the usual variability compared to the long-term means (1981-2010 and 1991-2020), with the exception of 2020, which recorded a lower amount of precipitation (92 %) compared to the long-term average (1991-2020).

While monthly precipitation fluctuations were most pronounced, the total annual amount did not vary substantially compared to long-term means (Table 1.2, Figure 1.6).

In contrast to temperature projections, predictions regarding changes in precipitation are less reliable due to Slovenia's location in the transition zone between northern and southern Europe. The signal of change in precipitation amount is slightly more pronounced seasonally. The most significant increase, by up to 40 %, is projected for winter under a moderately optimistic scenario. However, changes in summer precipitation are uncertain, with possible fluctuations in both directions (Bertalanič et al., 2019).

During the years 2018-2021, discharge levels at Sava Šentjakob were higher compared to long-term trends. The most significant deviations occurred during months with elevated discharge levels relative to the long-term averages. In contrast, deviations during months with lower discharge levels were more subtle (Figure 1.7). Additionally, the average yearly water temperatures at this location were higher for 1.6 °C, 1.4 °C, 1.3 °C and 1.1 °C, respectively compared to the long-term average (1981-2010).

At the Iška river at the Iška vas station (Figure 1.7), systematic measurements of discharge and temperature began only in 2001. In contrast, the discharge at Iška during the study period was lower compared to the long-term average (2001-2021) and was higher only 11 times during the four-year study period. The highest deviations were observed during spring time. Additionally, the average yearly water temperatures at this location were higher by 1.2 °C, 1.0 °C, 1.0 °C and 0.5 °C, respectively compared to the long-term average (2001-2021).

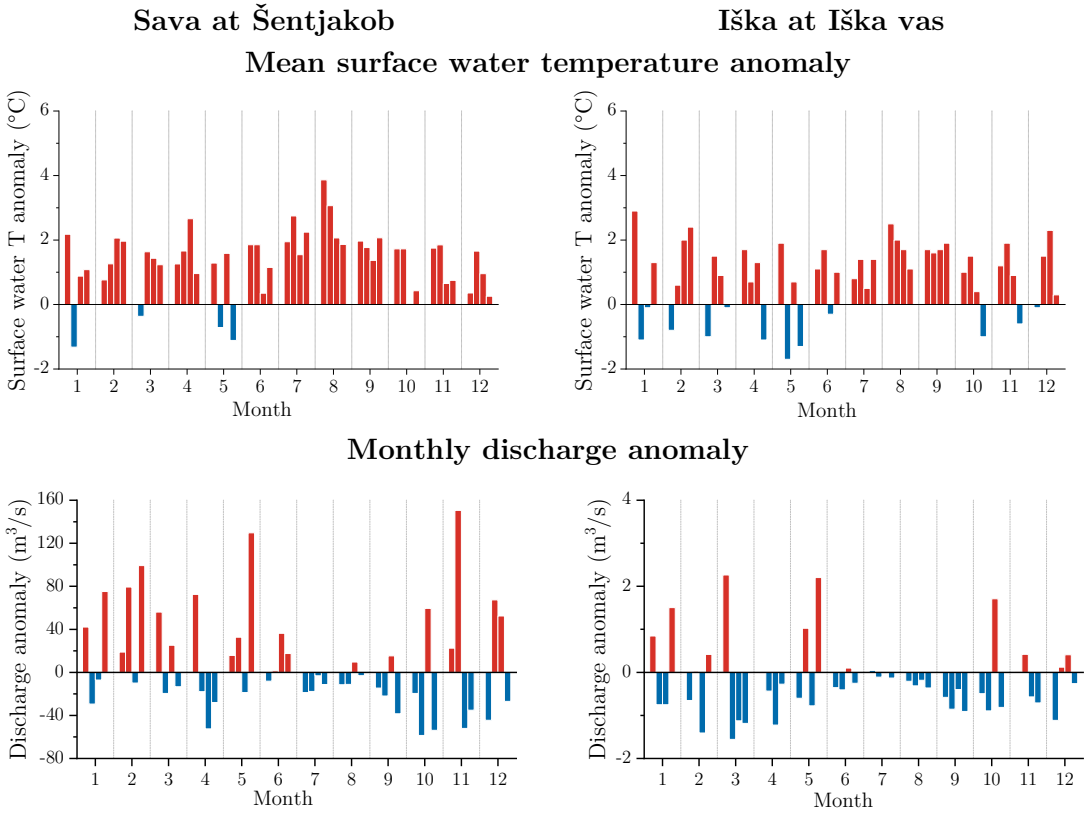

Figure 1.7: Mean surface water temperature and monthly discarge anomaly for period 2018, 2019, 2020 and 2021 based on long term average 1981-2010 for Sava River (left figures) and long term average 2001-2021 for the Iška River (right figures).

1.4 Sampling and Analytical Procedures

These sections provide an overview of the methodology, sampling techniques and analyses conducted in the study. A summary of the previous investigations performed in the study area is presented as a review paper in Chapter 3.1. Specific applications of methods to the individual field sites and information on the subsequent data processing can be found in Chapters 3.2 to 3.5.

1.4.1 Sampling

In this work, water samples were collected from precipitation, surface water, groundwater and different parts of water supply system (wells, joint exits from water pumping stations, reservoirs, water treatment locations, drinking fountains and taps) to determine their isotopic composition. The workflow of the sampling is presented in Figure 1.8.

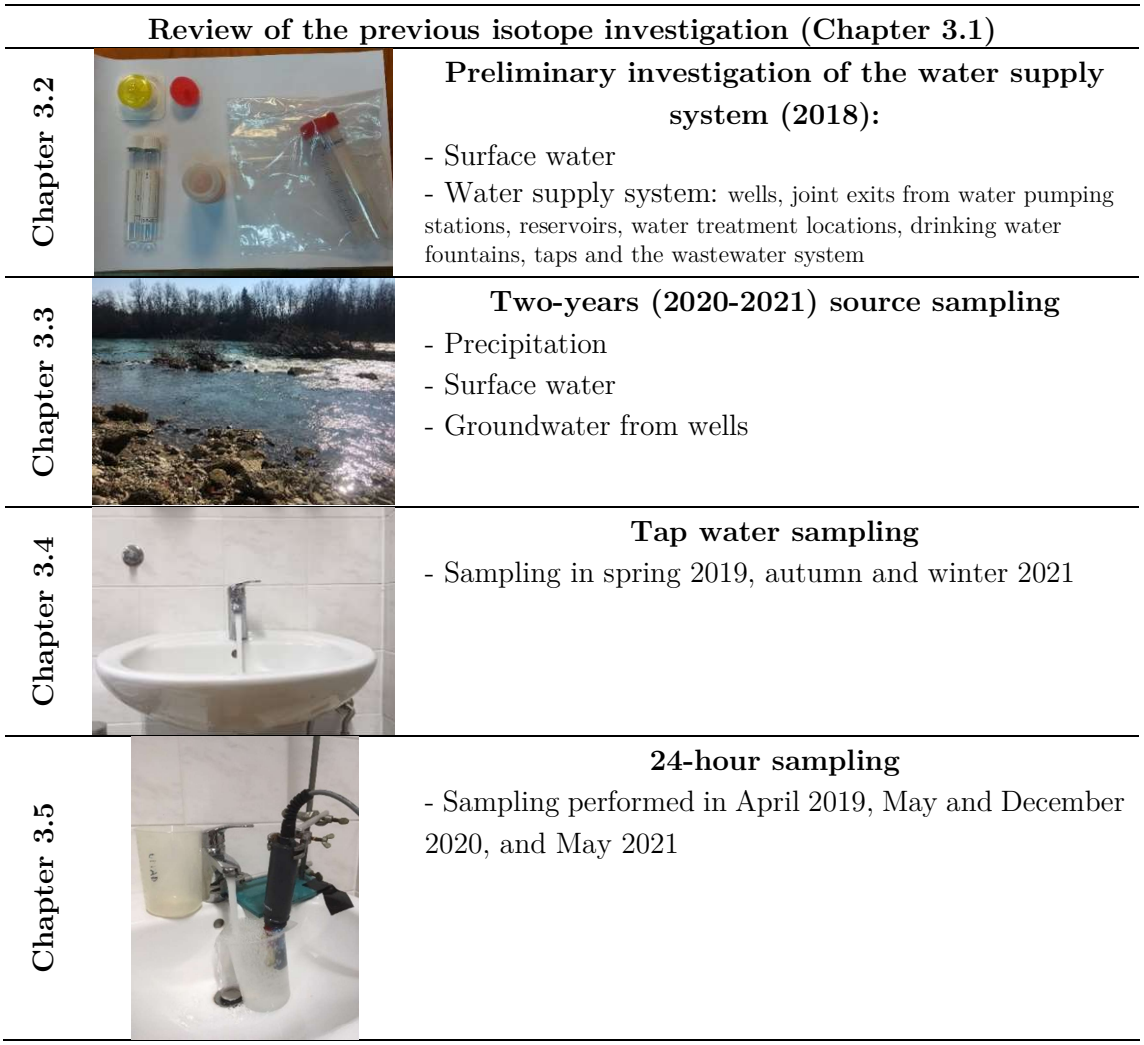

Figure 1.8: Conceptual graphic of the sampling campaigns and experiments.

The investigation of the Ljubljana water supply system started in 2018, after the review of previous isotope results. Sampling sites were selected based on the expertise of personnel from JP VOKA SNAGA d.o.o. The selection process considered both the type of the sampling site (TSS) (e.g., well, water treatment location, reservoirs, taps) and the type of water supply area (WSA) (e.g., Kleče, Hrastje, Šentvid). To ensure comprehensive coverage

of the entire WSS, additional three locations were selected along the River Sava and at the outflow from a wastewater treatment plant (CČN). For more detailed information, please refer to Chapter 3.2.

Following the initial screening of the system, a two-year monitoring program was conducted, during which samples from precipitation, surface water, and groundwater were collected between 2020 and 2021. Grab samples from surface water were taken directly from streams at three locations: Brod and Šentjakob on the Sava River and Iška vas on the Iška River (Figure 1.9). Groundwater samples were collected from five wellfields: Kleče, Brest, Hrastje, Jarški prod and Šentvid (Figure 1.10). Various experiments were conducted within the water supply system, including 24-hour sampling and tap water sampling.

Figure 1.9: Sampling locations of the Sava River at a) Brod, b) Šentjakob and c) the Iška River at Iška vas.

Figure 1.10: Wellfields Jarški prod and Šentvid in Ljubljana from outside and inside, respectively.

1.4.1.1 Tap water experiments

Tap water sampling was performed three times in the Municipality of Ljubljana (MOL). The first sampling occurred in March 2019, representing the spring season, while the subsequent samplings in September and December 2021 represented autumn and winter. The investigation focused on collecting tap water (TW) samples.

1.4.1.2 24-hour sampling experiment

The first 24-hour sampling aimed to investigate hourly variability in water samples collected from 9 am on April 24th until 9 am on April 25th 2019, from a tap at the Jožef Stefan Institute (JSI) (Figure 1.10). At this location, water was mixed from Kleče and Brest wellfields. The experiment involved collecting the first sample after running the tap for 60 seconds (1 minute). For more detailed information, please refer to Chapter 3.5. Sampling was then repeated three times, in May and December 2020, and May 2021. During this period, the water came only from the Kleče wellfield, so no mixing of sources was observer.

1.4.2 Measurements

1.4.2.1 Determination of stable isotope composition of oxygen and hydrogen

All water samples were collected in 30- or 60-ml HDPE bottles. The isotope composition of oxygen and hydrogen was determined according to the modified IAEA Technical procedure note no. 43 (Tanweer, Gröning, Van Duren, Jaklitsch, & Pöltenstein, 2009) using the CO_2-H_2O (Avak & Brand, 1995; Epstein & Mayeda, 1953) and H_2-H_2O (Coplen, Wildman, & Chen, 1991) equilibration techniques. All analyses were performed at the Jožef Stefan Institute using a dual inlet isotope ratio mass spectrometer (DI-IRMS, Finnigan MAT DELTA plus Finnigan MAT GmbH, Bremen, Germany) with an automated H_2-H_2O and CO_2-H_2O equilibrator HDOeq48 Equilibration Unit (custom built by M. Jaklitsch) and water bath temperature at 18 °C. The equilibration of H_2-H_2O and CO_2-H_2O lasted for 2 and 6 hours, respectively.

All measurements were performed together with routinely measured samples and laboratory reference materials (LRMs) calibrated periodically against IAEA calibration standards on the VSMOW/SLAP scale. This standards are stored in stainless steel containers under N_2 gas pressure for long-term water storage (Gröning, 2018). The results were normalized to VSMOW/SLAP using a Laboratory Information Management System for Light Stable Isotopes (LIMS) program (Coplen, 2017). For normalisation (N) and independent quality control (QC), we used LRMs with defined isotope values and estimated measurement uncertainty calculated by Kragten method (Carter & Barwick, 2011) (Table 1.3) and commercial LRM provided by the USGS (Nigro, Žagar, & Vreča, 2024).

1.4.2.2 Other analytical methods

Other methods were performed to complement the hydrometric and isotopic data. In the field, temperature (T), pH and electrical conductivity (EC) were measured. In the laboratories of the Departments of Environmental Sciences (IJS), additional parameters were analzed; namely stable isotope composition of carbon in dissolved inorganic carbon ($\delta^{13}C_{DIC}$), elemental composition (Ca, Na, K, Mg, Ag, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, K, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sr, U, V, Zn) and the $^{87}Sr/^{86}Sr$ isotope ratio. A detail explanation of the methods is presented in Chapter 3.2 to Chapter 3.5.

Table 1.3: δ^2H and δ^{18}O defined values of JSI laboratory reference materials with their associated combined standard uncertainties. N stands for normalization, QC for quality control (Nigro et al., 2024).

JSI code	Material	δ^2H [‰]	δ^{18}O [‰]	Comment
W-3869	Distilled see water	$+2.9 \pm 0.9$	$+0.36 \pm 0.04$	N, defined
W-3871	Snow water Kranjska gora	-147.9 ± 0.6	-19.73 ± 0.02	N, defined
W-54	Snow water Kanin	-140.4 ± 0.7	-18.91 ± 0.03	N, defined
W-45	Milli-Q tap water Reaktor	-59.7 ± 0.7	-9.12 ± 0.03	QC, defined
W-53	Snow water Kanin	-140.4 ± 0.7	-18.91 ± 0.03	QC, defined
W-45	Milli-Q tap water Reaktor	-59.9 ± 0.7	-9.13 ± 0.03	QC, measured

1.5 Data Evaluation

Data was evaluated using various methods and software tools. Microsoft® office Excel 2016 was used to calculate basic descriptive statistical parameters. Statistical analyses, including Spearman correlation coefficient, hierarchical cluster analysis, and principal component analysis, were performed using OriginPro 2021 (OriginLab, Northampton, PA, USA). RStudio version 3.6.0 (RStudio Team, 2018) was used for the Kruskal-Wallis test followed by a Dunn post hoc test with Hochberg-Benjamin adjustment for multiple comparisons. For data visualization, both OriginPro 2021 and RStudio were used. The local meteoric water lines (LMWL) were calculated using the Python code available on GitHub (Pavšek & Vreča, 2022). Spatial data visualization was performed using QGIS Standalone Installer Version 3.4.

Chapter 2

Aims and Hypotheses

Previous isotopic investigations in the Ljubljana aquifers have been conducted in an unsystematic and short-term manner, providing information about the aquifer characterization, water sources and interactions. These data have helped improve conceptual models of the Ljubljana aquifer (Janža, 2009, 2022). Regular monitoring of the isotope composition of precipitation has been conducted since 1981 in Ljubljana, (Pezdič, 1999, 2003; Vreča, Bronić, Leis, & Brenčič, 2008; Vreča, Pavšek, & Kocman, 2022) but studies of other water cycle components, such us surface water and groundwater have been limited and sporadic. Additionally, no comprehensive isotopic investigation of both water sources and the water supply system has been carried out, leading to gaps in understanding water circulation, flow paths and storage in urban areas.

To address these gaps, this dissertation aims to use stable water isotopes (δ^2H and δ^{18}O), in combination with other physico-chemical parameters to investigate different components of urban water cycle in Ljubljana, from source to tap. Samples will be collected from multiple points within the water supply system, including wells, joint exits from water pumping stations, water treatment locations, reservoirs, drinking fountains and taps. Additionally, monthly sampling of surface water (the Sava and the Iška Rivers) and groundwater (Kleče, Hrastje, Brod, Jarški prod and Šentvid wellfields) will be conducted.

The general hypothesis is that the properties of water change from the source (wellfield) to end-user due to interplay of natural and anthropogenic processes in the aquifer, its recharge area, and the water supply system. These changes, reflected in the isotope composition and other physico-chemical properties, can be used to better understand water sources, evaluate changes and mixing within a complex water supply system, and assess the impact of anthropogenic activities and climate change on freshwater resources.
Moreover, this dissertation also addresses three sub-hypotheses, namely:

- Stable water isotopes can be used in the urban water supply systems and assess changes in the water cycle.
- Changes in the source contribution can be observed in the study area by determining the isotopic composition and other hydro-chemical parameters.
- The observed changes in the isotopic composition of water sources in the study area are correlated with climatic variations and trends.

The dissertation addresses the following questions:
1.) Can the different components of the urban water cycle be characterized by their different isotopic signatures?
2.) Can the unique isotope signatures be used to better define sources, pathways and interactions of water supply areas in the urban environments?
3.) Can we use stable water isotopes of specific tap water to link the primary source and water supply area?

The specific goals of this dissertation are:

- To synthesis and critically assess previous isotope investigations in the Ljubljana area, with emphasis on the use of δ^2H and δ^{18}O until 2019; identifying both good practices and main gaps (Chapter 3.1).
- To improve the assessment of freshwater resources for domestic supply using water isotopes and other physico-chemical measurements to better characterise sources and pathways in urban environments (Chapter 3.3).
- To gain insights into seasonal variations in source and changes in flow paths in urban area and the potential impact of climate change (Chapters 3.3 and 3.4).
- To determine the isotope composition of water within the water supply system and at the end-users (Chapters 3.2, 3.4 and 3.5).
- To create an isotopic database for future use (Chapter 3.6).
- To develop best-practice guidelines for integrating water isotopes to assist water managers in planning, designing and managing freshwater resources for domestic supply in urban environments (Chapter 3.7).

Chapter 3

Publications

The dissertation comprises five publications: four that have been published and one that has been submitted. The final two sections include a data map and best practice guidelines designed for stakeholders. The publications are listed in such a way that their consecutive appearances follow the general hypotheses and objectives of the thesis.

The first publication provides a synthesis and critical assessment of previous isotope investigations in the Ljubljana area (Chapter 3.1). Based on the literature review and insights from employees of the public utility JP VOKA SNAGA regarding the water supply system, a preliminary investigation of the system was proposed and performed in 2018. The results of this investigation are detailed in Chapter 3.2. Following this initial screening, a two-year sampling study was proposed, involving monthly sampling of all sources contributing to the groundwater and, consequently to the drinking water in Ljubljana. The sources included precipitation, surface water and groundwater from all wellfields at Ljubljansko polje and Ljubljansko barje. The findings of the study are presented in Chapter 3.3.

Chapters 3.4 and 3.5. present two types of experiments where tap water was sampled and analysed. First, tap water from across Ljubljana was collected during three sampling campaigns, with 273 samples collected using a citizen science approach (Chapter 3.4). Chapter 3.5. describes a 24-hour sampling experiment in which tap water was sampled every hour over a 24-hour period.

In all manuscripts, samples were collected to determine isotope composition of hydrogen ($\delta^{2}H$) and oxygen ($\delta^{18}O$) and were analysed using dual inlet isotope ratio mass spectrometry (DI-IRMS). Additional parameters investigated included temperature, electrical conductivity, total alkalinity, isotopic composition of carbon in dissolved inorganic carbon ($\delta^{13}C_{DIC}$), elemental composition and $^{87}Sr/^{86}Sr$ isotope ratios.

The work presented in the thesis is based on the Coordinated Research Project (CRP F33024) entitled “Use of Isotope Techniques for the Evaluation of Water Sources for Domestic Supply in Urban Areas” implemented by the IAEA Isotope Hydrology Section from 2018 to 2023. This five-year global assessment included representative urban studies in Canada, the USA, Costa Rica, Ecuador, Argentina, Ethiopia, Morocco, South Africa, Italy, Slovenia, Romania, Ukraine, India, Nepal, Vietnam, and China.

3.1 Manuscript: Synthesis of Past Isotope Hydrology Investigations in the Area of Ljubljana, Slovenia

This section presents a review paper authored by K. Nagode, T. Kanduč, S. Lojen, B. Bračič Železnik, B. Jamnik and P. Vreča published in Geologija in 2020. It examines 102 studies conducted in the area of Ljubljana aquifers between 1976 and 2019, with a specific focus in 41 papers that provided detailed data on stable isotopes of hydrogen, oxygen and carbon in groundwater, surface water and precipitation.

While numerous investigations have been conducted in the study area in the past, the results have been sporadic and often lacked important metadata (e.g., location of sampling, sampling date, measured parameters). Therefore, the primary goal of the manuscript was to summarize the methodologies used and the results obtained from these studies. We identified main gaps in the previous research, including the lack of long-term data sets, and large-scale isotopic data. Most investigations focused on samples collected for the determination of δ^{2}H and δ^{18}O, while $\delta^{13}C_{DIC}$ was rarely reported. 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. We also emphasized the importance of presenting numerical data with exact coordinates, as this is important for comparing newly gathered data with previous investigation.

The paper aims to improve the understanding of water circulation dynamics in Ljubljana's urban environment, which is crucial for effective water resource management. For the future investigations we recommend long-term and systematic monitoring, the expansion of isotopic studies, sharing of numerical data and enhanced collaboration and coordination.

I was responsible for updating the preselected references and summarizing the available literature. I also prepared the manuscript, including the creation of tables and figures.

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

Pregled preteklih izotopskih hidroloških raziskav na območju Ljubljane, Slovenija

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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-

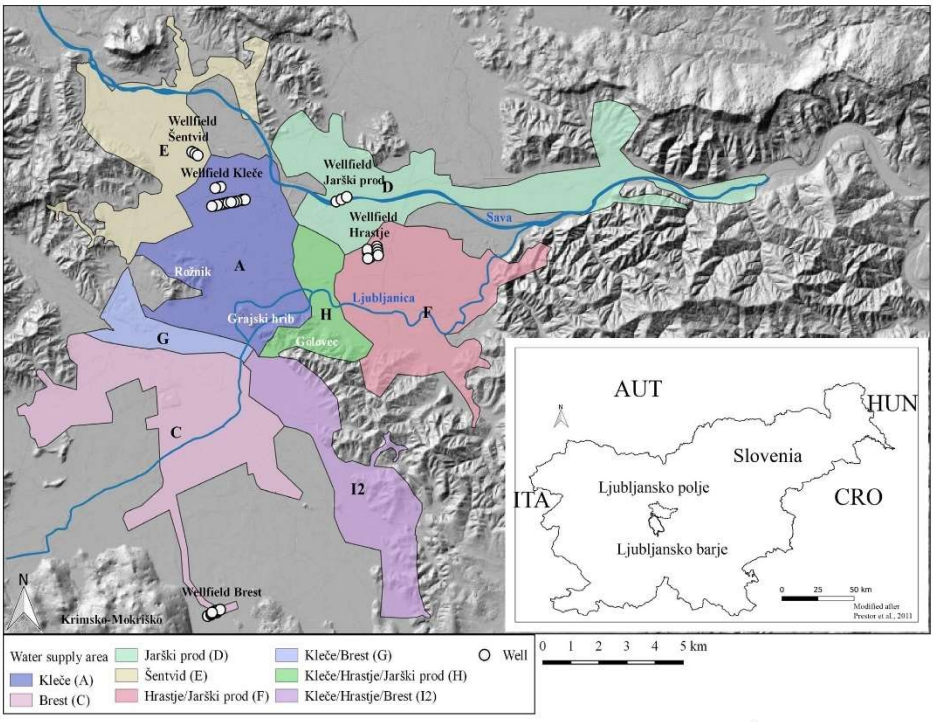

Fig. 1. Locations of the studied area with the main wellfields (Kleče, Hrastje, Brest, Jarški prod and Šentvid) and corresponding water supply areas in the Municipality of Ljubljana (wellfield Hrastje does not represent a unique water supply area). Source of topography: Geodetska uprava RS.

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.

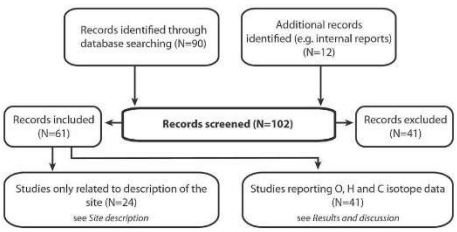

Fig. 2. Flowchart of study selection for detail review synthesis.

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.

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 *Analytical 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, SP = 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	$\delta^{18}O$, ($\delta^{3}H$)	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 $\delta^{2}H$ 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 $\delta^{2}H$. 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 $\delta^{2}H$ values. Pezdič (1998) reported $\delta^{18}O$ values of springs and surface river water of -9.65 and -8.82 ‰, while $\delta^{2}H$ values ranged from -67.4 to -61.2 ‰. The weighted means of $\delta^{18}O$ and $\delta^{2}H$ 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, $\delta^{18}O$, $\delta^{2}H$

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

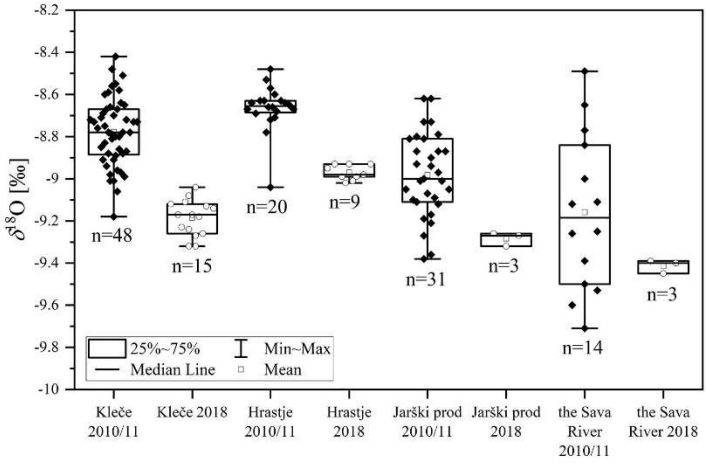

Fig. 3. Box plots of $\delta^{18}O$ values taken from Vrzel et al., 2018 (period 2010/2011) and from research performed in autumn 2018 for wells in Kleče, Hrastje, Jarški prod and the Sava River (Vreča et al., 2019a; 2019b).

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 $^3H/He$ 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 $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^{18}O$ ranged from -12.0 to -5.5 ‰. Trček (2005; 2017) monitored $\delta^{18}O$ values in precipitation from January 2003 to August 2004 and again from 2004 to 2014 at the Union Brewery. $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^{18}O$ and $\delta^{2}H$ 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.

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3.2 Manuscript: Multi-Isotope Characterization of Water in the Water Supply System of the City of Ljubljana, Slovenia

In this section, we present a paper authored by K. Nagode, T. Kanduč, B. Bračič Železnik, B. Jamnik, and P. Vreča published in the Water in 2022.

This study marks the first comprehensive stable isotope (H, O, and C) investigation of Ljubljana's urban water supply system (WSS), from source to tap. Sampling was conducted between September and November 2018 by JP VOKA SNAGA d.o.o. staff, JSI team members, and volunteers. The investigations focused on changes in temperature, electrical conductivity, total alkalinity, δ^2H, δ^{18}O, and $\delta^{13}C_{DIC}$ values. A total of 108 samples were collected from different points in the WSS, including wells, joint exits from water pumping stations, reservoirs, water treatment locations, drinking water fountains, taps and the wastewater system.

The results revealed that the ranges of δ^2H and δ^{18}O values were small, each well exhibited a unique fingerprint when additional parameters were considered. Statistically significant differences were observed between sampling months. The smallest temperature ranges were observed in wells compared to other WSS components, suggesting the system's susceptibility to external temperature changes. Other observed parameters showed higher variability within the wells than within the WSS, further indicating a more unified water system. Although precipitation's δ^2H, δ^{18}O signatures were seasonal, no such seasonal variation was observed within the WSS during the three-month sampling period. This limited timeframe also meant that the influence of meteorological and hydrological changes was minimal.

The isotope composition of groundwater at Ljubljansko polje depended on the well's location and the contribution of precipitation and River Sava water. This was particularly evident in the Hrastje, Jarški prod, and Šentvid wellfields, which showed more positive δ^{18}O values with distance from the River Sava. Higher alkalinity and more negative $\delta^{13}C_{DIC}$ values were noted at the Brest wellfield, with both parameters showing a negative correlation. $\delta^{13}C_{DIC}$ values enabled a distinction between river/groundwater interactions within the WSS and between shallower and deeper wells, as well as their distance from the riverbank.

To gain a better understanding of potential changes within the system, simultaneous sampling from source to tap is recommended, along with additional parameter measurements. Further observations are necessary to account for possible changes in the River Sava and the sensitivity of the aquifers to climate change. This preliminary study provides a foundational understanding of the differences between various groundwater sources and the WSS, offering baseline data for future research. In this study, also As was measured. Most results were below the detection limit, with measurable levels only observed in samples from the WSA Brest. Consequently, As concentration was subsequently used in the 24-hour experiment (Chapter 3.5).

The data gathered during this study have been published in an open repository Pangaea, titled "Multi-isotope characterization of water resources for domestic supply in Ljubljana, Slovenia." (Vreča et al., 2020)

In this paper I contributed with the sampling, performed the measurements for the determination of δ^2H and δ^{18}O using DI-IRMS, data evaluation, and writing the manuscript, including preparation of figures and tables. In addition, I was responsible for the preparation of the data and its submission.

water

MDPI

Article

Multi-Isotope Characterization of Water in the Water Supply System of the City of Ljubljana, Slovenia

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Abstract: Urban water supply systems (WSS) are complex and challenging to manage since the properties of water in the WSS change from source to the end user over time. However, understanding these changes requires a more profound knowledge of the WSS. This study describes the urban water cycle within the WSS of Ljubljana, Slovenia, where different water parameters such as temperature, electrical conductivity, total alkalinity, δ^2H, δ^{18}O, and $\delta^{13}C_{DIC}$ were monitored from September to November 2018. Altogether 108 samples were collected, including from the source (3) and at different levels of the WSS: wells (41), joint exits from water pumping stations (7), reservoirs (22), water treatment locations (2), drinking fountains (13), taps (19) and wastewater system (1). The data show that although the ranges of δ^2H and δ^{18}O values were small, each well is represented by a unique fingerprint when considering additional parameters. A statistically significant difference was observed between sampling months, and temperature and most parameters showed higher variability within the wells than across the WSS, suggesting a more unified WSS. Finally, based on $\delta^{13}C_{DIC}$ values, a distinction could be made between river/groundwater interactions within the WSS and between shallower and deeper wells and their distance from the river bank.

Keywords: urban water supply system; stable isotopes; hydrogen; oxygen; carbon; Ljubljana; Slovenia

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1. Introduction

Urban water supply systems (WSS) are complex and dynamic and are composed of multiple interdependent components, i.e., water resources, storage units, pumping stations, reservoirs, transfer lines, and channels and, like any other system, they are prone to physical disruption and pollution [1]. Rapid growth in populations and urbanization has resulted in a dramatic increase in water usage, putting considerable strain on existing WSS, which cannot adequately adapt to accommodate the new level of demand [2]. As a result, in many countries, WSS might become deficient and poorly understood [1]. The allocation and management of water sources are also increasingly challenging due to environmental factors such as pollution and climate change [3,4]. Therefore, what is needed is a multidisciplinary approach to address such issues. In this respect, stable isotopes can be used to complement other hydro-chemical information about the system [5]. The application of water isotopes (δ^{18}O and δ^2H) is based on the assumption that the isotopic signature of water is present with unique values that change with time and space [6,7]. This conservative behavior allows new insights into the mechanisms, pathways, and interactions of water bodies in urban systems [4,8]. Moreover, the isotopic composition of carbon in dissolved inorganic carbon ($\delta^{13}C_{DIC}$) is important in deciphering the origin of carbon in the water system since HCO_3^- is the primary species leaching from carbonate rocks [9].

Applying the stable isotope approach in urban water settings has increased in recent years and, as a consequence, yielded promising results. For example, stable isotope values of tap water were used to identify and quantitatively characterize the water sources, water management practices, and structure of different WSS and quantify the effects of climate variability [3,4,8,10,11]. In addition, Leslie and others [12] used the stable isotope values in municipal water to delineate the residence time of water in a WSS based on the lag between precipitation and residential tap water over time. In most cases, these systems are investigated by sampling sources and tap water, and so far, only Sánchez-Murillo et al. [11] have investigated other engineering features, i.e., storage units or tanks, transfer lines/pumping units, over a short period (over 2–3 days).

The provision of water for domestic supply in urban areas is complex and usually involves many sources (i.e., precipitation, surface water, and groundwater). The WSS for Ljubljana, the capital city of Slovenia, is no exception and is still in use today despite being designed more than 100 years ago. The main source of drinking water for the city is the groundwater from the Ljubljansko polje aquifer, although some of it derives from the Ljubljansko barje aquifer in the southern part of Ljubljana [13]. So far, only short−term investigations of the WSS have been performed that focus on groundwater dynamics, modeling [14,15] and chemical and isotope investigations to characterize the aquifers, sources, and water interactions for the aquifers' water supply [14,16–20]. Despite the usefulness of stable isotopes (H, O, C) for managing water resources, Slovenian regulation does not require the analysis of stable isotopes in drinking water. Consequently, as concluded by a thorough review of past investigations [19], no systematic investigation of the isotope composition of drinking water in Ljubljana from "source to tap" has been performed.

In this paper, the results of a short, preliminary investigation of Ljubljana's WSS from well to tap are presented. The aim was to perform a systematic assessment of the use of stable isotopes and other physicochemical properties to evaluate water sources, pathways, and interactions to improve water supply management. More specifically, the paper addresses the following research questions: Can isotopic signatures characterize different urban water cycle components? Can the unique isotopic signatures be used to define better the sources, pathways, and interactions between water bodies (e.g., groundwater and river water) in urban environments and WSS? The data provided also represents an initial database for future comparison of the WSS.

2. Materials and Methods

2.1. Site Description

Sampling was performed in two sections of the Ljubljana basin: the Ljubljansko polje (LP), an unconfined alluvial aquifer in the northern part of the and the Ljubljansko barje (LB), a confined aquifer in the southern part of the basin (Figure 1) [15]. A detailed description of the aquifers is given in [19,21]. The aquifers are separated by the hills Golovec, Grajski hrib and Rožnik. The hills and the bedrock of the LP are composed of impermeable Permian and Carboniferous schist, claystone, and sandstone [22]. It was formed by tectonic subsidence and filled with Pleistocene and Holocene alluvial sediments of up to 120 m in thickness. The aquifer is generally recharged from infiltration of precipitation, the River Sava (north-western part) and via lateral inflow from the Ljubljansko barje multi-aquifer system [15]. The Ljubljansko barje is a depression formed by tectonic subsidence and filled by alluvial and lacustrine sediments during the Pleistocene and Holocene epochs. The heterogeneity of sediments means that the hydrogeological conditions in the LB are more complicated than in the LP [16,22].

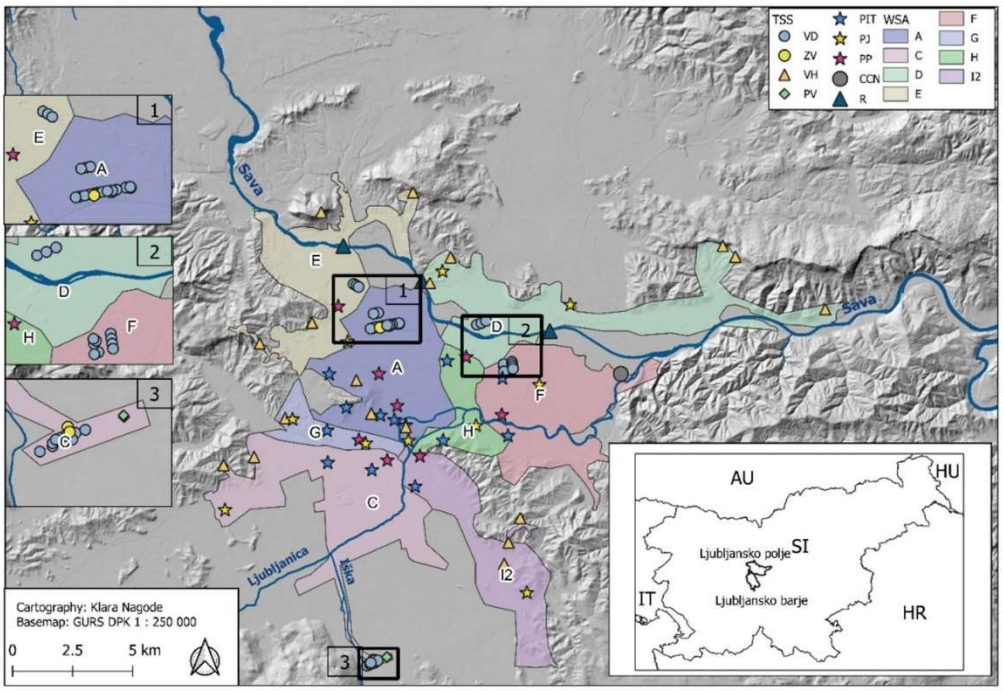


Figure 1. Sampling locations for the different water supply areas (WSA) and type of sampling site (TSS). Zoom locations represent the distribution of wells in the respective wellfields. VD = well, ZV = joint exit from the water pumping station, VH = reservoir, PV = water treatment location, PIT = drinking water fountain, PJ = tap in a public building, PP = tap in a private building, CČN = water treatment plant, R = river; A = Kleče, C = Brest, D = Jarški prod, E = Šentvid, F = Hrastje/Jarški prod, G = Kleče/Brest, H = Kleče/Hrastje/Jarški prod, I2 = Kleče/Hrastje/Brest.

The largest water company in Slovenia in terms of users is the Public Water Utility JP VOKA SNAGA d.o.o. Drinking water has been supplied to users in Ljubljana since 1890. Currently, the majority of the groundwater is extracted from the Kleče (A) wellfield at LP, while the contribution of other wellfields at LP; Hrastje (B), Jarški prod (D) and Šentvid (E) and from LB from Brest (C) is lower (Figure 1). Water is pumped from 44 wells and is distributed through more than 1100 km of supply network [23], and it takes a few hours for water from the wellfield to reach the end-user. Well depths typically range from 30 to 105 m below the surface, with pumping rates from 15 to 92 L/s. The perforated screens in the pumping wells vary at LP from 200 to 290 m a.s.l. Their elevation is between 281.4 and 310.0 m a.s.l. In the LB, the screens are located between 290 m and 270 m a.s.l. for shallow wells and 270 to 195 m a.s.l. for deeper wells (e.g., Brest 2a and Brest 4a). Their elevation is between 299.5 and 301.9 m a.s.l. (Supplementary Figure S1). In the central system, certain settlements are continuously supplied with drinking water from a single wellfield (A, C, D, and E), while others are supplied from two or more wellfields: F, G, H, and I2 (Figure 1) [20]. In Ljubljana, WSS also includes other components: joint exits from water pumping stations (ZV), reservoirs (VH), water treatment locations (PV), drinking water fountains (PIT) and taps in public buildings (PJ) and private buildings (PP).

2.2. Selection of Sampling Sites and Sampling

Based on the knowledge of the JP VOKA SNAGA d.o.o. personnel and previous investigations of the WSS, 97 sampling sites, which are used for the regular monitoring of drinking water, were selected for investigation (Figure 1). Sampling sites were selected

according to (a) the type of sampling site (TSS) in the WSS and (b) the type of water supply area (WSA). Based on TSS, the initial selection included wells (VD, 44 samples), joint exits from water pumping stations (ZV; 7 samples), reservoirs (VH; 23 samples), water treatment locations (PV; 2 samples), drinking water fountains (PIT; 13 samples) and taps in public (PJ; 10 samples) and private buildings (PP; 8 samples). The sampling of the WSA initially included 4 main wellfields: Kleče (A; N = 35), Brest (C; N = 22), Jarški prod (D; N = 10) and Šentvid (E; N = 11) and four areas where water is mixed from two or three different WSA: Hrastje/Jarški prod (F; N = 5), Kleče/Brest (G; N = 5), Kleče/Hrastje/Jarški prod (H; N = 3) and Kleče/Hrastje/Brest (I2; N = 6). Wells from the Hrastje wellfield (B; N = 10) were also included, although it does not represent a unique WSA.

In order to cover the whole WSS, an additional three locations along the River Sava (R; locations Brod, Črnuče and Šentjakob) and at the outflow from a wastewater treatment plant (CČN) were selected. Data collection focused on a 3-month period between 6 September 2018 and 29 November 2018. Altogether, 8, 10 and 12 sampling campaigns were performed in September, October and November 2018, respectively. Samples at four sites were not collected, and one site (PJ) was sampled twice. The final collection of samples included sampling in VD (41), ZV (7), VH (22), PV (2), PIT (13), PJ (11) and PP (8). In total, 104 samples were collected at 103 locations. The majority of well samples (41) were collected in September, while eight samples from Kleče and six from Brest were collected in October and November 2018. In the field, temperature (T) and electrical conductivity (EC) measurements were collected, while pH, total alkalinity (TA), isotope composition of hydrogen (δ^2H), oxygen (δ^{18}O) and carbon in the dissolved inorganic carbon ($\delta^{13}C_{DIC}$) were measured in the laboratory. Metadata and results are presented in [24]. Water samples from the various components of the WSS (93 sites in the WSS and at the outflow of CČN) were collected by JP VOKA SNAGA d.o.o., while the JSI team members and volunteers performed sampling at PP and two locations at PJ. From 2016 to 2018, daily air temperature and precipitation data were obtained from the Environmental Agency of the Republic of Slovenia for the station at Ljubljana–Bežigrad [25]. In addition, monthly composite precipitation samples were collected at Ljubljana-Reactor, where monitoring has been performed since 1981 [26–28].

2.3. In-Situ Measurements

Temperature (T) and electrical conductivity (EC) were determined together in-situ using an Ultrameter II^{TM} 6PFC^{E} (MIRON L Company, Carlsbad, CA, USA). The measurement accuracy was ±0.1 °C for T and ±1% for EC. However, T and EC were not measured for all tap water samples (10). Samples were collected using the following protocol: taps were opened for 5 min [11] before sampling to avoid stagnant water.

2.4. Analytical Procedures

2.4.1. Determination of Total Alkalinity (TA)

To determine the TA, each sample was passed through a 0.45 µm nylon filter into an HDPE bottle and kept refrigerated until analyzed. First, the pH was measured (SevenCompactTM pH/Ion S220, Mettler-Toledo 8603 Schwanzenbach, Switzerland, Rating 9–12 V, made by Mettler Toledo group). The TA was then measured by Gran titration [29] with a precision of ±1%. Sample repeatability was ±0.1 mM.

2.4.2. Determination of δ^2H, δ^{18}O and d-Excess

δ^2H and δ^{18}O values were determined according to [20]. The results are expressed using the standard δ notation (in‰):

$$\delta_{sample}\ (‰) = (R_{sample}/R_{standard} - 1) \times 1000 \quad (1)$$

R_{sample} and $R_{standard}$ are the isotope ratios ($^2H/^1H$ and $^{18}O/^{16}O$) of a heavy isotope to a light isotope in a sample measured against an international standard. Materials

used for normalization and reference materials are described in [20]. The average sample repeatability was 0.3‰ for δ^2H and 0.02‰ for δ^{18}O. Deuterium excess (d-excess) was calculated as d-excess [‰] = δ^2H − 8 × δ^{18}O [30]. The overall uncertainties were estimated to be less than 1‰, 0.05‰ and 1.01‰ for δ^2H, δ^{18}O and d-excess, respectively.

2.4.3. Determination of $\delta^{13}C_{DIC}$

A Europa Scientific isotope ratio mass spectrometer (Sercon Limited, Crewe, UK) coupled with a TG − preparation module was used to measure the amount of carbon in dissolved inorganic carbon ($\delta^{13}C_{DIC}$). In brief, phosphoric acid (100%) was added (100−200 µL) to a septum tube and purged with pure He. A water sample (5 mL) was then injected into the tube, and CO_2 was measured directly from the headspace. One-point normalization to Carlo Erba was performed. The $\delta^{13}C_{DIC}$ of the dissolved CO_2 was directly measured from the headspace. A standard solution of Na_2CO_3 (Carlo Erba) with a known $\delta^{13}C_{DIC}$ value of −10.8‰ ± 0.2 was used for calibration [31,32]. The average sample repeatability for $\delta^{13}C_{DIC}$ was 0.1‰. The results are expressed in the standard δ notation as reported in Section 2.4.2.

2.5. Data Evaluation

Metadata and data were deposited in the Pangea database [24]. Descriptive statistics were used for the determination of the median (Me), standard deviation (SD), minimum (min), maximum (max) and range. The distribution of δ^2H versus δ^{18}O data was compared to the global meteoric water line (GMWL), identified by Craig [33] as $\delta^2H = 8 \times \delta^{18}O + 10$. A local meteoric water line (LMWL) for Ljubljana was calculated from the amount-weighted reduced major axis (PWRMA; 2016–2018) [34] using the python code deposited in GitHub [35]. In addition, we used the LMWL for the Kredarica station (46.378784, 13.848628, 2514 m a.s.l.) for further evaluation [26]. Spearman's correlation analysis was used to identify correlations between determined parameters and the whole WSS, wells in LB and LP and other components of the WSS, respectively. The significance level was $p < 0.05$. Statistical differences between groups (different parameters, components of the WSS and WSA) were assessed using the non-parametric Kruskal-Wallis test followed by a Dunn post hoc test with Hochberg-Benjamin adjustment of the *p*-values for multiple comparisons. All statistical analyses and visualization of the results were performed using RStudio version 3.6.0 (RStudio Team, 2018) using the stats package (R Core Team, Vienna, Austria, 2019) and OriginPro 2021 software (OriginLab, Northampton, PA, USA).

3. Results and Discussion

3.1. Meteorology and Hydrology

The Ljubljana basin has a Subcontinental climate [36], with a mean annual precipitation of 1362 mm and an annual mean temperature of 10.9 °C for the period 1981 to 2010 [37]. The driest and wettest months are January (69 mm) and October and November (147 mm), respectively, while the lowest and the highest temperatures recorded are in January (0.03 °C) and in July (average: 21.2 °C).

In Slovenia, the average air temperature in 2018 was the second-highest compared to 1981–2010, with a mean annual temperature of 1.5 °C above the national average [38]. In September, October, and November 2018, the average temperatures were 1.6 °C, 1.9 °C, and 2.6 °C above the long−term normal (1981–2010). In addition, only 85% (126 mm), 85% (125 mm) and 84% (109 mm) of precipitation fell, respectively, compared to the average for the same months during 1981–2010 [39–41]. In the spring and summer seasons prior to sampling (March–May and June–August), the average precipitation exceeded the average for the previous three years during the same period. In contrast, the average precipitation amount was lower during the sampling period (September–November) than the same period during the previous three years. The same trend is also observed for December–February (Table 1). However, the temperature difference is not that significant when

comparing 2018 to the previous three-year period except for December–February, where the average difference was 0.5 °C (Table 1).

Table 1. Mean precipitation (mm), mean air temperature (°C), and mean isotope composition of precipitation for the three-month periods during 2016–18 and 2018, respectively.

Year	Parameters	December–February	March–May	June–August	September–November
2016–2018	P [mm]	98.2	104.8	119.8	146.7
	T [°C]	1.8	12.5	22.0	11.9
	$\delta^{18}O$ [‰]	−10.91	−7.93	−5.60	−8.27
	$\delta^{2}H$ [‰]	−76.5	−53.8	−35.6	−53.0
2018	P [mm]	72.5	118.6	148.0	119.8
	T [°C]	2.3	12.6	22.0	13.0
	$\delta^{18}O$ [‰]	−10.88	−7.18	−5.95	−7.20
	$\delta^{2}H$ [‰]	−76.2	−47.8	−38.7	−44.3

The water flow in the River Sava varied between 28 m^3/s to 907 m^3/s from 2016 to 2018 and from 30 m^3/s to 741 m^3/s from September–November, 2018 [42]. As observed for precipitation, the average monthly river discharges in September 2018 were about 40% lower than during the so-called long-term period between 1981 and 2010. Only one sizeable precipitation event occurred in September 2018; however, it did not cause a significant increase in water flow. In October 2018, the river had a small discharge, which increased due to many precipitation events at the end of the month (Figure 2). In November 2018, the discharge slowly decreased, with an additional increase through the end of the month. Again, the average monthly discharge was lower than during the long-term period.

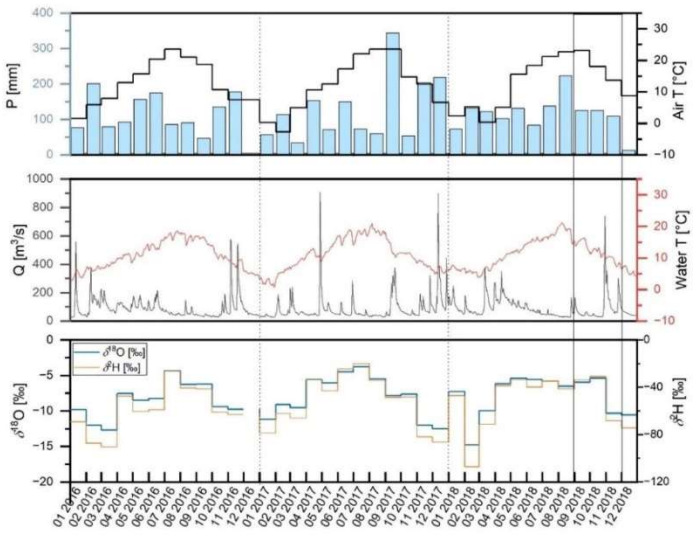


Figure 2. Monthly precipitation totals (mm), average monthly air temperature (°C), water flow (m^3/s), water temperature (°C) and $\delta^{2}H$, $\delta^{18}O$ in precipitation during 2016–2018. The sampling period September–November 2018 is marked with black lines.

3.2. Isotope Composition of Precipitation

Values of $\delta^{2}H$, $\delta^{18}O$ (Figure 2), and d-excess for precipitation ranged between −107.2‰ and −20.0‰, between −14.79‰ and −3.75‰ and between 4.7 to 14.9‰ for the period 2016–2018, respectively. The most positive isotope signature is characteristic for warmer

summer months and a more negative signature for colder winter months (Table 1). When comparing seasonal differences during 2018 to the previous three-year averages (Table 1), we observe the highest difference for September–November 2018, i.e., the more positive δ^2H and δ^{18}O values, which can be attributed to the higher average air temperature in 2018. The local water meteoric water lines (LMWL) for Ljubljana and Kredarica in the period 2016–2018 were calculated using PWRMA [26,35] and are: $\delta^2H = (7.82 \pm 0.16) \times \delta^{18}O + (9.61 \pm 1.37)$ ($r^2 = 0.99$; N = 35) and $\delta^2H = (8.42 \pm 0.19) \times \delta^{18}O + (18.98 \pm 2.09)$ ($r^2 = 0.99$; N = 34) (Figure 3). The LMWL for the Ljubljana plot is parallel to the GMWL, while the LMWL for Kredarica is plotted above the LMWL for Ljubljana, suggesting different moisture sources in the upper River Sava drainage area than in Ljubljana.

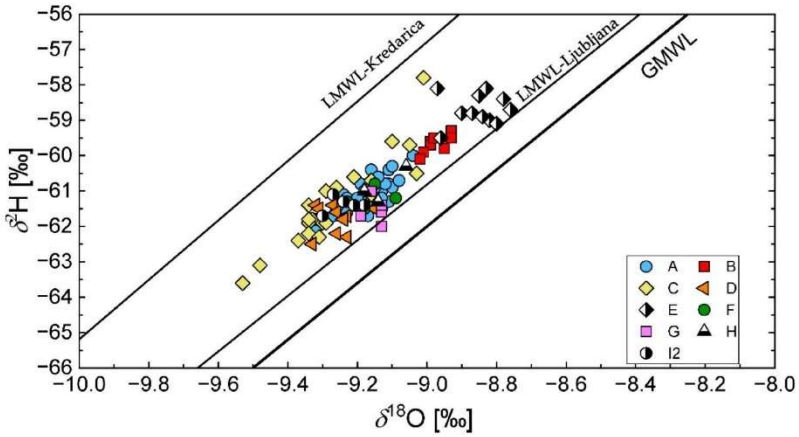


Figure 3. Dual isotope plot of the whole water supply system samples compared to the global meteoric water line (GMWL) and local meteoric water line (LMWL) from Ljubljana (2016–2018) and Kredarica (2016–2018). A = Kleče, B = Hrastje, C = Brest, D = Jarški prod, E = Šentvid, F = Hrastje/Jarški prod, G = Kleče/Brest, H = Kleče/Hrastje/Jarški prod and I2 = Kleče/Hrastje/Brest.

3.3. The Whole Urban Water Supply System

The sample data set of T, EC, pH, TA, δ^2H, δ^{18}O, d-excess and $\delta^{13}C_{DIC,}$ is presented in [24]. Their median (Me), standard deviation (SD), minimum (min), maximum (max) and ranges are presented in Table 2, while the WSA and TSS averages are presented in [43]. In addition, Table 2 also contains data for CČN and the three sampling locations along the River Sava (Šentjakob, Črnuče and Brod).

Table 2. Basic statistic parameters for temperature (°C), electrical conductivity (µS/cm), pH, total alkalinity (mM), and isotope composition of oxygen (δ^{18}O) and hydrogen (δ^2H), d-excess and isotopic composition of carbon in dissolved inorganic carbon ($\delta^{13}C_{DIC}$) for all components in the system and the actual values for CČN and locations at the River Sava.

	T (°C)	EC (µS/cm)	pH	TA (mM)	δ^2H (‰)	δ^{18}O (‰)	*d* (‰)	$\delta^{13}C_{DIC}$ (‰)
Median	12.7	508.55	7.7	4.9	−61.2	−9.16	12.3	−12.9
Standard deviation	1.5	58.1	0.2	0.7	1.1	0.15	0.5	1.0
Minimum	10.3	365.2	7.2	3.4	−63.6	−9.53	11.0	−15.3
Maximum	17.4	660	8.4	7.4	−57.8	−8.76	14.3	−9.4
Range	7.1	294.8	1.2	4.0	5.8	0.77	3.3	5.9
Sava 1–Šentjakob	15.0	345	8.17	3.3	−63.0	−9.40	12.2	−8.0
Sava 2–Črnuče	15.1	345	8.23	3.4	−62.4	−9.39	12.7	−9.2
Sava 3–Brod	15.1	343	8.24	3.3	−63.3	−9.45	12.3	−7.7
CČN	21.7	1086	9.9	5.9	−58.2	−8.68	11.2	−11.9

The outflow from CČN had the highest values of T, EC, pH, and TA, while the values of δ^2H, δ^{18}O and $\delta^{13}C_{DIC}$ were lower compared to the median values for the whole system (Table 2). Similarly, T and pH values are higher at the three sampling locations along the River Sava, while EC and TA values are lower than the median values for the whole system. Distinct differences could be observed between more enriched δ^2H and δ^{18}O values for the whole system compared to more depleted surface water resulting from different system processes. In addition, other processes (i.e., mixing surface water with precipitation) can cause more positive values observed in other components of the WSS. The average d-excess of the River Sava is 12.3‰ reflecting the contribution of precipitation of the mixed Atlantic−Mediterranean origin [44]. The $\delta^{13}C_{DIC}$ values of surface water and wastewater effluent from the CČN treatment plant are more positive than the median values of the whole system. Data for surface water (three locations) and from the CČN were omitted in further evaluation.

The highest water temperature in the WSS was observed for samples collected in September 2018, corresponding to the highest daily air temperature for that month. The highest EC and pH values were also measured in September 2018, with median values of 508.6 µS/cm and 7.7, respectively. Isotopic signatures were positive during September 2018, with mean values of −60.3‰, −9.10‰, and −12.4‰ for δ^2H, δ^{18}O, and $\delta^{13}C_{DIC}$, respectively. In contrast, the most negative isotopic compositions were determined in November 2018 with −61.3‰, −9.21‰, and −13.1‰, respectively. A strong positive correlation ($\geq$0.7; $p \leq 0.001$) was observed between EC and TA and δ^2H and δ^{18}O, while a strong negative correlation (≥ -0.6; $p \leq 0.001$) was observed between TA and $\delta^{13}C_{DIC}$ (Figure 4a). Associations between sampling months and δ^2H and δ^{18}O values were tested. However, differences were only statistically significant for δ^2H. A statistically significant correlation was observed between sampling months and $\delta^{13}C_{DIC}$. Total alkalinity ranged from 3.4 mM to 7.4 mM. The highest alkalinity is observed at Brest wellfields, while lower alkalinity is observed at the Hrastje wellfields. In this study, the $\delta^{13}C_{DIC}$ values ranged from −15.3‰ (Brest-9) to −9.4‰ (VD-Kleče 7) with a median of -12.9 ± 1‰. The lowest $\delta^{13}C_{DIC}$ values were recorded at Brest wellfield, while the highest $\delta^{13}C_{DIC}$ was observed at Kleče wellfield (Figure 5b). The total alkalinity (Table 2) is much lower in river water samples (3.3 mM to 3.4 mM) than in groundwater samples (3.4 mM to 7.4 mM). The $\delta^{13}C_{DIC}$ values in river water (9.2 to −7.7‰) are higher than in groundwater (–15.3 to −9.4‰) due to the equilibration of CO_2 with the atmosphere [45].

Plotting δ^2H and δ^{18}O data from all sampling locations in the dual-isotope space (Figure 3) revealed slight differences between different WSA; however, the differences were significant for δ^2H and δ^{18}O between some WSA ($p \leq 0.001$). The most enriched values were observed for samples from the WSA Šentvid. Samples collected from this WSA are statistically significantly different from other WSA except for Hrastje WSA (Figure 5a). The highest range is observed for samples collected at WSA Brest (0.52‰) with the most negative values of δ^{18}O and δ^2H. All samples plot below the LMWL-Kredarica [26], representing the upper part of the River Sava recharge area and above GMWL and LMWL-Ljubljana (Figure 3). However, we observed no statistically significant difference between components and δ^2H, δ^{18}O or $\delta^{13}C_{DIC}$, while a statistically significant difference ($p \leq 0.05$) was observed between d-excess and different components in the WSS.

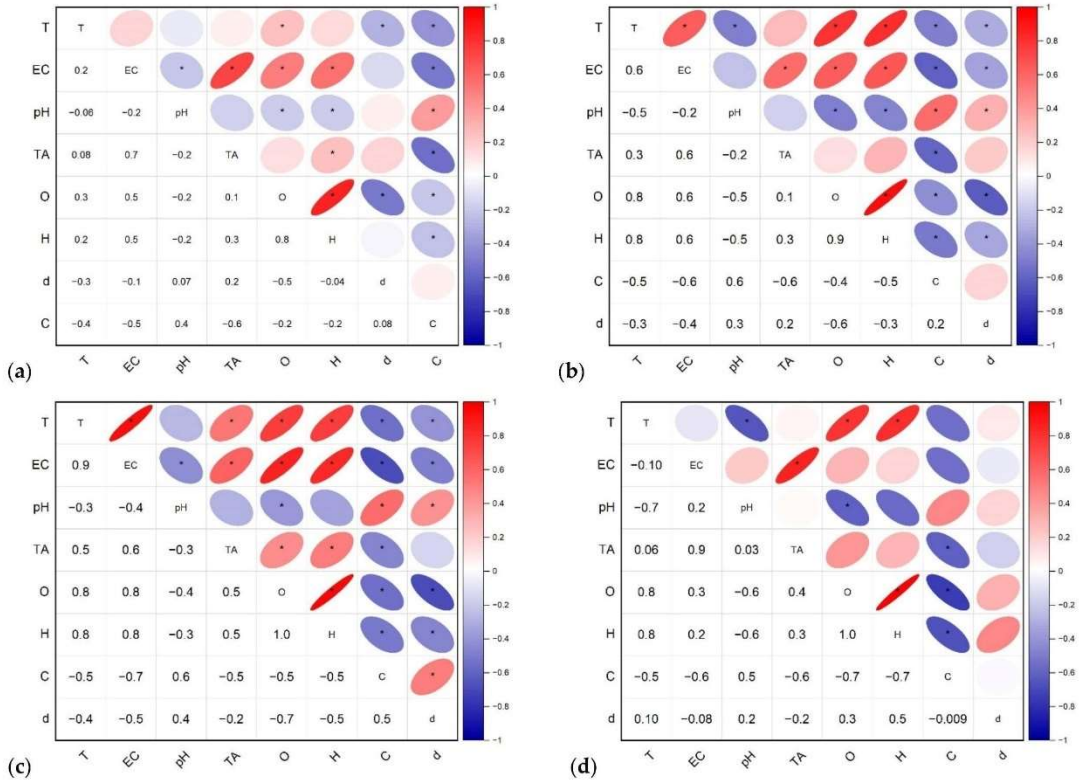


Figure 4. Spearman correlation matrix between determined parameters and (**a**) the whole urban water supply system (N = 104); wells at (**b**) Ljubljansko barje and Ljubljansko polje (N = 41); (**c**) Ljubljansko polje (N = 30); (**d**) Ljubljansko barje (N = 11). * $p \leq 0.05$. H, O and C represent δ^2H, δ^{18}O and $\delta^{13}C_{DIC}$, respectively.

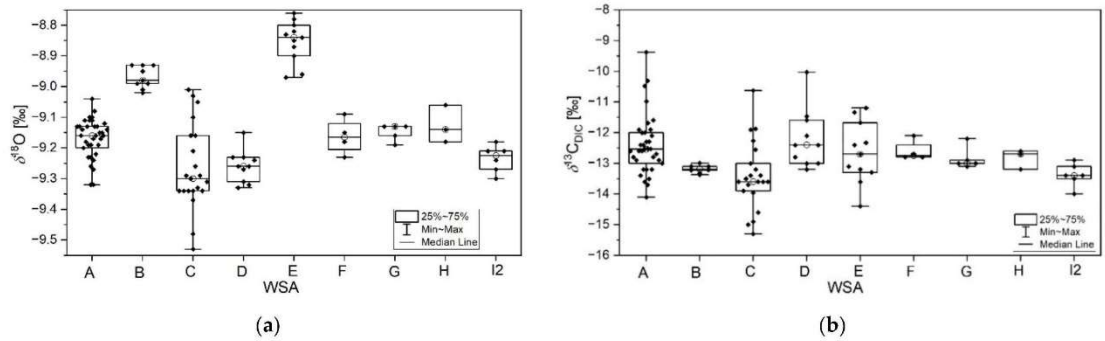
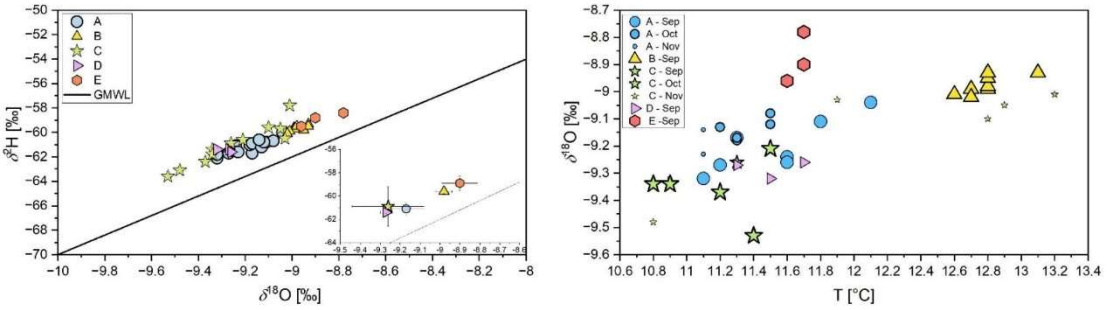


Figure 5. Distribution of (**a**) δ^{18}O and (**b**) $\delta^{13}C_{DIC}$ regarding different WSA for the whole system (N = 97). For the explanation of the abbreviations, see Section 2.2.

3.3.1. Characteristics of the Groundwater from Wells

An objective of this research was to sample all 44 active wells in the WSS from both aquifers. However, water samples were only collected from 41 wells. The isotopic composition ranged from −63.6‰ to −57.8‰, from −9.53‰ to −8.75‰ and from 11.7 to

14.3 for δ^2H, δ^{18}O and *d*, respectively. The groundwater is scattered along the LMWL. The same median d-excess of 12‰ was observed for the LP aquifer and the River Sava at all three locations observed in the investigation [14]. Again, the most positive δ^{18}O value can be observed for the Šentvid wellfield (E), followed by the Hrastje wellfield (B) (Figure 6a); moreover, this can also be observed when the median values of wells regarding WSA are plotted (Figure 6a). The most negative values were observed from the deeper wells in Brest: Brest 2a and Brest 4a (S1) [24], which were observed by [17] and attributed to the recharge from higher altitudes.



(**a**) (**b**)

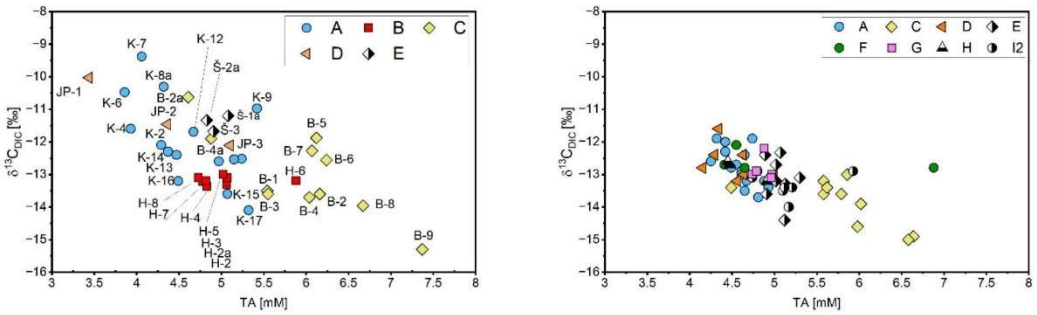
Figure 6. (**a**) Dual isotope plot of wells compared to GMWL. The small picture presents medians of wells regarding the respective wellfield. (**b**) δ^{18}O vs. T for wells from different wellfields. Different sized symbols represent different sampling months. A = Kleče, B = Hrastje, C = Brest, D = Jarški prod and E = Šentvid.

In the Hrastje, Jarški prod and Šentvid wellfields, more positive isotopes values correlate with distance from the River Sava and EC. Conversely, in the Kleče wellfield, no such trend can be observed where in general, δ^{18}O is decreasing from the outer wells to the central part (Kleče-7) (S1). The outermost well, Kleče-12, presents an exception in this trend with a more negative value. The same trend can be observed for EC values, which decrease with distance from the central part of the wellfield. Again, the Kleče-12 stands out with a more negative δ^{18}O value than the other outer wells. This finding is related to water extraction from the deeper parts of the aquifer (60–100 m). In the northern part of the Kleče wellfield, δ^{18}O and EC values decrease with the distance from the River Sava (S1) [24].

When δ^{18}O is plotted against temperature, the highest temperatures were recorded for those wells sampled in September 2018 from the Hrastje wellfield. In addition, high temperatures were also recorded at Brest-1, Brest-2, and Brest-3 in November 2018 (Figure 6b). The reason can be that these wells are shallower (S1). Also, the $\delta^{13}C_{DIC}$ values in groundwater ranged from −15.3‰ to −9.4‰ (Figure 7), specifically, from −14.1‰ to −9.4‰ in the LP and −15.3‰ to −10.6‰ in LB.

The Kleče wellfield is the most important tap water source in the LP and is annually monitored for major cations, anions, organic pollutants, and microbiological parameters. Basic physical and chemical parameters (EC, concentrations of Ca^{2+}, Mg^{2+}, HCO_3^- and pH) indicate that the fundamental properties of groundwater in the area (S1) depend on the location of the well inside the wellfield [46]. Monitoring results [46] also show that the lowest pH and EC values occur in the central part (Kleče-4); the same low value was also observed in the present study, where $\delta^{13}C_{DIC}$ values were −11.6‰ at Kleče-4 (Figure 7a). In the central part of the wellfield, higher $\delta^{13}C_{DIC}$ values are likely due to equilibration with river water. At Kleče-3, higher EC levels and $\delta^{13}C_{DIC}$ values of −12.6‰ (measured in this study) are due to only a few meters of filter section in the saturated zone [46], indicating a higher soil CO_2 contribution. Kleče-12 deviates from other wells and covers aquifers from a depth of 60 to 100 m (S1) with a $\delta^{13}C_{DIC}$ value of −11.7‰. Kleče-17 has a similar recharge

area as Kleče-11 and 10 and has a similar chemical composition [46]. This observation is also reflected in more negative $\delta^{13}C_{DIC}$ values determined in the present study [24]. In the Hrastje well field, the $\delta^{13}C_{DIC}$ values of groundwater are, due to longer residence time of the surface water, more homogeneous in comparison to the Kleče wellfield where the $\delta^{13}C_{DIC}$ values are more scattered (−13.6 to −9.4‰).



(a)-well **(b)-system**

Figure 7. Relation between $\delta^{13}C_{DIC}$ and TA for samples collected from wells (N = 41) (**a**) other components of the WSS system (N = 63) (**b**). A = Kleče, B = Hrastje, C = Brest, D = Jarški prod, E = Šentvid, F = Hrastje/Jarški prod, G = Kleče/Brest, H = Kleče/Hrastje/Jarški prod and I2 = Kleče/Hrastje/Brest.

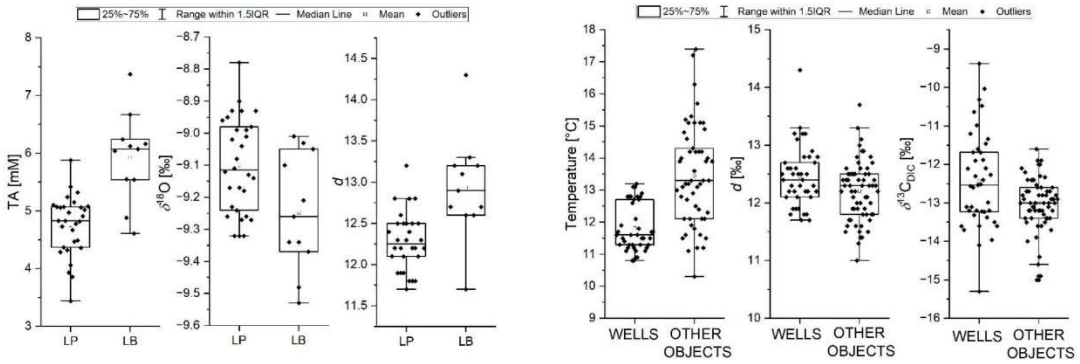
At LB, higher EC and TA (Figure 7a) values were detected in Brest-8 (608.2 µS/cm, 8.33) and Brest-9 (660 µS/cm, 7.22) that capture water from the shallow aquifer. The most positive $\delta^{13}C_{DIC}$ (−10.6‰) was observed at Brest-2a (Figure 7a). Brest-4a captures groundwater from depths of 30.3 to 99.3 m (S1) and represents a much broader area than Brest-2a. As a consequence, Brest-4a had lower pH (7.63) and $\delta^{13}C_{DIC}$ (−11.9‰) values compared to Brest-2a (7.82 and −10.6‰, respectively). Brest-9 had the most negative $\delta^{13}C_{DIC}$ value (−15.3‰), indicating the highest level of soil CO_2. Also, long-term monitoring (2011–2019) revealed that Ca^{2+}, Mg^{2+}, and HCO_3^- were higher in shallower wells than in deeper wells, while the trend was the opposite for pH values. Basic hydro-chemical properties of drinking water in the Holocene aquifer in Brest, especially in shallower wells, are influenced by the Iška River and vary depending on the distance from the river [47]. Therefore, the effect of river water was most apparent in Brest-1 with a $\delta^{13}C_{DIC}$ value of −13.5‰ [48]. Unfortunately, the $\delta^{13}C_{DIC}$ value in the River Iška was not measured.

The Šentvid wellfield has $\delta^{13}C_{DIC}$ values from −11.7 to −11.2‰, while a broader range of values is observed at Jarški prod (−12.1 to −10.0‰). The lowest EC was measured at the Jarški prod WSS. The WSS at Šentvid has higher EC values than the WSS at Kleče since the WSS at Šentvid is positioned outside the main groundwater flow at LP [48]. Higher $\delta^{13}C_{DIC}$ values were also observed at Jarški prod-1, 2 and 3 due to their distance from the river water. A higher $\delta^{13}C_{DIC}$ value (−10.0‰) was also observed at Jarški prod–1 (closer to the River Sava), while at Jarški prod–3, $\delta^{13}C_{DIC}$ values were more negative due mainly to recharge from precipitation being comparable to $\delta^{13}C_{DIC}$ values from wells located at the Šentvid wellfield [48].

The $\delta^{13}C_{DIC}$ values in the River Sava (Table 2) were more positive (−9.2‰ to −7.7‰) than those in wells in LP and LB, suggesting that $\delta^{13}C_{DIC}$ values in groundwater are influenced by water-soil-rock interactions, i.e., degradation of organic matter and carbonate dissolution [49]. At the same time, in river water, equilibration of CO_2 occurs [45].

In the present study, a significant ($r > 0.6$) positive correlation between well parameters was observed between T and EC, $\delta^{18}O$ and $\delta^{2}H$, EC and TA, $\delta^{18}O$ and $\delta^{2}H$, pH and $\delta^{13}C_{DIC}$ and between $\delta^{18}O$ and $\delta^{2}H$. Strong (>−0.7) statistically significant negative correlation was observed between $\delta^{13}C_{DIC}$ and EC and TA and between $\delta^{18}O$ and d, with Spearman's

rank coefficients (rs) ($p \leq 0.005$; Figure 4b). When we compare parameters only for LP and LB aquifers (Figure 4c,d), the correlation results change more for LB. The LB aquifer is presented by a strong significant positive correlation between TA and EC and $\delta^{18}O$ and $\delta^{2}H$. Also, a strong significant negative correlation is observed between pH and T, $\delta^{18}O$ and $\delta^{2}H$, and between $\delta^{13}C_{DIC}$ and $\delta^{18}O$ and $\delta^{2}H$ (Figure 4d). A statistically significant difference is also observed between LP and LB ($p \leq 0.05$) regarding TA, $\delta^{18}O$ and d-excess (Figure 8a).



(**a**) (**b**)

Figure 8. (**a**) Observed statistically significant differences for TA, $\delta^{18}O$, and d-excess between wells presented at Ljubljansko polje (LP; N = 30) and Ljubljansko barje (LB; N = 11). (**b**) Observed statistically significant differences in T, d-excess, and $\delta^{13}C_{DIC}$ between wells (N = 41) and other components in the WSS (N = 63).

Associations were also tested between the wellfields and T, EC, $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C_{DIC}$. Statistically significant differences were observed for T, EC, TA, $\delta^{18}O$, $\delta^{2}H$, d-excess, and $\delta^{13}C_{DIC}$ ($p \leq 0.05$), but not between all locations. The highest median T and EC were observed for wells in Hrastje, while the median TA and *d* were the lowest. The wells in Hrastje, T, pH, TA, and d-excess all showed the smallest range of values. Small ranges in values are also observed for $\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C_{DIC}$ in wells from Hrastje, Jarški prod, and Šentvid. Except for Kleče and Brest, which were collected over three months, all other samples were collected during the same month.

Samples collected in October and November from the wells in Kleče and Brest wells were excluded from the dataset for further evaluation to see if such associations changed. In September 2018, 7, 9, 5, 3, and 3, water samples were collected from wells in Kleče, Hrastje, Brest, Jarški prod, and Šentvid, respectively. In addition to T, EC, TA, $\delta^{18}O$, $\delta^{2}H$, d-excess, and $\delta^{13}C_{DIC}$, there are also significant differences in pH ($p \leq 0.05$). Again, a high range of $\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C_{DIC}$ values were observed in Kleče and Brest, suggesting that the well water from each wellfield is compositionally different. In the Brest wellfield, this is likely a consequence of water extraction at different depths [17]. In addition, the well's position defines the unique properties of the groundwater, which can also be seen using other in-situ parameters (T, EC). Moreover, in the Kleče and Brest wellfields, differences can result from different proportions of the source water in each well [14].

3.3.2. Characteristics of Other Components in the Water Supply System

After the water is pumped from the wells, it is distributed to the end users through the WSS. Other components sampled included joint exits from the water pumping station, reservoirs, water treatment locations, water fountains, and water taps. The observed median temperature was 13.5 °C and is statistically different from the wells (1.7 °C higher; Figure 8b), while the median EC and TA values were lower than the well values, although

the differences were insignificant. In addition, $\delta^{18}O$, $\delta^{2}H$, and d-excess values ranged from −9.34‰ to −8.76‰, from −62.5‰ to −58.1‰, and from 11.0 to 13.7, respectively. The observed ranges are smaller than those in the wells, indicating a more homogenous drinking water composition. The median values were more positive for samples collected at LP than LB in all components. Likewise, the differences between LP and LB are also statistically significant. This comparison did not include samples collected at the water treatment locations since they were sampled only at LB. Also, no statistically significant difference in $\delta^{18}O$ and $\delta^{2}H$ values between other WSS components and wells were observed.

The $\delta^{13}C_{DIC}$ values of other components in the system were between −15.0‰ and −11.6‰ (Figure 7b), a range smaller than that observed in the wells. The only statistically significant differences were found between LB and LP, with more negative $\delta^{13}C_{DIC}$ values recorded at LB due to the influence of organic matter degradation in Brest-9 and other shallow wells in the Brest well field: Brest-1-8 [9]. The samples collected at LB also have high TA values (Figure 8a). The $\delta^{13}C_{DIC}$ from water taps ranged from −14.6 to −11.9‰ (Figure 7b) with an average value of −12.9‰, indicating a more significant contribution from the soil. However, carbonate precipitation within the WSS could have a prominent effect on enrichment with ^{12}C [50]. Water fountains had $\delta^{13}C_{DIC}$ from −13.7 to −12.1‰, with more negative $\delta^{13}C_{DIC}$ vales observed for Brest and more positive values from Kleče. The $\delta^{13}C_{DIC}$ values in the reservoirs ranged from −14.4 to −11.6‰ depending on the water supply well, e.g., the Kleče, Šentvid, and Jarški prod wellfields. Among all wellfields, Brest has the most negative $\delta^{13}C_{DIC}$ (Figure 7a).

In addition to T, a statistically significant difference is observed between wells and other components in the WSS for d-excess and $\delta^{13}C_{DIC}$ (Figure 8b), while no statistically significant differences for the other parameters were observed. A strong significant positive correlation ($\geq$0.7; $p \leq 0.001$) was observed between EC and TA and $\delta^{2}H$ and $\delta^{18}O$, while a strong negative correlation (≥ -0.6; $p \leq 0.001$) was observed between TA and $\delta^{13}C_{DIC}$. A higher temperature range in all components in the system is observed, meaning that the temperature in wells is more stable and not affected by the outside temperature. Moreover, the highest temperature was observed in the Hrastje wellfield but is the most variable in the Brest wellfield [24].

4. Conclusions

This study presents the first stable isotope (H, O, and C) investigation of water in the whole urban WSS in Ljubljana, Slovenia, from source to tap. Sampling was performed mainly by JP VOKA SNAGA d.o.o. staff, JSI team members, and volunteers over three months. The results show changes in meteorological and hydrological conditions that could influence the isotope composition of water collected at different locations across the WSS, from well to tap at the end user. The study is important for consumers and water supply managers.

This investigation combines in-situ (i.e., T and EC), stable isotope (i.e., $\delta^{18}O$, $\delta^{2}H$, and $\delta^{13}C_{DIC}$), and total alkalinity data in order to evaluate whether different components (i.e., water treatment location, reservoirs, water taps, preparation of water, drinking water collector, drinking water fountains) to characterize the urban water cycle. Sampling included a collection of 104 water samples from 103 locations from wells, joint exits from the water pumping station, reservoirs, water treatment locations, drinking water fountains, and taps. Sampling was performed at almost all active wells (41 of 44) included in the WSS for the first time. In addition, sampling was also performed at the Sava River, wastewater treatment plant, and precipitation.

The smallest temperature ranges were observed for wells compared to other components of WSS. This suggests that the system itself is more susceptible to the outside temperature. All other observed parameters show higher variability within the wells than the WSS, which suggests that the water is more unified within the WSS. The $\delta^{18}O$ and $\delta^{2}H$ signatures of precipitation are seasonal, but no such observation could be determined in the WSS due to the limited three-month sampling period. In addition, very little or

no effect of meteorological and hydrological changes can be observed. The results show that the isotope composition at LP depends on the location of the well as the fraction of the precipitation and the River Sava is different. The latter was observed at the Hrastje, Jarški prod, and Šentvid wellfields that show increasing $\delta^{18}O$ values with distance from the River Sava.

Higher alkalinity and more negative $\delta^{13}C_{DIC}$ were observed at the Brest wellfield. Both parameters (TA and $\delta^{13}C_{DIC}$) are negatively correlated. In all investigated wellfields, both processes: degradation of organic matter and dissolution of carbonates, influence to $\delta^{13}C_{DIC}$ value. In addition, precipitation of carbonates within WSS could not be excluded. These phenomena shift the $\delta^{13}C_{DIC}$ values in groundwater to values that are more negative. $\delta^{13}C_{DIC}$ values are a powerful tool for distinguishing between river/groundwater interactions within a WSS and between shallower and deeper wells, including their distance from river water. The interpretation of $\delta^{13}C_{DIC}$ in WSS at LB and LP also depends on other factors such as the depth of filters, pumping rates, and the well's location.

To understand better the possible changes within the system, sampling from source to tap should be performed simultaneously, with samples being collected for additional parameters. Also, additional observations would be advisable due to possible changes in the River Sava (gaining or losing stream) to the LP and the sensitivity of the LP and LB aquifer to climate changes. This preliminary investigation presents a basic understanding of the differences between different groundwater and the WSS and provides baseline information for future investigations.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14132064/s1. Figure S1: The locations of the active wells at Ljubljansko polje and Ljubljansko barje (Atlas okolja (gov.si) and depth of perforated screens in wells (JP VOKA SNAGA d.o.o.).

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Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are openly available in PANGAEA at https://doi.pangaea.de/10.1594/PANGAEA.914586 [24] (accessed on 27 June 2022).

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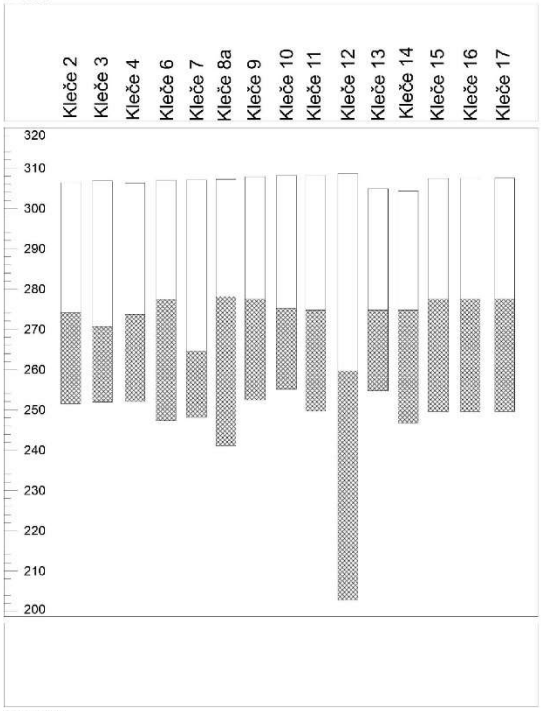
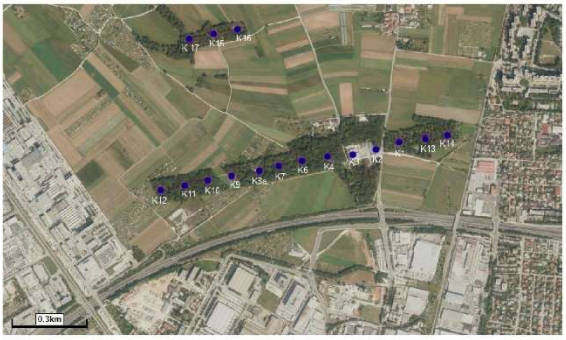
Figures S1 – The locations of the active wells at Ljubljansko polje and Ljubljansko barje (Atlas okolja (gov.si) and depth of perforated screens in wells (JP VOKA SNAGA d.o.o.)

Names of sampled wells:

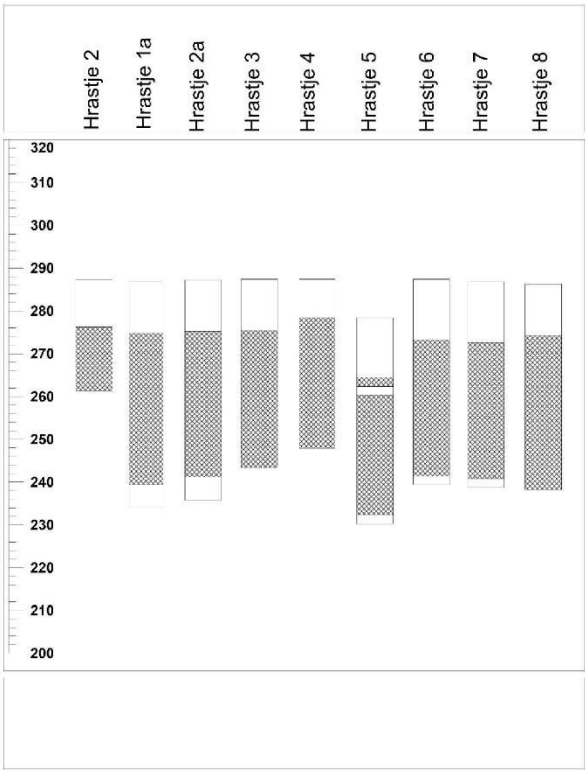
Kleče	Hrastje	Brest	Jarški prod	Šentvid
•VD Kleče-2	•VD Hrastje-1a	•VD Brest-1	•VD Jarški prod-1	• VD Šentvid-1a
•VD Kleče-3	•VD Hrastje-2	•VD Brest-2	•VD Jarški prod-2	• VD Šentvid-2a
•VD Kleče-4	•VD Hrastje-2a	•VD Brest-3	•VD Jarški prod-3	• VD Šentvid-3
•VD Kleče-6	•VD Hrastje-3	•VD Brest-4		
•VD Kleče-7	•VD Hrastje-4	•VD Brest-5		
•VD Kleče-8a	•VD Hrastje-5	•VD Brest-6		
•VD Kleče-9	•VD Hrastje-6	•VD Brest-7		
•VD Kleče-11	•VD Hrastje-7	•VD Brest-8		
•VD Kleče-10	•VD Hrastje-8	•VD Brest-9		
•VD Kleče-12		•VD Brest-2a		
•VD Kleče-13		•VD Brest-4a		
•VD Kleče-14				
•VD Kleče-15				
•VD Kleče-16				
•VD Kleče-17				

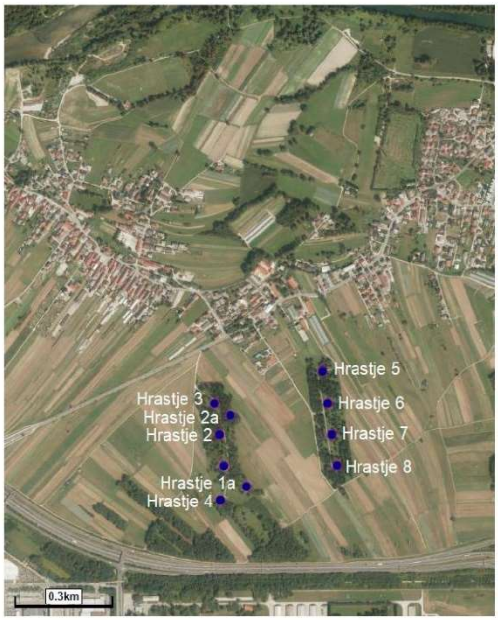
Kleče



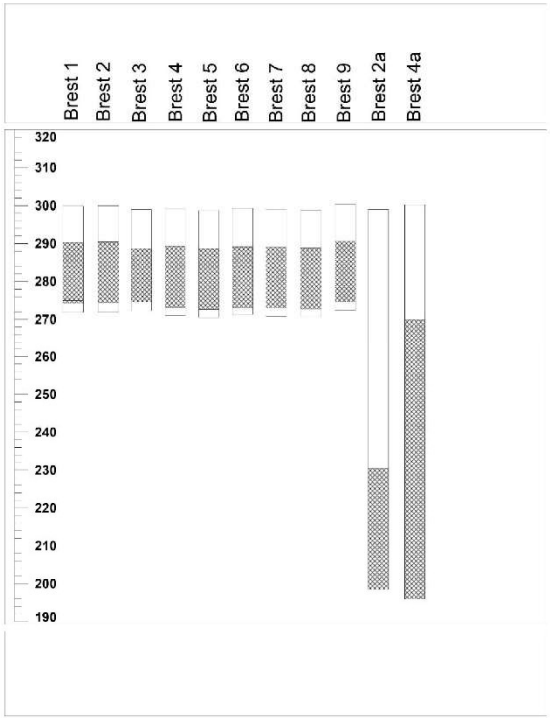


Hrastje

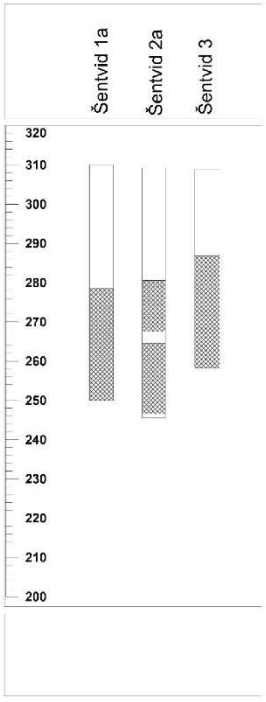


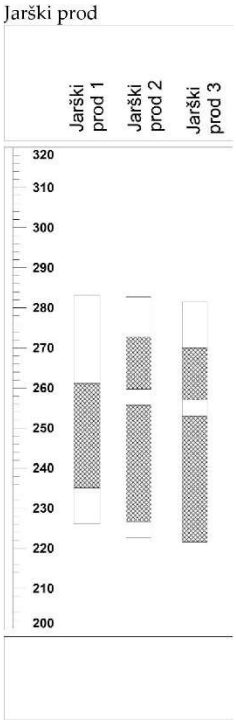


Brest



Šentvid




Jarški prod
Jarški prod 1
Jarški prod 2
Jarški prod 3
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310
300
290
280
270
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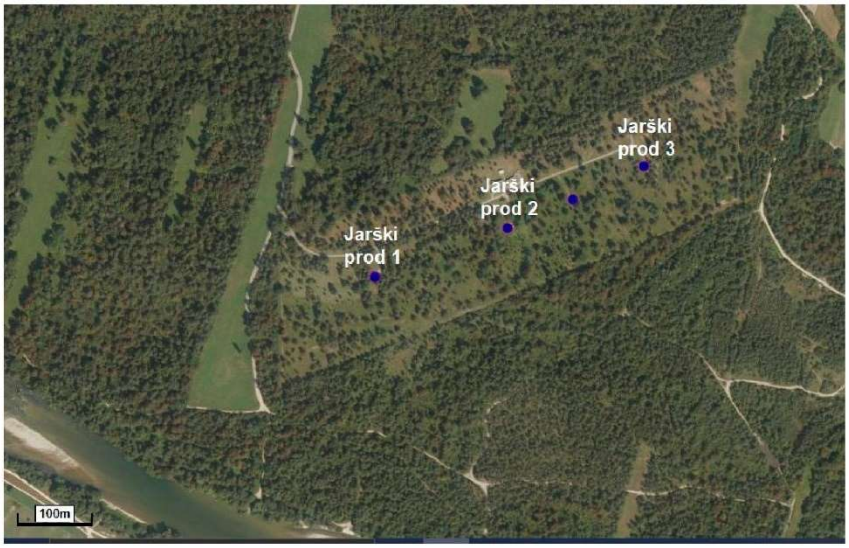
220
210
200


Jarški prod 3
Jarški prod 2
Jarški prod 1
100m

3.3 Manuscript: Unravelling the Sources Contributing to the Urban Water Supply: An Isotope Perspective from Ljubljana, Slovenia

In this section, we present a paper authored by K. Žagar, L. Ortega, B. Jamnik, B. Bračič Železnik and P. Vreča published in the Journal of Hydrology in 2024. The paper addresses the isotopic investigation of the main sources contributing to the drinking water in Ljubljana. Monthly sampling was conducted from precipitation, surface water and groundwater, between 2020 and 2021. Groundwater sampling included all five wellfields (Kleče, Hrastje, Brest, Jarški prod and Šentvid) that supply drinking water to the city. Additionally, two surface water sampling locations at the Sava River and one location and the Iška River were selected, while precipitation was collected at Ljubljana Reaktor.

During the study period, we observed significant temperature changes that aligned with climate projections, along with variations in precipitation patterns that influenced the isotope composition. Surface water characteristics indicated influence from upper catchment recharge, with the Sava River and precipitation monthly variability contributing to groundwater sources in the Ljubljansko polje aquifer. On the other hand, the isotope data suggest precipitation is a major recharge source of shallow wells at the Brest wellfield.

One important finding was also the significantly longer mean residence time of surface water as previously reported, with an estimated duration of three to four years. This extended residence time has implications for understanding the sustainability and replenishment rates of the aquifer. Additionally, the investigations revealed that the contributions of surface water and local precipitation to groundwater have changed over time, indicating a dynamic interaction between these sources and the aquifer system. Understanding these dynamics is essential for sustainable water resource management, especially in urban areas where human activities affect groundwater recharge and water quality.

The results reported in this paper can be used by water managers to improve the understanding of water dynamics in urban areas. In addition, these findings have implications for national strategic planning including water infrastructure construction, such as dams and wellfields. Future urban development and population growth will also place additional pressure on water sources.

The data gathered during this study have been published in an open repository Pangaea. The surface water sampling dataset is titled “Isotopic characterisation of the Sava and Iška River at Ljubljansko polje and Ljubljansko barje, Slovenia, during 2020-2021 sampling campaign” (Žagar et al., 2022b). The groundwater data sampling dataset is titled “Isotopic characterisation of groundwater at Ljubljansko polje and Ljubljansko barje, Slovenia, during 2020-2021 sampling campaign” (Žagar et al., 2022a).

In this paper I contributed to developing the research question, performed monthly surface water sampling, accompanied the technical personnel four times for groundwater sampling in protected wellfields, performed measurements for δ^{2}H and δ^{18}O determination using DI-IRMS, evaluated the data, and prepared the manuscript, including the figures and tables.

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Research papers

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

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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 (δ^2H and δ^{18}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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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 km^2 and 129.3 km^2, 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 Ljubljanica 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 m^3/s and 700 m^3/s (Jamnik et al., 2003), and is strongly interconnected with the groundwater (Bračič Železnik and Jamnik, 2005). The other important river in the Lp aquifer is the Ljubljanica, 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 Ljubljanica 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 Ljubljanica 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 m^3/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 (Bračič Železnik et al., 2005; Bračič 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 Permo–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.

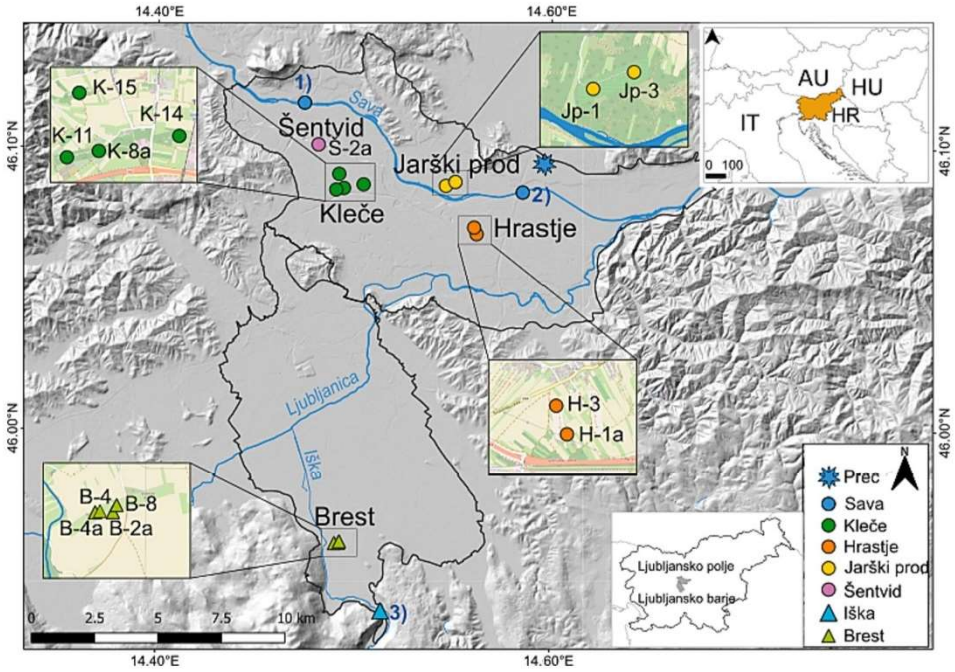

Fig. 1. a) Location of Slovenia in Europe; b) Sampling area in Slovenia with Ljubljansko polje and Ljubljansko barje aquifer; c) Sampling locations of precipitation (Prec), surface water at two rivers (Sava at Brod (1) and Šentjakob (2) and Iška River at Iška vas (3)) and sampling wells in Kleče (K), Brest (B), Hrastje (H), Jarški prod (Jp) and Šentvid (Š) 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 (Šram, 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 3–7 x 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 m^3/day, 7139 m^3/day, 4385 m^3/day and 7047 m^3/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 x 10^{-3} m/s and 2 x 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 m^3/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 ($\delta^{18}O$ and $\delta^{2}H$) 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 $\delta^{2}H$ and $\delta^{18}O$ 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 Burkle TM angular beaker attached to a BurkleTM telescopic rod (Bürkle 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 µS/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 Šentvid 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 ($\delta^{18}O$ and $\delta^{2}H$) were determined on all 328 water samples using the H_2-H_2O (Coplen et al., 1991) and CO_2-H_2O (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 H_2-H_2O and CO_2-H_2O 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 $\delta^{2}H$ and 0.04 ‰ for $\delta^{18}O$. 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 $\delta^{2}H$ and 0.02 ‰ for $\delta^{18}O$. The deuterium excess (d-excess) was calculated as d-excess [‰] = $\delta^{2}H - 8 \times \delta^{18}O$ (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 Šentvid 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 $\varepsilon \leq 5$ %.

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): $\delta^{2}H = 8 \times \delta^{18}O + 10$ (Craig, 1961).

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

$$\delta_{GW}(t) = p\delta_R(t) + (1-p)\delta_P(t) \quad (1)$$

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:

$$p = (\overline{\delta}_{GW} - \overline{\delta}_P)/(\overline{\delta}_R - \overline{\delta}_P) \quad (2)$$

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).

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

Mean residence time – Seasonal trends in $\delta^{18}O$ 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 $\delta^{18}O$ variations in precipitation and surface water and is defined as:

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

where $\delta^{18}O$ is modelled $\delta^{18}O$ (‰), X is the weighted mean annual amplitude, c is the radial frequency f 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:

$$T = c^{-1}[(Az_2/Az_1)^{-2} - 1]^{0.5} \quad (5)$$

where Az_1 is the amplitude of precipitation $\delta^{18}O$ (‰), Az_2 is the amplitude of the surface water $\delta^{18}O$ (‰), and c is the radial frequency of annual fluctuations as defined in the Eq (4).

3. Results

The hydrochemical and isotopic ($\delta^{2}H$ and $\delta^{18}O$) 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 $\delta^{2}H$–$\delta^{18}O$. Mean air temperature (°C), amount of precipitation (mm), and mean isotope composition of $\delta^{18}O$ (‰) and $\delta^{2}H$ (‰) 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 $\delta^{18}O$ (‰) and $\delta^{2}H$ (‰) 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 $\delta^{18}O$ (‰)	Mean weighted $\delta^{2}H$ (‰)
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 $\delta^{18}O$ and $\delta^{2}H$ 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 $\delta^{18}O$ and $\delta^{2}H$ 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, $\delta^{2}H$ and $\delta^{18}O$ 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 $\delta^{2}H = (7.23\pm0.16)\ \delta^{18}O + (5.06\pm1.44)$ $R^2 = 0.99$, 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 m^3/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 m^3/s. The discharge then decreased to 293.2 m^3/s in autumn 2021. The discharge showed no seasonal variation, with daily means ranging from 31.6 to 385.7 m^3/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 m^3/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 225 to 372 $\mu S/cm^{-1}$, 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 $\delta^{2}H$ and $\delta^{18}O$ in precipitation, the monthly surface water isotope patterns were significantly dampened with no pronounced seasonality and with an overall variability of 3.2 ‰ for $\delta^{2}H$ and 0.61 ‰ for $\delta^{18}O$ during the 2−year sampling period (Fig. 2). The lowest $\delta^{18}O$ occurred in June 2021, with a value of −9.62 ‰. The mean seasonal signal for $\delta^{18}O$ 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 m^3/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 graduate decrease in autumn 2021 (Fig. 2). The EC was higher than in the Sava River, ranging from 358 to 423 $\mu s/cm^{-1}$. 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 $\delta^{18}O$ −9.15 ‰ and −59.9 ‰ for $\delta^{2}H$. 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.

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 $\delta^{18}O$ (‰), $\delta^{2}H$ (‰) 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)	$\delta^{18}O$ (‰)				$\delta^{2}H$ (‰)				d − excess (‰)
								Mean	SD	Min	Max	Mean	SD	Min	Max	Mean
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
Šentvid 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

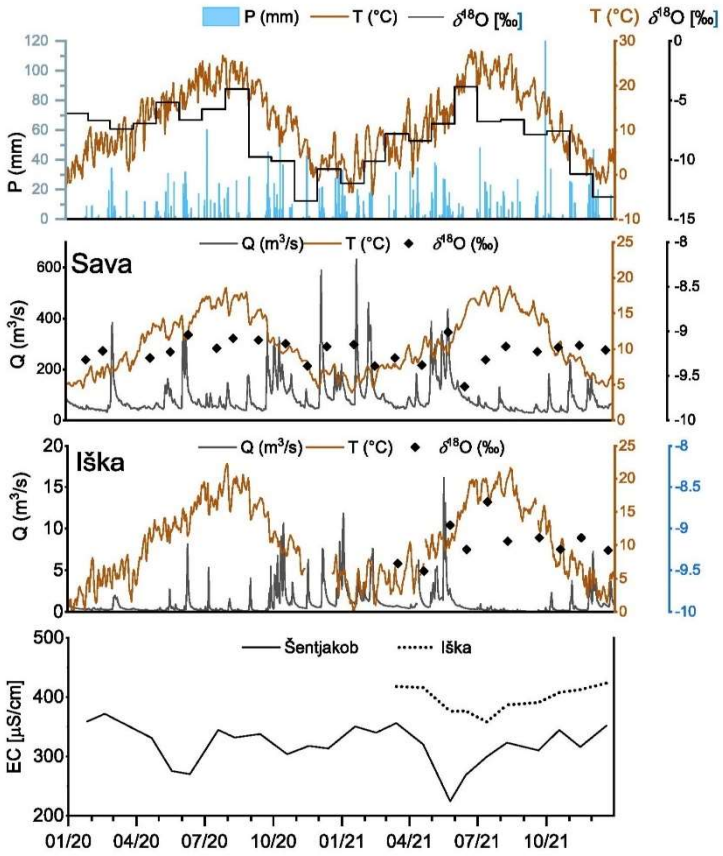

Fig. 2. Time series of the daily amount of precipitation, air temperature, surface water discharge (ARSO, 2021) and surface water temperature for the Sava and Iška River, $\delta^{18}O$ in precipitation and surface water and electrical conductivity in the Sava and Iška River over the 2-year study period. 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{2}H$ and $\delta^{18}O$ 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 $\delta^{18}O$ 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 ‰

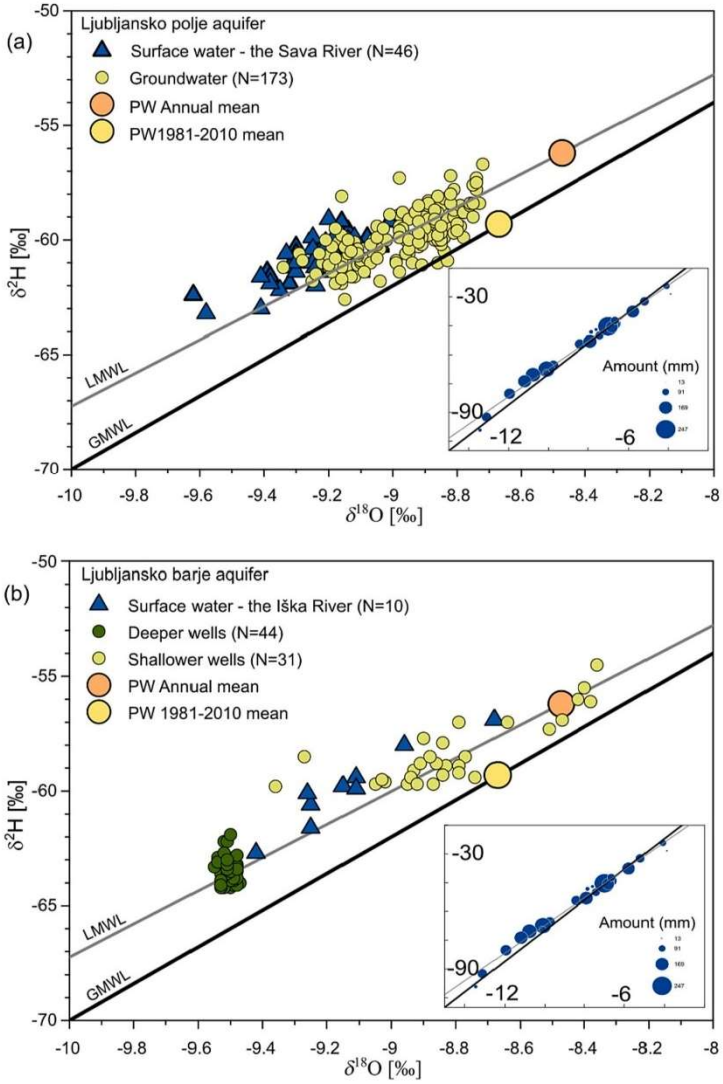

Fig. 3. Dual isotope plot showing the isotope composition of i) precipitation (blue circular dots), precipitation weighted (PW) mean for the period 1981–2010 (yellow circle) and 2020–2021 (orange circle), ii) surface water and iii) groundwater regarding the seasons for a) Lp aquifer and b) Lb aquifer (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-HCO_3 facies and the Lb aquifer as a Ca−Mg−HCO_3 facies. The Lp aquifer has higher SO_4^{2-}, 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 NO_3^- values compared to other Lp aquifer wells. Likewise, higher NO_3^-, EC values and Cl- concentration are notable at K-11 and K-14 compared to other wells in the Kleče wellfield. Higher NO_3 content can be attributed to fertilisers used in the area, while the concentration of Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, EC and NO_3^- 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 SO_4^{2-} levels. However, higher NO_3^- 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 Ca^{2+} and Mg^{2+}

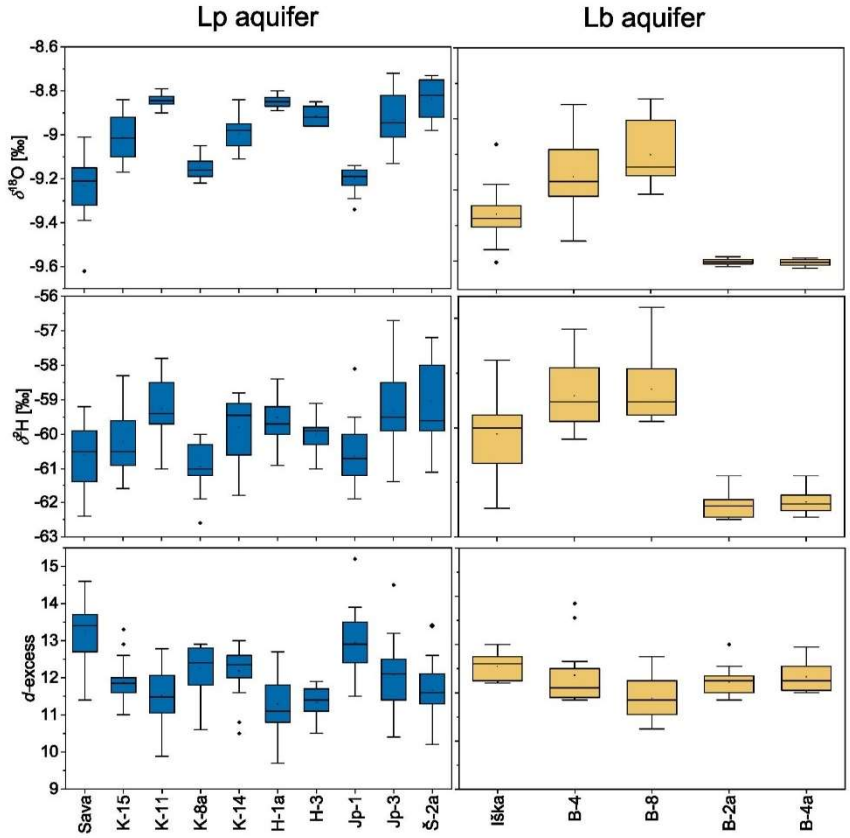

Fig. 4. Boxplots comparing the isotopic composition of surface water and groundwater at the Lp aquifer (left) and Lb aquifer (right) during 2020–2021 monthly sampling. For abbreviations, see Table 2.

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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ and $\delta^{2}H$ 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 $LMWL_{PWRMA}$ $\delta^2H = (7.23\pm0.16)\ \delta^{18}O + (5.06\pm1.44)$ for the study periods deviates from the long-term $LMWL_{PWRMA}$ $\delta^2H = (8.09\pm0.07)\ \delta^{18}O + (10.62\pm0.6)$ 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

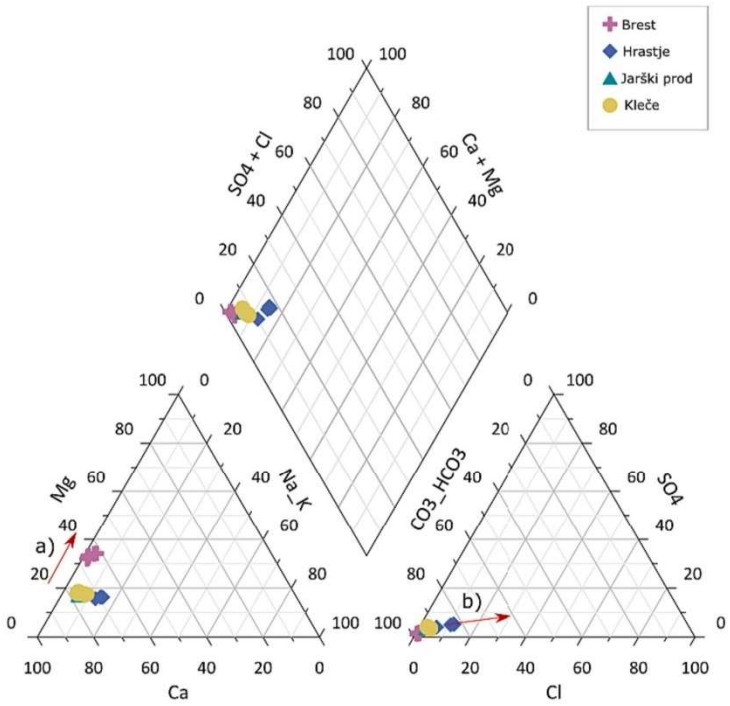

Fig. 5. Piper diagram of samples that represent different hydrogeological units. The letters refer to the main processes inducing: (a) dissolution of limestones (Ca > 50 %) or dolostones (Ca = Mg > 50 % and Mg > 50 %) and (b) ionic exchange.

reflected in the fluctuations of the d-excess, i.e., form 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 $\delta^{18}O$ of precipitation and those observed in the Sava River, along with the temporal fluctuation in $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ values of surface water oversimplify temporal variations. The estimated amplitudes in $\delta^{18}O$ 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 $\delta^{18}O$ and temperature, water flow and precipitation were also observed, suggesting that other processes are influencing the $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ and $\delta^{2}H$ 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

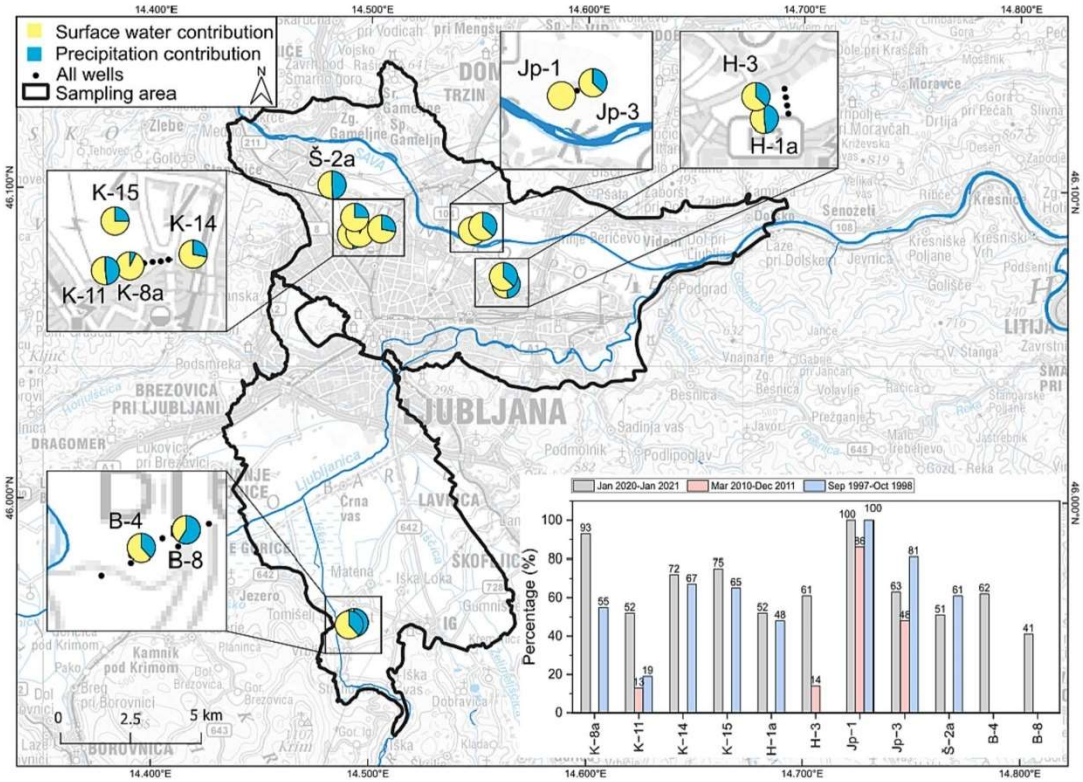

Fig. 6. Spatial distribution of estimated contributions of identified groundwater end-members: precipitation (blue) and surface water (yellow) between 2020 and 2021. On the right side, the inserted graph represents the percentage of surface water contribution to the respective well compared to the investigations (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; Vrzel 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 (Tipple 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 an the link for the reviewers is provided in Cover letter..

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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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Table 1. Hydrochemical data of the groundwater samples studied in the Ljubljansko polje and Ljubljansko barje aquifer.

Name	Date	Sampling depth	EC field (mS/cm)	pH lab	T field (°C)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	Cl^{-} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^{-} (mg/L)	NO_3^{-} (mg/L)	Br^{-} (mg/L)
VD Brest-1	1.04.2021	9.65-25.65	381	7.5	9.4	50	27	1.6	0.97	3.22	4.54	276	4.92	0.026
VD Brest-2a	23.06.2020	68.5-100.50	396	7.6	11.5	53	27	0.86	0.48	1.94	3.92	280	8.86	LOQ=0.008
VD Brest-2a	11.11.2020	68.5-100.50	390	7.7	11.2	52	26	0.71	0.46	1.86	3.82	284	8.28	0.011
VD Brest-2a	9.03.2021	68.5-100.50				53	27	0.81	0.43	1.82	3.74	276		
VD Brest-2a	1.04.2021	68.5-100.50	386	7.6	11.4	52	26	0.85	0.43	1.68	3.62	284	6.64	0.03
VD Brest-2a	12.04.2021	68.5-100.50				52	26	0.83	0.43	1.79	3.71	282		
VD Brest-3	23.06.2020	10.35-24.35	415	7.4	10.4	53	29	1.3	1.5	2.79	5.79	293	7	LOQ=0.008
VD Brest-3	11.11.2020	10.35-24.35	508	7.3	12.8	65	36	2.2	1.8	3.66	5.94	362	12.9	0.019
VD Brest-3	1.04.2021	10.35-24.35	384	7.5	10.4	49	27	1.7	1.4	3.34	4.38	275	5.27	0.024
VD Brest-4a	23.06.2020	30.30-100.5	382	7.6	11.4	51	25	0.83	0.49	1.81	3.96	271	6.73	LOQ=0.008
VD Brest-4a	11.11.2020	30.30-100.5	384	7.6	11.1	52	25	0.78	0.51	1.86	3.93	278	6.91	0.013
VD Brest-4a	9.03.2021	30.30-100.5				51	25	0.83	0.49	1.86	3.81	273		
VD Brest-4a	1.04.2021	30.30-100.5	376	7.6	11.1	51	25	0.84	0.52	1.83	3.82	264	6.38	0.032
VD Brest-4a	12.04.2021	30.30-100.5				51	25	0.83	0.48	1.79	3.79	276		
VD Brest-8	25.11.2020	9.95-25.95				78	38							
VD Brest-8	24.11.2021	9.95-25.95				68	34							
VD Hrastje-1a	15.06.2020	12-47.4	564	7.4	13.4	84	20	16	1.3	36.9	17.6	294	18.3	0.032
VD Hrastje-1a	5.11.2020	12-47.4	565	7.4	13.2	85	20	16	1.4	40.2	18.9	292	21.2	0.033
VD Hrastje-1a	24.03.2021	12-47.4	560	7.4	13.1	84	20	17	1.4	41.4	18.5	295	20.6	0.055
VD Hrastje-3	15.06.2020	12-44	519	7.4	12.9	82	18	13	1.6	20.6	13.9	305	17.7	0.014
VD JP-1	15.06.2020	22-48	333	7.7	11.4	55	12	3.6	0.74	5.8	10.8	216	5.8	LOQ=0.008
VD JP-1	19.10.2020	22-48				56	13							
VD JP-1	24.03.2021	22-48	340	7.7	10.9	57	13	3.6	0.71	5.66	11.5	224	5.8	0.017
VD JP-3	24.02.2020	11.5-24.5 & 28.5-59.9				43	20							
VD JP-3	15.06.2020	11.5-24.5 & 28.5-59.9	454	7.6	11.8	76	18	5	0.93	7.74	10.7	300	7.71	0.01
VD JP-3	19.10.2020	11.5-24.5 & 28.5-59.9				81	19							
VD JP-3	5.11.2020	11.5-24.5 & 28.5-59.9	495	7.5	11.4	84	19	5.8	1.1	9.52	11.9	326	11	0.019
VD JP-3	24.03.2021	11.5-24.5 & 28.5-59.9	478	7.5	11.2	81	19	5.5	0.991	10.2	11.8	313	10.9	0.039
VD Kleče-11	9.06.2020	33.2-58.2	520	7.4	11.8	84	20	8.8	1.3	14.5	11.6	314	21	0.013
VD Kleče-11	3.11.2020	33.2-58.2	516	7.4	11.7	85	20	8.3	1.3	14.3	12.7	317	22.1	0.022
VD Kleče-11	22.03.2021	33.2-58.2	518	7.4	11.5	85	20	8.2	1.3	13.6	12.6	324	23.1	0.019
VD Kleče-14	3.11.2020	29.4-57.4	414	7.5	11.5	68	16	4.9	1.5	8.59	10.9	264	12.5	0.011
VD Kleče-15	31.03.2021	28.9-56.9				77	17							
VD Kleče-8a	9.06.2020	29.3-66.3	392	7.6	11.3	65	15	3.8	0.67	7.73	10.9	252	9.03	0.008
VD Kleče-8a	3.11.2020	29.3-66.3	395	7.6	11.3	65	16	3.8	0.74	7.42	11.2	257	9.7	0.012
VD Kleče-8a	22.03.2021	29.3-66.3	375	7.6	10.8	63	15	3.5	0.63	6.79	11.4	240	7.84	0.012
VD Šentvid-2a	26.02.2020	28.6-41.6 &44.6-62.6				80	18							
VD Šentvid-2a	12.10.2020	28.6-41.6 &44.6-62.6				77	17							
VD Šentvid-2a	4.02.2021	28.6-41.6 &44.6-62.6				84	19							

3.4 Manuscript: Hydrogen and Oxygen Isotopes in Tap Water: Insights into Urban Water Supply Structure and Management

This section represents an important research, currently under review in Science of The Total Environment. The paper is authored by K. Žagar, L. Ortega, J. van Rooyen and P. Vreča.

This study investigates the spatiotemporal isotopic composition of tap water in Ljubljana, using a citizen science approach to enhance urban water management strategies. The primary aims were to test the feasibility of the sampling protocol, characterize isotopic variations in tap water, and explore the boundaries of water sources within the city. $\delta^{2}H$ and $\delta^{18}O$ values serve as tracers, revealing distinct water supply areas and reflecting varied water management practices. Through the involvement of 145 participants, 273 samples were collected across three different seasons (spring, autumn and winter). The isotopic analysis showed coherent patterns that indicate low residence times and rapid water movement through the system. Significant differences in isotopic compositions were observed between water supply areas and seasons, suggesting that water source mixing and management practices influence tap water isotopic signatures.

Comparisons with previous studies showed an increase in isotopic values over time, which may correlate with climate trends, change in the recharge dynamics and water management changes. The research confirms that isotope data can provide insights into water supply boundaries and the dynamics of urban water systems, which are not fixed and can change based on demand and system conditions.

This study contributes valuable data on urban water supply dynamics and demonstrates the effectiveness of a citizen science approach for extensive and efficient data collection. The results advocate for longer-term monitoring of tap water isotopic composition to better understand and manage the impacts of climate change and human activities on water resources, ultimately aiding in sustainable urban water management practices.

In this paper I contributed to finding the participants, preparing all sampling materials and paperwork, gathering samples, evaluating the data, performing measurements for $\delta^{2}H$ and $\delta^{18}O$ determination using DI-IRMS, preparing the manuscript, including the figures and tables.

Hydrogen and Oxygen Isotopes in Tap Water: Insights into Urban Water Supply Structure and Management

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Abstract

Sustainable water supply strategies require a clear understanding of the links between water consumers and sources, particularly in regions vulnerable to climate change. In Ljubljana, Slovenia, where the water supply system is heavily dependent on groundwater, climate change is causing shifts in temperature and precipitation patterns. This study uses stable isotope ratios of hydrogen and oxygen (δ^2H and $\delta^{18}O$) in tap water to investigate these connections. The primary objective was to characterized isotopic variations in Ljubljana's tap water during three different seasons, and investigate water source boundaries, using a citizen science approach. The results demonstrated that isotopic analysis effectively distinguishes between water sources, offering valuable insights into Ljubljana's adaptable water supply system. The study revealed distinct water supply areas (WSAs) with coherent spatiotemporal patterns, reflecting variations in sources and water management practices influenced by demand and system pressure. Altogether, the research demonstrates a straightforward method that provide a substantial number of samples and effectively indicates water management strategies and climate impacts within urban water systems.

Key words: urban hydrology, tap water, hydrogen, oxygen, isotopes, sustainability

1. INTRODUCTION

In an era marked by escalating global challenges, effective urban water management has become increasingly urgent. The sufficiency and safety of domestic water supplies present a significant challenge due to climate change, rapid urbanization, population growth, and land use changes (Esquivel-Hernández et al., 2018; Pelling et al., 2022). Issues such as pipe leakage, high rates of unaccounted water loss in distribution networks, inadequate sewage system and wastewater treatment facilities further impact the problem (Hoekstra et al., 2018; Krueger et al., 2019). As a result, urban water scarcity is expected to increase significantly. This creates a critical need for innovative solutions and further research, such as the application of water isotopes, to address these challenges.

Stable isotope ratios of hydrogen and oxygen (δ^2H and $\delta^{18}O$), are important tracer in many fields of hydrology. They can provide information to water managers about the sources and interactions between water bodies as well as vulnerabilities to environmental change (Bhuiyan et al., 2023; Bowen et al., 2019, 2007; Jasechko, 2019). Studies on the isotope characteristics of tap water and its relationship with the precipitation have been conducted on a national scale e.g. in the United States, China, and South Africa (Landwehr et al., 2014; Wang et al., 2018; Zhao et al., 2017). However, these studies are based on relatively sparse sampling sites. The findings suggest that higher resolution is needed to determine city-wide water isotopic ranges, and to offer valuable insights to water managers regarding water sources, mixing dynamics, residence times, and aquifer interconnectivity (Ueda and Bell, 2016). Consequently, efforts are now being directed towards investigating tap water on regional al local scales (Du et al., 2019b; Shakya et al., 2022; Tipple et al., 2017).

Stable isotopes in tap water were reported in many studies. It was observed that isotopes ratios in tap water are influenced by natural processes and human activities, and on annual basis correlate with local precipitation (Wang et al., 2018). Contrary, the seasonal and monthly variations in tap water depend on water sources, with surface water showing more variability, while groundwater less (Du et al., 2019a; Wang et al., 2018). Tap water isotopes also provided information of local water management responses to drought (Tipple et al., 2017), and while isotopic analysis may not directly reveal water quality information, it offers valuable insights to water managers regarding water sources, mixing dynamics, residence times, and aquifer interconnectivity, enhancing overall system understanding.

Characterization of spatial and temporal patterns of water supply is important, especially in regions vulnerable to climate change. In Ljubljana, high susceptibility to climate variations is due to its positioned in an area influenced by three different climates; sub-Mediterranean, Alpine and Continental climate type. Observations indicate a trend towards warmer climates with more pronounced dry winters and summers (Bertalanič et al., 2019; Dolinar, 2018). As climate change progresses, there will be an additional impact of water resources in Ljubljana, where the water supply system relies heavily on the groundwater sources (Nagode et al., 2020). During the 2020-2021 characterization of spatiotemporal patterns of water sources it was observed, that a shift in groundwater source distribution, compared to previous investigations (Urbanc and Jamnik, 2002; Vrzel et al., 2018).

For this study, tap water samples were collected during three samplings representing spring, autumn and winter seasons in Ljubljana. This study uses the hydrogen and oxygen stable isotopes (δ^2H and $\delta^{18}O$) to analyse the spatiotemporal isotopic composition of tap water aiming to test the feasibility of the proposed protocol and implementation of city science in tap water

70 investigation, characterize variations in isotopic composition, and investigate water source
71 boundaries. This research promises to provide new insights into urban water management and
72 advance our understanding of water resource dynamics in complex urban environments.

73 **2. WATER SUPPLY CONTEXT**

74 Tap water sampling was performed in the Ljubljana basin, Slovenia (Figure 1), where the
75 capital, Ljubljana is located. The basin is divided into the Ljubljansko polje aquifer in the north
76 and the Ljubljansko barje aquifer in the south (Nagode et al., 2020), covering an area of
77 approximately 109 km^2 and 129 km^2 (ARSO, 2004). The current population exceeds 300.000
78 and is expected to grow.

79 The Ljubljansko polje tectonic depression, formed in the early Pleistocene, consists of Permian
80 and Carboniferous slate claystone and sandstone. During the Pleistocene and Holocene, the
81 Sava River filled this depression with silty-sandy gravels and sandy gravel with lenses of
82 conglomerate (Žlebnik, 1971). The fluvial sediment thickness varies, exceeding 100 meters in
83 the center (Bračič Železnik et al., 2005). The unconfined aquifer, with an intergranular porosity,
84 has a groundwater table fluctuating 20-25 meters below the surface. Significant watercourses
85 include the Sava and Ljubljanica Rivers, with the Sava River providing substantial recharge to
86 the aquifer (Jamnik et al., 2000; Nagode et al., 2020; Vrzel et al., 2018). Contrary, Ljubljansko
87 barje is filled with diverse sediments from the Pleistocene and Holocene periods. The area's
88 geology includes Upper Triassic dolomite and Jurassic limestone in the south, west, and
89 center, and Triassic and Permo-Carboniferous shaly mudstone, quartz sandstone, and
90 conglomerate in the north and east (Mencej, 1988). This complex geology forms a multi-layer
91 aquifer system influenced by the Ljubljanica and Iška Rivers. Based on the groundwater level
92 measurements, four distinct aquifers can be identified: Holocene gravel aquifer with a free
93 groundwater level, upper Pleistocene aquifer with an artesian groundwater level in the central
94 area, lower Pleistocene aquifer with subartesian groundwater level and Karst-fissured
95 carbonate aquifer (Bračič Železnik, 2016). The Ljubljanica river only flows through the
96 Ljubljansko barje aquifer, where one of the most important affluent is the Iška river, that
97 recharges the wellfield positioned on the Ljubljansko barje aquifer (Janža, 2022). Groundwater
98 dynamics are affected by precipitation infiltration and deep percolation from karst formations
99 from the hinterland (Cerar and Urbanc, 2013).

100 The region has a temperate climate with an annual precipitation of 1362 mm and mean
101 temperature of 10.9 °C (1981-2010 period) (Bertalanič et al., 2019). The climate is seasonal,
102 with warm summer and cold winters. During the study period (2019-2021), mean temperature
103 were 12.1 °C and yearly precipitation was 1361 mm, slightly than long-term averages (Table
104 1).

105 Table 1: Annual mean temperature, annual total precipitation and the deviation from the 30-year mean
106 measure in Ljubljana. The annual values are calculated for the individual year (1 January to 31
107 December) (source: ARSO climate data).

Year	Mean Temperature (°C)	Deviation (°C)	Mean Precipitation (mm)	Deviation (mm)
2019	12.5	1.6	1379	17
2020	12.1	1.2	1262	-100
2021	11.5	0.6	1442	80
1981-2010	10.9	n.a.	1362	n.a.

108

109 Public utility VOKA SNAGA d.o.o. (VOKA SNAGA) controls and monitors the distribution of
110 drinking water to Ljubljana and its surroundings. The central drinking water supply system
111 comprises different water supply areas (WSA), each receiving water from a single water supply
112 facility or two or more water supply facilities, depending on the demand and pressure
113 conditions in the system. The transit time of water is not defined in the distribution system,
114 however, on its way from the pumping stations to the users, it is not kept in the network for
115 more than a few hours (JP VOKA SNAGA, 2013).

116 Water is supplied from five main wellfields: Kleče (A), Hrastje (B), Brest (C), Jarški prod (D)
117 and Šentvid (E). With the exception of Hrastje, each wellfield corresponds to a distinct water
118 supply area (Figure 1). In 2019, the central water supply system was divided into nine WSAs:
119 Kleče (A), Hrastje (B), Brest (C), Jarški prod (D), Šentvid (E), Hrastje/Jarški prod (F),
120 Kleče/Brest (G), Kleče/Hrastje/Jarški prod (H), Kleče/Hrastje/Brest (I2). This division was
121 revised in 2020, resulting in the creation of one additional WSA and modifications to the
122 existing areas, changing their sizes. The newly established areas include ten WSAs (Figure
123 1): Kleče (A1), Hrastje (B1), Brest (C1), Jarški prod (D1), Šentvid (E1), Hrastje/Kleče (F1),
124 Kleče/Brest (G1), Kleče/Hrastje (H1), Kleče/Brest/Hrastje (I3) and Kleče/Jarški prod (DA). For
125 information on the source of tap water, residents can use the online application *Where does*
126 *the water comes from* (https://www.vokasnaga.si/od-kod-pritece-voda, *In Slovene*). In 2019,
127 water abstraction from the wells amounted to 30692865 m^3, which was higher than the
128 29595107 m^3 abstracted in 2021, despite an increase in the number of users (Jamnik and
129 Žitnik, 2021; JP VOKA SNAGA, 2013). The decrease in water demand during the second and
130 third sampling campaign can be attributed to the COVID-19 pandemic, which led to the closure
131 of many public buildings in Ljubljana.

132 **3. METHODS**

133 ***3.1. Collection of samples***

134 Three city-wide sampling campaigns were undertaken across Ljubljana water supply system
135 as part of this study. These took place in March 2019, September 2021 and December 2021,
136 corresponding to the spring, autumn and winter seasons, respectively. In total, 92, 90, and 91
137 samples were collected during the first, second and the third sampling campaign, respectively.
138 Two hundred and seventy-three water samples for spatial and temporal characterization were
139 obtained from 145 different participants in Ljubljana, with 37 of the participants contributing in
140 all three sampling campaigns. The majority of samples were collected from taps in private
141 homes with two additional samples per campaign collected from public buildings
142 (Supplementary material).

143 Before the first survey, the sampling protocol (Supplementary 1) was established with the
144 following criteria: a) a target of 100 samples, distributed proportionally based on the population
145 of each specific WSA; b) samples are to be collected between 07:00 and 08:00 AM; c) water
146 must be allowed to flow for at least 210 s before sampling.

147 The population data used for proportional distribution was based on figures from 2017 (Jamnik
148 and Žitnik, 2018) (Table S2). This was the most recent data available at the time the first
149 sampling protocol was defined.

150 Tap water samples were collected through citizen science approach. Each participant was
151 supplied with a returnable envelope containing a letter with the description of the research,
152 consensuses statements, sample sheet (Supplementary 2) and sampling bottle with sampling
153 protocol. In all three campaigns, water was collected in 60 ml HDPE bottles. Some participants
154 left the water running for less or more than 210 s. Upon completion of sampling, the volunteers
155 had to return completed and signed copy of consensuses, sample of tap water and completed
156 sample sheet. Samples were returned in the following days of the sampling and checked for
157 any signs of leakage.

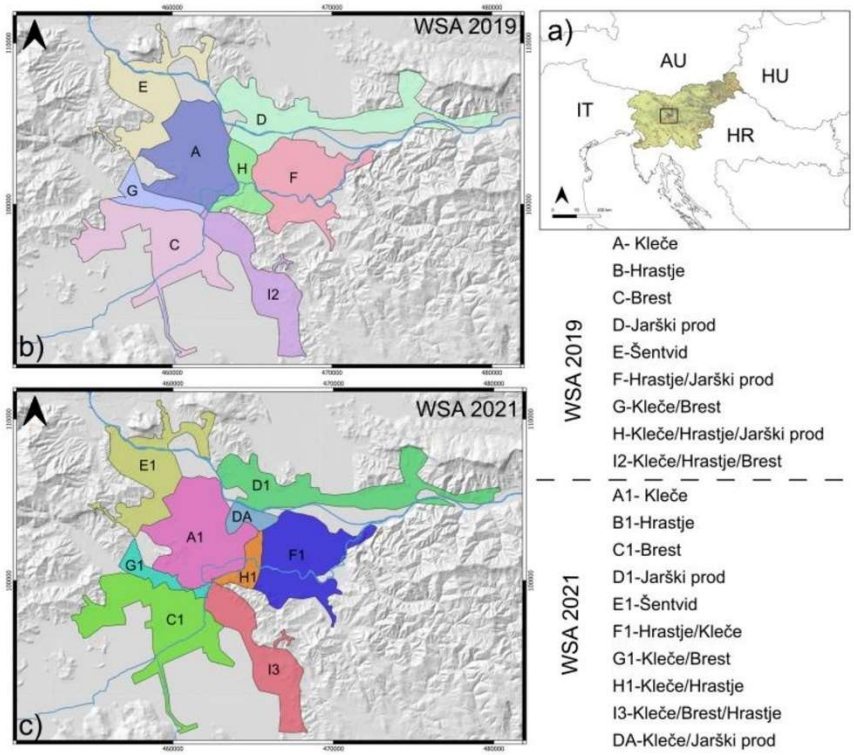


Figure 1: Locations of sampling sites: a) Ljubljana sampling site, b) tap water sampling site with eight water supply areas in 2019; and c) tap water sampling sites with nine water supply areas 2021.

Samples were obtained from all water supply areas in 2019, while due to changes in the water supply areas in 2020, no samples were obtained from Kleče-Jarški prod (DA) WSA in 2021 (Figure 1). Highest number of samples were in all three campaigns collected from Kleče, the biggest WSA in Ljubljana with majority of inhabitants living in this area (Figure 1, Table S2).

During the data evaluation, one sample collected in September 2021 from the Brest WSA (C1) showed more positive values compared to other samples from the same water supply area. Upon closer examination, we found that this sample was located near the adjacent water supply area and exhibited characteristics similar to samples from that area Kleče/Brest (G1). Therefore, we decided to exclude this sample from Brest area in further evaluations.

3.2. Isotope Analysis

Prior to analysis, samples were stored at 5 °C in refrigerator. The H and O isotope ratios of samples were measured within a few weeks of their collection at the Jožef Stefan Institute using a dual inlet isotope ratio mass spectrometer (DI IRMS, Finnigan MAT DELTA plus Finnigan MAT GmbH, Bremen, Germany) with an automated H_2-H_2O and CO_2-H_2O equilibrator HDOeq 48 Equilibration Unit (custom built by M. Jaklitsch). The water vapor trap was cooled to –55 °C. H_2 and CO_2 gases were used as working standards. Samples (3 mL) were allowed to equilibrate for 2 (H_2-H_2O) and 6 (CO_2-H_2O) hours before analysis. All measurements were performed as independent duplicates and together with laboratory reference materials (LRM) calibrated periodically against primary IAEA calibration standards to VSMOW/SLAP scale. Results were normalized to VSMOW/SLAP using Laboratory Information Management System for Light Stable Isotopes (LIMS program) and expressed in the standard δ notation (in ‰). Analysed tap water samples were normalized against two in-house LRMs. For the quality control, two in-house reference materials were used with known $\delta^{18}O$ and $\delta^{2}H$ and commercial reference material (USGS 45 and USGS 47). The maximum uncertainty of in-house LRMs used for normalization of data and independent quality control was calculated by Kragten method (Carter and Barwick, 2011) amounts to 0.04 ‰ for $\delta^{18}O$ and 0.9 ‰ for $\delta^{2}H$. The mean sample repeatability for all measurements was 0.02 ‰ and 0.3 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively. The performance of the method is satisfactory as proven by successful regular testing in worldwide inter-comparisons WICO2016 and WICO2020 (Wassenaar et al., 2021, 2018).

3.3. Data evaluation

Temperature and precipitation data for the period 2019-2021 were obtained from the Slovenian Environment Agency, Ljubljana Bežigrad (ARSO). Additionally, local meteoric water lines (LMWL) for the Ljubljana Reaktor (46.094612, 14.597046) and Kredarica stations (46.378784, 13.848628, 2514 m a.s.l.) were used for further evaluation (Jožef Stefan Institute archive, unpublished data). The Kredarica station is used as the station that represent the upper part of the River Sava recharge area. The LMWLs were calculated for the selected period using precipitation-weighted reduced major axis regression analysis ($LMWL_{PWRMA}$) via a Python script (Pavšek and Vreča, 2022, Vreča et al. 2022). Statistical differences between water supply areas were assessed using the non-parametric Kruskal-Wallis test followed by a Dunn post hoc test with Hochberg-Benjamin adjustment of the p-values for multiple comparisons. The d-excess values were calculated as d-excess = $\delta^{18}O$ - 8*$\delta^{2}H$ (Dansgaard, 1964). For comparison of tap water results, data from 2014 tap water sampling was used (Vreča et al., 2019). To analyse the isotope variability between the source and tap water, we used groundwater data collected from 2020 to 2021 (Žagar et al., 2024, 2022). To generate the

gradient maps, the Jenk's natural breaks method (Jenks and Caspall, 1971) was set to five classes. This method presented an optimal classification as the number of classes can reflect the number of water supply facilities. The maps were generated using QGIS v.3.28.1.

A simple linear mixing model was employed to quantify the relative contribution from deeper and shallower wells within Brest wellfield, based on the groundwater data gathered between 2020-2021 (Žagar et al., 2022). This was achieved by using the $\delta^{18}O$ values from the two end-members as follows:

$$O_T = x_D O_D + x_s O_s$$

$$1 = x_D + x_s$$

In these equations, the subscript T denotes the isotopic composition of the tap water mixture, while, D and S represent isotopic compositions of the water sources from the deeper and shallower wells within and Brest wellfield (Žagar et al., 2024).

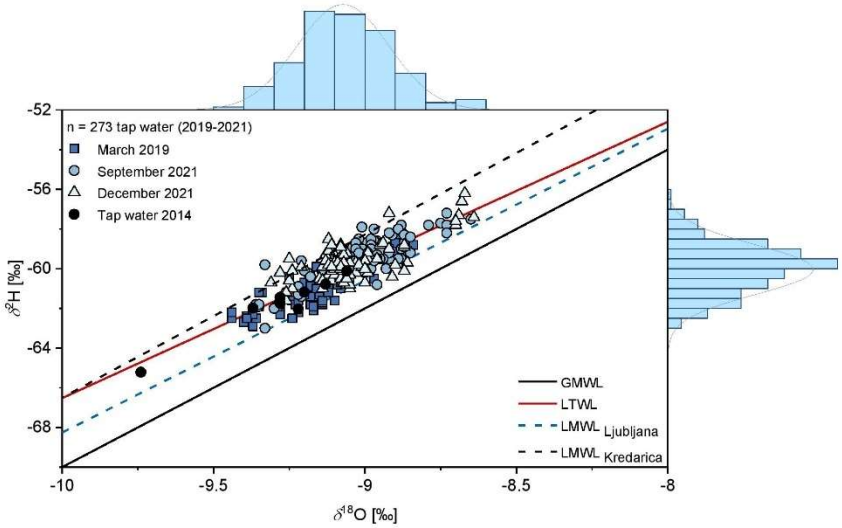
All statistical analyses and visualization of the results were performed using RStudio version 3.6.0 (RStudio Team, 2018) using the stats package (R Core Team, Vienna, Austria, 2019) and OriginPro 2021 software (OriginLab, Northampton, PA, USA).

4. RESULTS

4.1. Isotopic Composition of Tap Water Across Seasons and Water Supply Areas

Based on data from 273 samples obtained across three seasons (Table S1), the δ values span from -63.0 ‰ to -56.2 ‰ and from -9.44 ‰ to -8.64 ‰ for δ^2H and $\delta^{18}O$, respectively (Figure 2). The d-excess, a parameter for the evaporation of waters, ranged from 10.9 ‰ to 14.8 ‰, with average value of 12.5 ‰. The local tap water line (LTWL) in Ljubljana (Figure 3), was calculated based on all (N=273) tap water samples using ordinary lest square regression line: δ^2H= 6.96 x $\delta^{18}O$ + 3.08 (r^2=0.72, p<0.001).

A majority of the tap water data cluster above the global meteoric water line (GMWL, Craig 1961) and the LMWL, as defined by data collected during 2019-2021 period (δ^2H=7.62±0.19x$\delta^{18}O$ + 8.25±1.58, N=36, r^2=0.99, p<0.001). The small subset of samples falls below the LMWL. In addition, majority of samples plot below the Kredarica $LMWL_{PWRMA}$ as defined by data collected during 2019-2021 (δ^2H=8.22±0.27 $\delta^{18}O$ + 15.7±2.8, N=36, r=0.98, p<0.001) (Figure 2). Kredarica LMWL represents the station that is positioned in the upper part of the River Sava recharge area.

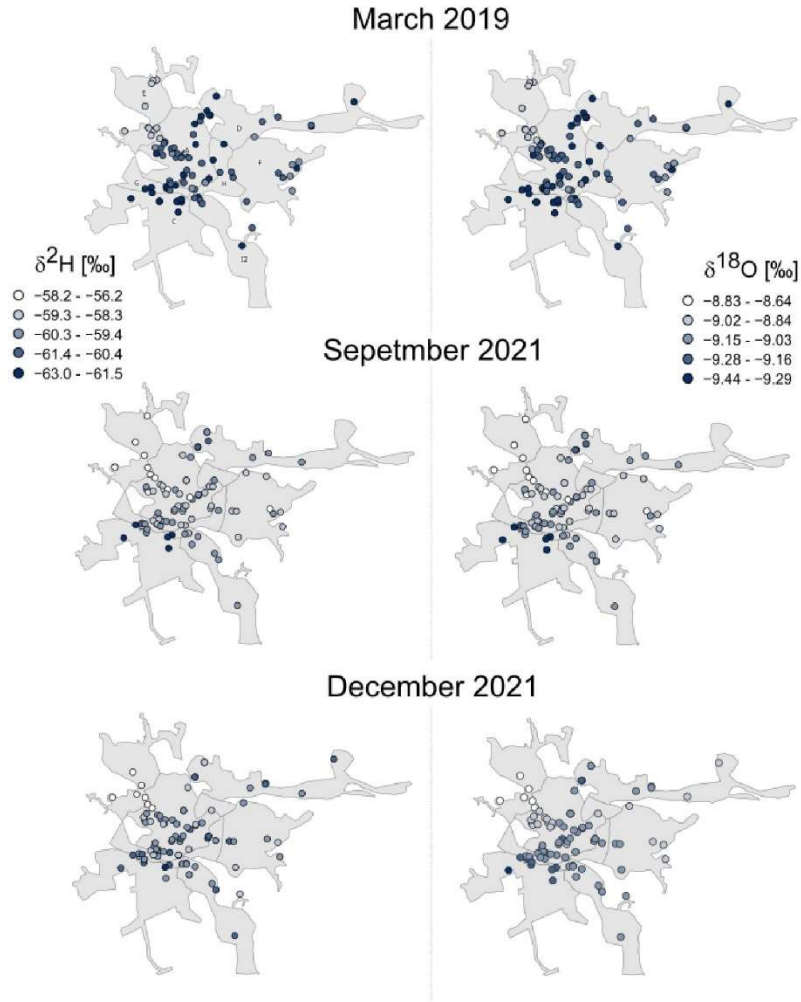


239

240 *Figure 2: Isotopic composition of tap water samples across Ljubljana area during all three*
241 *campaigns. The black line represents global meteoric water line (GMWL), the blue dash line*
242 *represents the local meteoric water line ($LMWL_{PWRMA}$) for Ljubljana in 2019-21 period, the black*
243 *dash line represents the local meteoric water line ($LMWL_{PWRMA}$) for Kredarica in 2019-21 period*
244 *and the red line is the local tap water line (LTWL).*

245 The mean values of δ^2H and $\delta^{18}O$ varied between the different seasons. Overall, we noted a
246 positive trend, with the March samples being the most negative and September and December
247 samples more positive (-61.0 ‰, -59.4 ‰ and -59.7 ‰, and -9.16 ‰, -9.00 ‰ and -9.05 ‰,
248 respectively) (Figure 2).

249 The tap water collected in March 2019 at Brest WSA had the most negative δ^2H and $\delta^{18}O$
250 values, while the most positive values were observed in December 2021 at Šentvid WSA
251 (Figure 3). The tap water in all three-sampling campaign showed small isotope range, with
252 even smaller range between the individual WSA. The overall range was the lowest in March
253 (0.60 ‰ and 4.5 ‰ for $\delta^{18}O$ and δ^2H, respectively) and the highest in September (0.71 ‰ and
254 5.8 ‰ for $\delta^{18}O$ and δ^2H, respectively). The highest isotopic values were consistently observed
255 on the north-western site (Šentvid WSA), while the most negative values were presented on
256 the southern part (Figure 3).



257

258 Figure 3: Observed $\delta^{18}O$ and $\delta^{2}H$ of tap water samples during all three campaigns collected
259 across Ljubljana WSA.

260 ***4.2 Statistical Analysis of Isotopic Variations Among Water Supply Areas***

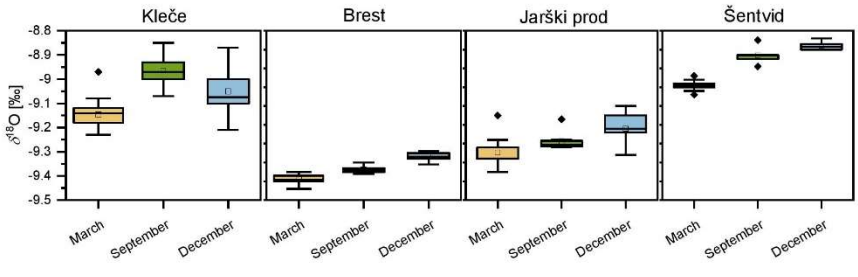
261 To determine if the WSAs and sampling seasons are statistically significant, a comparison was
262 conducted, revealing significant differences, with Šentvid WSA being the most distinct from the
263 others. This evaluation was consistent across all four main WSAs: Kleče, Brest, Jarški prod,

and Šentvid. There was a statistically significant difference ($p<0.01$) for Kleče WSA between all seasons, while for Brest and Jarški prod ($p<0.05$) differences were observed between March and December. For Šentvid, significant differences were found between March and September, as well as between March and December (Figure 4).

We observe the most positive values for Kleče WSA in December, while for the other areas (Brest, Jarški prod and Šentvid) the most positive values were in September. Overall, across all campaigns, the most positive values were consistently observed for the Šentvid WSA, showing significant deviation from the other groups.

Table 2: Mean and standard deviation of $\delta^{18}O$ and $\delta^{2}H$ for each water supply area (WSA) based on three different campaigns. For WSA abbreviations see 2.2.

WSA	n	δ^2H [‰] Mean ± SD	δ^{18}O [‰] Mean ± SD	WSA	n	δ^2H [‰] Mean ± SD	δ^{18}O [‰] Mean ± SD	n	δ^2H [‰] Mean ± SD	δ^{18}O [‰] Mean ± SD
		March 2019				September 2021			December 2021	
A	35	-61.1 ± 0.6	-9.15 ± 0.05	A1	45	-59 ± 0.6	-8.96 ± 0.05	44	-59.8 ± 0.6	-9.05 ± 0.07
B	0	/	/	B1	0	/	/	0	/	/
C	9	-62.5 ± 0.3	-9.39 ± 0.03	C1	7	-61.4 ± 1.2	-9.29 ± 0.13	7	-60.8 ± 0.8	-9.27 ± 0.02
D	9	-61.4 ± 0.6	-9.25 ± 0.09	D1	8	-60.5 ± 0.6	-9.19 ± 0.05	9	-60.1 ± 0.9	-9.12 ± 0.09
E	11	-58.9 ± 0.3	-8.89 ± 0.03	E1	6	-57.7 ± 0.3	-8.73 ± 0.05	6	-57.2 ± 0.6	-8.68 ± 0.02
F	11	-60.7 ± 0.6	-9.13 ± 0.06	F1	9	-59 ± 0.4	-8.95 ± 0.06	7	-59.7 ± 0.7	-8.98 ± 0.11
G	6	-61.6 ± 0.6	-9.2 ± 0.09	G1	7	-59.7 ± 0.6	-8.99 ± 0.02	8	-59.8 ± 0.5	-9.11 ± 0.07
H	5	-61.5 ± 0.7	-9.17 ± 0.03	H1	1	-60.2	-9	1	-60	-9.08
I2	6	-61.4 ± 0.6	-9.24 ± 0.04	I3	7	-9.06 ± 0.06	-59.7 ± 0.6	9	-60 ± 0.6	-9.09 ± 0.03
				DA	0	/	/	0	/	/



277 *Figure 4: $\delta^{18}O$ boxplot of tap water from four main WSA (Kleče, Brest, Jarški prod and Šentvid)*
278 *based on different seasons. The graphs show overlaps between seasons, however the*
279 *statistical evaluation showed that the differences are statistically significant.*

280 **5. DISCUSSION**

281 Data obtained during three surveys in Ljubljana was gathered using a citizen science approach
282 as reported by Landwehr et al. (2014), West et al. (2014), and Zhao et al. (2017). This method
283 allows sampling across a large area within a short period, which would not be feasible
284 otherwise (Warner et al., 2024). In total, 273 samples were collected around the city with the
285 majority gathered during one hour in March 2019, September 2021 and December 2021. While
286 this method allowed us to collect 273 samples in a very short period, the limitations of such
287 approach, including potential variability in sampling consistency should be acknowledged.
288 Nonetheless, the large dataset gathered in March 2019, September and December 2021
289 provided a robust foundation for analysing temporal and spatial isotopic variations. The short
290 sampling period allowed us to investigate temporal and spatial variability more effectively
291 compared to studies that conducted sampling over multiple days (Tipple et al., 2017). Some
292 studies, however, reported collecting majority of samples within one day (Jameel et al., 2016;
293 Landwehr et al., 2014). In our study, the tap water was running for at least 210s, in contrast to
294 other studies where water was running for ~ 5 s (Landwehr et al., 2014; Zhao et al., 2017) or
295 ~ 15 s (Jameel et al., 2016).

296 The isotopic differences in tap water, particularly the variances of 0.80 ‰ and 6.8 ‰ for $\delta^{18}O$
297 and $\delta^{2}H$, reveal seasonal and spatial fluctuations within the city's water supply system (Figure
298 5). While in Ljubljana, precipitation shows a positive isotopic signal during the summer and a
299 negative signal in the winter (Vreča et al., 2014), the pattern in tap water differs. Notably, the
300 most negative isotopic signal in tap water was observed in samples collected during the spring,
301 rather than winter.

302 Moreover, the similarities of isotopic signal between sources and tap water suggest a low
303 residence time for water in the system, indicating that water moves rapidly from source to tap.
304 This rapid movement, coupled with clear mixing of water from different sources, emphasize
305 the efficiency of the water distribution system but also raises questions about its vulnerability
306 to external changes, such as shifts in precipitation patterns or potential contamination events.

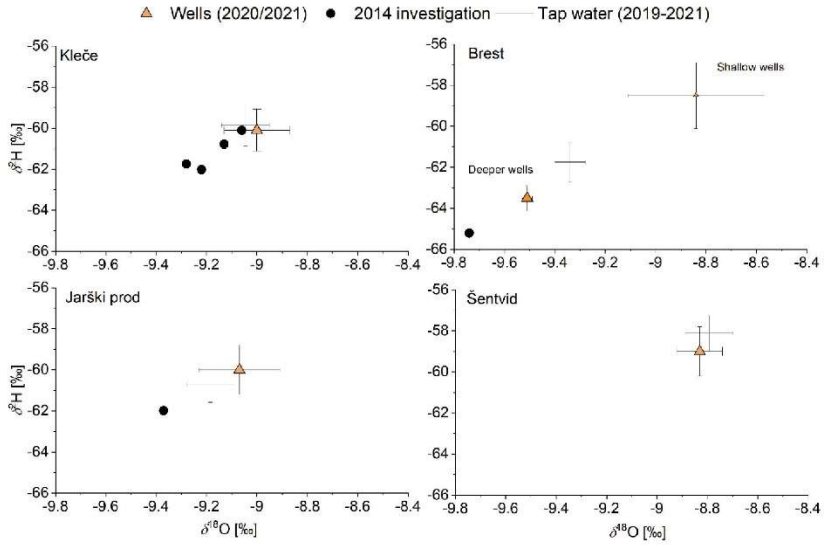
307 A single sampling of tap water was conducted over Slovenia between June 26, 2014, and July
308 15, 2014. In Ljubljana eight samples were collected during this period: four from Kleče WSA,
309 one from Brest and Jarški prod WSA and two from Hrastje/Jarški prod WSA. Our study from
310 2019 to 2021 revealed a noticeable increase in the isotopic values of tap water compared to

311 this data (Vreča et al., 2019). The 2014 samples were collected during an unusual
312 meteorological year characterized by high temperatures and exceptional precipitation (1851
313 mm), which likely influenced the more negative isotopic signals observed in the tap water. An
314 increase in the isotope values of the tap water was also observed in Salt Lake Valley over a
315 five-year period (Ehleringer et al., 2016). This comparison emphasizes the sensitivity of the
316 water supply system to climatic conditions, highlighting the need for continuous monitoring,
317 especially as climate change may lead to more frequent and severe weather anomalies.

318 ***Implications for Groundwater Sustainability***

319 Our study identified differences in isotopic composition between water supply areas in
320 Ljubljana. In the Kleče WSA, the isotopic values of groundwater (Žagar et al., 2024) and tap
321 water were almost identical, indicating efficient mixing and rapid distribution. However, in areas
322 like Jarški prod and Šentvid, we observed more negative or more positive tap water values
323 compared to groundwater, which might be due to isotopic fractionation caused by temperature
324 differences within the water system. This suggests that some parts of the system might be
325 more sensitive to temperature changes, which could affect the quality of the water over time.

326 In the Brest WSA (Figure 5 and 6), where water is drawn from both deep (depths of more than
327 100 m (Nagode et al., 2022)) and shallow wells, our analysis shows that most of the tap water
328 comes from deeper wells – sometimes up to 90%. This heavy reliance on deeper groundwater
329 is concerning because it suggests that the deeper aquifer, which has a longer residence time
330 and is less easily replenished, could be at risk of depletion if current extraction rates continue
331 or increase. As Ljubljana's population grows and water demand rises, this dependency on
332 deep aquifers could pose a significant risk to the city's long-term water security.



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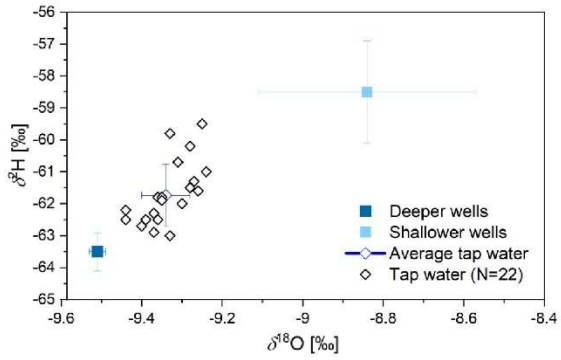
334 Figure 5: Comparison of tap water samples collected during our study (2019-2021) with
335 groundwater wells representative of the respective water supply areas (Žagar et al., 2022) and
336 previous tap water samples collected during 2014 investigation (Vreča et al., 2019) in Kleče,
337 Brest, Jarški prod and Šentvid.



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339 Figure 6: Mixing relation for tap water samples collected at Brest water supply area and mean
340 values for groundwater collected at deeper and shallower wells during 2020-2021 study (Žagar
341 et al., 2024).

342 ***Implications for Future Water Management***

343 In Slovenia, groundwater is a critical resource, providing 97% of the country's domestic water
344 supply. Ljubljana, the capital, relies entirely on groundwater for its drinking water, which
345 currently meets high standards (Žagar et al., 2024). However, this dependence on a single
346 water source makes the city vulnerable to changes brought about by urban development and
347 climate change.

348 Slovenia is experiencing a temperature rise that is accelerating faster than the global average,
349 with further increase expected based on the climate projections (Bertalanič et al., 2019). Over
350 the last three decades, temperatures have risen significantly. While annual precipitation trends
351 show variability across different years and regions, shifts in seasonal precipitation are more
352 concerning (Cegnar et al., 2021). These climatic changes could impact the replenishment of
353 groundwater, a source generally considered stable and well-protected (Zektser and Everett,
354 2004). Maintaining the good quality of this water is crucial especially as future urban
355 development and climate changes may affect groundwater recharge from precipitation and
356 surface water sources (Žagar et al., 2024).

357 The water supply areas in Ljubljana are defined by a hydraulic model, but these boundaries
358 can shift depending on the operational status of wellfields and other system components. This
359 variability can influence water flow directions, affecting operational costs, primarily electricity,
360 and the safety of the water supply system, ensuring that high-quality water reaches the
361 consumers (water manager, personal communication). An example of this was observed in
362 September 2021, when a sample from the Brest WSA, near the border with the Kleče/Brest
363 WSA, showed characteristics similar to the Kleče/Brest area. It is suspected that during
364 sampling, the WSA borders shifted, causing the water at that location to be supplied from two
365 different sources.

366 Long-term infrastructure changes are planned for the area, including constructing a
367 wastewater collection system upstream and across the Ljubljansko polje aquifer, building a
368 hydropower plant on the River Sava upstream of Ljubljana, and improving the current water
369 distribution system. In Ljubljana, actual water losses in the water supply system were 29.6 %
370 in 2019 (Vodovod Kanalizacija Snaga, 2020) and reduced to 26.2 % in 2021 (JP VOKA
371 SNAGA, 2022). Therefore, this study provides a baseline for future investigations into the
372 Ljubljana aquifers and the sustainability of the city's water supply.

373 **6. CONCLUSIONS**

374 Water isotopes have been widely used in various natural applications across a broad range of
375 temporal and spatial scales. However, their application to estimate the anthropogenic urban

water cycles has been limited, with only a few investigations primary conducted over extensive spatial scales (Bowen et al., 2007; de Wet et al., 2020). To enhance our sampling efforts, we adopted a citizen science approach, engaging 145 volunteers who collected 273 samples across Ljubljana during three seasons: spring, autumn, and winter. Volunteers provided essential details, including date, time, location, and building information. The samples required no special pre-treatment, needing only to be stored in a cool, dark place.

This approach allowed for extensive collection of a large dataset, offering valuable insights into the dynamics of Ljubljana's water supply system. The δ^2H and $\delta^{18}O$ values effectively distinguish between different water supply areas, reflecting spatiotemporal dynamics and the characteristics of sources and management practices. Water managers indicated that the water supply areas are flexible, influenced by demand and system pressure. Thus, our isotope data provides additional insights into these dynamic boundaries and serve as a supplementary tool for validating physical models of system operation.

In Ljubljansko polje, wells penetrate similar depths, while in Ljubljansko barje, water is abstracted from both shallower and deeper wells, with deeper wells reaching depths of more than 100 meters. Isotopic data indicated that deeper wells contributed majority of tap water during the sampling period, highlighting the importance for careful monitoring of groundwater extraction.

Given Slovenia's rapid temperature increases, ongoing monitoring of tap water isotopes is essential to assess the impact of human activity and climate change on water resources. While our study successfully mapped the isotopic signature of tap water, the small variation observed highlight the need for long-term monitoring to better understand and manage unaccounted water losses within the distribution network.

7. CREDIT AUTHOR STATEMENT

Conceptualization, K.Ž., P.V., L.O.; Methodology, K.Ž., P.V.; Formal analysis, K.Ž.; Investigation, K.Ž., P.V.; Resources, P.V.; Data curation; K.Ž.; Writing - original draft, K.Ž.; and Writing - review & editing, P.V., L.O., J.V.R.; Visualization, K.Ž.; Supervision, P.V., L.O.; Project administration, K.Ž., P.V.; Funding acquisition, P.V., L.O.

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3.5 Manuscript: Daily Fluctuations in the Isotope and Elemental Composition of Tap Water in Ljubljana, Slovenia

In this section, we present a paper authored by K. Nagode, T. Kanduč, T. Zuliani, B. Bračič Železnik, B. Jamnik, and P. Vreča published in the Water in 2021.

Until 2018, no studies had investigated the Ljubljana WSS or attempted to explain possible isotopic and elemental compositional changes in water during its journey from source to tap. This study used a multi-tracer approach to investigate the daily variability in the isotope and elemental composition of tap water at one location. It is the first study in Slovenia to specifically address water isotopes, building on the 2018 preliminary investigation. Samples were collected from a tap at Jožef Stefan Institute where water was mixing from two aquifers with different recharge areas and geochemical facies. Samples were collected for determination of pH, δ^2H, δ^{18}O, d-excess, $\delta^{13}C_{DIC}$, and $^{87}Sr/^{86}Sr$ ratios and major and trace elements at hourly intervals over a 24 h period. The study aims to provide information to water managers about the origins of drinking water and the contribution of different wellfields based on evaluated parameters. The information is important to ensure a safe water supply as it helps managers effectively plan and implement changes in the water distribution system and mitigate any adverse effects.

The results of this experiment showed that, stable isotopes of water alone cannot be used due to similarity in isotope signatures between the two source waters. However, the concentrations of certain elements, though low, provided more detailed information. Based on temporal differences, four distinct groups were identified: one with higher values at the beginning and end of the day and lower values in between, another with lower values at the beginning and end and higher values in between, a third with higher values at the beginning of the experiment, and a final group with no specific pattern. δ^2H and δ^{18}O showed a significant correlations with Ca, K, As, Li, Ni, and U. Higher contributions from Kleče were noted at the beginning and end of the experiment, while Brest contributed more between 12:00 and 18:00. This variability confirmed the assumptions of water managers about the mixing of water in the investigated area. The study demonstrated that elements such as Na, Cr, and As could serve as proxies for determining the mixing ratios of water from the two wellfields.

The experiment was repeated three times afterwards, first during the COVID-19 pandemic when the provisions and the distribution changed due to the closure of public buildings in Ljubljana. During this period, water was distributed to this location only from the Kleče wellfield.

In this publication I prepared sampling design, performed 24-hour sampling, analyse sampling for the determination of δ^2H and δ^{18}O using DI-IRMS, evaluated the data and prepared the manuscript, including the figures and tables.

water

MDPI

Article

Daily Fluctuations in the Isotope and Elemental Composition of Tap Water in Ljubljana, Slovenia

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Abstract: The isotope and elemental composition of tap water reflects its multiple distinct inputs and provides a link between infrastructure and the environment over a range of scales. For example, on a local scale, they can be helpful in understanding the geological, hydrogeological, and hydrological conditions and monitor the proper functioning of the water supply system (WSS). However, despite this, studies examining the urban water system remain limited. This study sought to address this knowledge gap by performing a 24 h multiparameter analysis of tap water extracted from a region where the mixing of groundwater between two recharge areas occurs. This work included measurements of temperature and electrical conductivity, as well as pH, δ^2H, δ^{18}O, *d*, $\delta^{13}C_{DIC}$, and $^{87}Sr/^{86}Sr$ ratios and major and trace elements at hourly intervals over a 24 h period. Although the data show only slight variations in the measured parameters, four groups were distinguishable using visual grouping, and multivariate analysis (Spearman correlation coefficient analysis, hierarchical cluster analysis, and principal components analysis). Finally, changes in the mixing ratios of the two sources were estimated using a linear mixing model. The results confirm that the relative contribution from each source varied considerably over 24 h.

Keywords: tap water; stable isotopes; hydrogen; oxygen; carbon; multi-elemental analysis; $^{87}Sr/^{86}Sr$ ratio; mixing model; Ljubljana; Slovenia

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1. Introduction

Increasing demand for drinking water and the complexity and heterogeneity of the urban water supply system (WSS), often with its fragmented and ageing infrastructure [1,2], represent a significant challenge for water supply managers as the system is susceptible to contamination or physical interruption [3]. Usually, the physical structure and the necessary information about the WSS are known but in large systems or in developing countries, where this information is either missing or difficult to obtain, methods are needed to study complex WSS without having an in-depth knowledge of the physical infrastructure [4].

Stable water isotope analysis has proven to be a useful tool in understanding hydrological processes [4–6]. This is because stable isotope ratios of hydrogen ($^2H/^1H$) and oxygen ($^{18}O/^{16}O$) in water provide a characteristic signature that can be used to investigate the origin of different water sources that contribute to the stream, natural, and artificial mixing of waters, sources of the groundwater recharge and to quantify the variability of climate change [4,6,7].

The isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$), the main species in water draining carbonate aquifers, is also helpful for assessing the origin of water. The primary processes that affect the carbon isotope composition are the dissolution of carbonates, the microbial decomposition of organic matter and its removal via carbonate

precipitation [8]. The $\delta^{13}C_{DIC}$ is indicative of the biogeochemical processes within the aquifer, especially in carbonate-rock aquifers [9–11]. Other than these three studies, little information was available at the outset of this investigation relating to the $\delta^{13}C_{DIC}$ of tap water. Similarly, the $^{87}Sr/^{86}Sr$ can connect local geology to a specific recharge area and provide a better understanding of the processes that impact waters affected by human management [12,13]. Knowing the concentration of the minor and major elements in water can also provide complementary information to the isotope composition [14].

More recently, water isotopes have been used to understand the origin of tap water, [6,15,16]. Unlike surface water with an isotopic composition similar to regional precipitation [6,15], the isotope information provided by tap water is not so easy to interpret, as it can represent contributions from different water sources and different static and dynamic regions, e.g., regions supplied predominantly by one source compared with regions experiencing active mixing between various sources [4,16]. Differences in water isotopes can be used to investigate different inputs into the system (i.e., lakes, precipitation, surface water) as different processes affect the isotope composition (seasonal changes in recharge, contribution of meteoric waters, temperature, and humidity) [15]. Elemental signatures related to the geological (lithology), hydrogeological and hydrological background can also be used to distinguish specific aquifers. Although it is essential to know the elemental composition of the different water sources, it is also necessary to consider the contribution made by elements leaching from pipe scale, e.g., Ca, S, Mn, Zn, P, Mg, Al, and Fe. Human activities can also alter the water composition (i.e., accidental spills, supply contamination) [4]. However, care is needed in any interpretation of elemental composition since urban water is subject to contamination by natural water supplies, water losses from the supply system, prolong retention times, and dead-end areas [17].

In urban areas, conducting field studies remains challenging as constraining the water fluxes requires the monitoring of vast areas. Therefore, simultaneous field studies are also needed covering the heterogenic and complex WSS where the researchers or the water system managers perform monitoring and sampling over spatiotemporal scales. In addition, there is a need to understand the water transport dynamics in the WSS and establish a spatially distributed multiparameter data set for a defined period.

In Ljubljana, Slovenia's capital city (population approximately 330,000), the primary source of drinking water is groundwater. The contribution that surface water and precipitation makes to groundwater changes through the hydrological year [18]. Within the area, some contaminations were defined: hexavalent chromium plumes, nitrate and new emerging pollutants, and desethyl-atrazine plumes [19]. In the city, water consumption varies daily; however, the time it takes for water from the wellfield to reach the city centre is no more than few hours (personal communication, VOKA SNAGA manager). Regular monitoring of drinking water quality in the WSS, based on demands of national regulations [20] that are harmonized with of European Drinking Water Directive [21], does require analysis of elements related to the pollution of drinking water (i.e., Cd, Cr, Fe, Pb, Mn) as high concentrations of toxic metals in water pose a risk to health [22]. The management of the groundwater quality at the functional urban area and the feasible measures for decreasing of the concentration of relevant contaminants were discussed recently [23,24].

Until 2018, no studies had looked at the Ljubljana WSS or attempted to explain possible isotopic and elemental compositional changes in water during its journey from "source to tap" [25]. Then, in 2018, the first multi-tracer investigation of urban water from different sources was performed by Vreča et al. [26,27], revealing that certain elements, e.g., As, B, Li, and Sr, are characteristic of a specific source or recharge area. Surprisingly, only Du et al. [16] report the hourly fluctuations in water isotopes, but no one has investigated changes in $\delta^{13}C_{DIC}$ or changes in the elemental composition coupled with stable isotopes ($\delta^{13}C_{DIC}$, $\delta^{18}O$, $\delta^{2}H$) in tap water.

This study's overarching goal was to use a multi-tracer approach to investigate the daily variability in the isotope and elemental composition of tap water. It is the first study of its kind in Slovenia looking specifically at water isotopes and building on our 2018 study.

The study also gave the opportunity to collect samples of tap water from the mixing of two aquifers with different recharge areas and geochemical facies. The mixing of water of different origin at this location is known to the water managers, who are interested in information on drinking water origins, for various reasons. The more information they have, the safer the water supply they are able to implement. This is important for when they have to control planned changes in the water distribution net, review the consequences of unintended changes, and take measures to mitigate any adverse effects. The main aims of this study were to characterize the daily geochemical variability of tap water over time and identify geochemical tracers to estimate the mixing ratio of water sources at the selected location.

2. Materials and Methods

2.1. Site Description

Hourly samples of tap water were collected from the main building's basement at Jožef Stefan Institute (JSI in Figure 1), Ljubljana, Slovenia (lat: 46.04207, long: 14.487400). The water originates from two different wellfields: Kleče and Brest (Figure 1), located in aquifers with different hydrogeological characteristics. Kleče is located in the Ljubljansko polje aquifer and Brest on the Ljubljansko barje aquifer. Two rivers bind the Ljubljansko polje: the River Ljubljanica to the south and the River Sava to the north in the eastern part of the Ljubljana basin. The basin was formed by tectonic subsidence in the early Pleistocene and is composed of Permian and Carboniferous slate claystone and sandstone [28]. The Pleistocene and Holocene fluvial sediments, accumulated by the River Sava, form highly permeable partially cemented sand and gravel with lenses of conglomerate [29]. The aquifer is recharged by both precipitation and the River Sava, mainly in the north-western part. It is also recharged via lateral inflow from the Ljubljansko barje multi-aquifer system in the south [30,31].

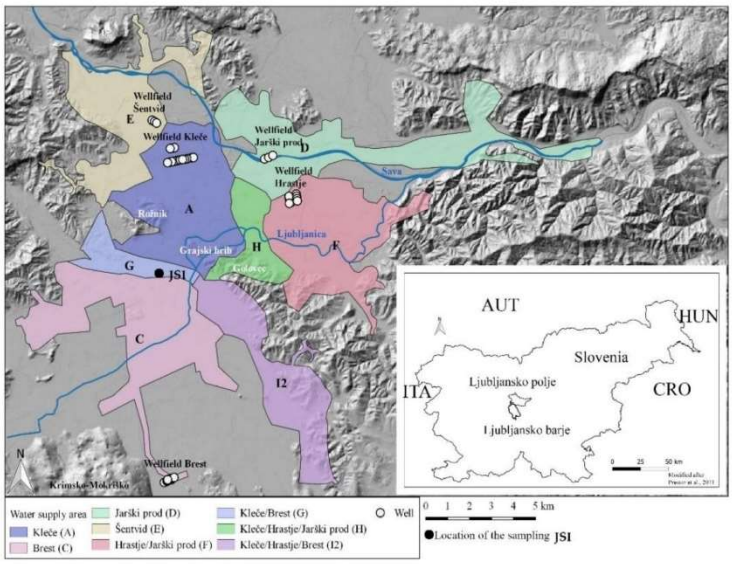

Figure 1. Study area showing the main wellfields (marked with circles) and water supply areas (A to I2). The sampling location is marked with a black dot (JSI).

The depression of the Ljubljansko barje is located on the southern part of the Ljubljansko polje; it formed within the permeable limestone and dolomite basement and was filled by alluvial, marshy, and lacustrine sediments during the Pleistocene and Holocene. The upper Holocene aquifers are recharged directly from precipitation and surface streams, while the lower aquifer is recharged from the karst recharge area [32]. Sediments in this area are heterogeneous, and the hydrogeological conditions are more complex than on the Ljubljansko polje [33].

The Ljubljana WSS consists of water supply facilities, 44 wells, eight minor pumping stations, and more than 1100 km of supply network [34]. Groundwater is exploited at the Ljubljansko polje from the Kleče, Hrastje, Jarški prod and Šentvid wellfields and at Ljubljansko barje from the Brest wellfield (Figure 1). In the central system, some settlements are continuously supplied with drinking water from a single wellfield (A, C, D, and E), while others are supplied from two or more wellfields (F, G, H, and I2) [33].

2.2. In-Situ Measurements and Water Sampling

Monitoring of tap water was performed from 09:00 on 24 April 2019 until 09:00 on 25 April 2019. In-situ temperature (T), electrical conductivity (EC), and pH were measured every full hour, using a Hanna HI 9829 Multiparameter instrument (Woonsocket, RI, USA), with an accuracy of ±0.15 °C, ±1 µS/cm and ±0.02, respectively. Quick calibration of the instrument was performed after 4 h, at 13:10.

Before collecting the first sample, the tap water was allowed to run for 60 s. Samples were then collected every hour. In total, 25 water samples were collected. The samples for δ^2H and δ^{18}O analysis were stored in prewashed 30 mL high-density polyethylene (HDPE) bottles and stored at room temperature. Samples for $\delta^{13}C_{DIC}$ were filtered on-site through a 0.45 µm nylon filter into 12 mL glass exetainers. In contrast, samples for determining the multi-elemental composition and $^{87}Sr/^{86}Sr$ ratios were collected in prewashed 50 mL polypropylene (PP) centrifuge tubes and acidified using HNO_3 (68% *v*/*v*, suprapur, Carlo Erba Reagents, Val de Reuil, France). All samples were stored at 4–6 °C.

2.3. Analytical Procedures

The δ^2H, δ^{18}O, $\delta^{13}C_{DIC}$, $^{87}Sr/^{86}Sr$ isotope ratios and major and trace element concentrations were determined at the Department of Environmental Sciences at Jožef Stefan Institute.

2.3.1. Determination of δ^2H, δ^{18}O and *d*-Excess

δ^2H and δ^{18}O were determined according to the modified IAEA Technical procedure note no. 43 [35], using the H_2-H_2O [36] and CO_2-H_2O [37,38] equilibration techniques. Measurements were performed on a dual inlet isotope ratio mass spectrometer (DI IRMS, Finnigan MAT DELTA plus Finnigan MAT GmbH, Bremen, Germany) with an automated H_2-H_2O and CO_2-H_2O equilibrator HDOeq 48 Equilibration Unit (custom built by M. Jaklitsch). The water bath was set to 18 °C. The water vapor trap was cooled to –55 °C. H_2 (IAEA) and CO_2 (Messer 4.5) gases were used as working standards. Samples (3 mL) were allowed to equilibrate for 2 (H_2-H_2O) and 6 (CO_2-H_2O) hours before analysis.

All measurements were performed together with laboratory reference materials (LRM) calibrated periodically against primary IAEA calibration standards to the VSMOW/SLAP scale. The defined isotope values and measurement uncertainty of LRMs were used to normalize the data, and independent quality control was calculated using the Kragten method [39–41]. All samples were measured in duplicate. The results were normalized to VSMOW/SLAP using LIMS (Laboratory Information Management System for Light Stable Isotopes) program and expressed in the standard δ notation (in ‰) using the conventional delta notation:

$$\delta_{sample}(‰) = (R_{sample}/R_{standard} - 1) \times 1000 \quad (1)$$

R_{sample} and $R_{standard}$ are the isotope ratios ($^2H/^1H$, $^{18}O/^{16}O$) of a heavy isotope to a light isotope in a sample and an international standard. For normalization, the method uses

LRMs calibrated to the VSMOW/SLAP scale, namely W-3869 with defined isotope values and estimated measurement uncertainty $\delta^2H = +2.5 \pm 0.7‰$ and $\delta\ ^{18}O = +0.36 \pm 0.04‰$, and W-3871 with values of $\delta^2H = -148.1 \pm 0.7‰$ and $\delta^{18}O = -19.73 \pm 0.02‰$. LRM W-45 with defined isotope values and estimated measurement uncertainty of $\delta^2H = -60.6 \pm 0.7‰$ and $\delta^{18}O = -9.12 \pm 0.04‰$, and commercial reference materials USGS 45, USGS 46, and USGS 47 were used. The average sample repeatability for δ^2H 0.2‰ and $\delta^{18}O$ was 0.01‰. Deuterium excess (d) was calculated as $d\ [‰] = \delta^2H - 8 \times \delta^{18}O$ [42].

2.3.2. Determination of $\delta^{13}C_{DIC}$

$\delta^{13}C_{DIC}$ was determined according to modified [43] and [44] methods. Saturated phosphoric acid (100%) was added (100–200 µL) to a septum-sealed tube and purged with pure He. A water sample (1 mL) was then injected into the tube, and the isotope composition of CO_2 measured directly from the headspace using a continuous flow IsoPrime100 stable isotope mass spectrometer (CF IRMS) coupled with the MultiFlow Bio equilibration unit. The results were normalized to VPDB and expressed in the standard δ notation in ‰ (see Section 2.3.1). A standard solution of Na_2CO_3 (Carlo Erba reagents, Val de Reuil, France) with a known $\delta^{13}C_{DIC}$ of $-10.8 \pm 0.2‰$ was used to determine the optimal extraction procedure for tap water samples. The average sample repeatability was 0.1‰.

2.3.3. Determination of Major and Trace Elements

Four major (Ca, Na, K, Mg) and 23 trace elements concentrations (Ag, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, K, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sr, U, V, and Zn) were determined using an Agilent 7900x inductively coupled plasma mass spectrometer (ICP-MS, Agilent Technologies, Tokyo, Japan). To measure accuracy, two surface water reference materials: SLRS-5 (National Research Council Canada, Ottawa, ON, Canada) and SPS-SW1 (Spectrapure Standards, Manglerud, Norway), were analysed at the beginning, in the middle and at the end of the sequence. Recovery ranged from 97% to 102% for all elements, and the repeatability was better than 5%.

2.3.4. Determination of $^{87}Sr/^{86}Sr$ Isotope Ratios

Five samples were selected for $^{87}Sr/^{86}Sr$ isotope ratio analysis according to the Sr and Rb concentrations and their ratio (10:00, 17:00, 00:00, 03:00 and 08:00). The $^{87}Sr/^{86}Sr$ isotope ratio was determined using the method described in Zuliani et al. [12]. Briefly, water samples (from 0.1 to 1 mL) were evaporated to dryness and redissolved in 1 ml of 8M HNO_3. For Rb/Sr separation, Sr specific resin (Eichrom®, Triskem International, Bruz, France) was used. The $^{87}Sr/^{86}Sr$ isotope ratio was determined using a Nu plasma II multi-collector ICP-MS (Nu Instruments Ltd., Wrexham, UK) fitted with an Aridus II™ Desolvating Nebulizer System (Teledyne Cetac, Omaha, NE, USA). Measurements were performed following the standard-sample-standard bracketing method using a NIST SRM 987 $SrCO_3$ (0.71034 ± 0.00026, National Institute of Standards and Technology, Gaithersburg, MD, USA) as the standard. All samples were prepared in triplicate.

2.3.5. Data Evaluation

Metadata information is explained in Supplementary Table S1, and all data obtained are presented in Tables S2 and S3. Since the Ag content in most samples and Se in all samples (Table S3) were below the LOD, they were excluded from further data analysis. The data were analyzed using Microsoft® office Excel 2019 for basic descriptive statistics and OriginPro 2021 for multivariate analysis: Spearman correlation coefficient analysis (SCA), hierarchical cluster analysis (HCA), and principal components analysis (PCA). The HCA method was used to order data and create groups that share common properties. Euclidean distances were chosen as the distance between the different sampling times, and Ward's method was used to form the clusters.

Finally, the simple linear mixing model (SLMM) was used to quantify the relative contribution from each well (Kleče and Brest), using the long-term average concentrations of sodium (Na), chromium (Cr), and arsenic (As) in the two end-members as follows:

$$Na_{JSI} = x_K Na_K + y_B Na_B \quad (2)$$

$$1 = x_K + y_B \quad (3)$$

Here, the subscript JSI, K and B represent tap water mixture at the JSI and the two water sources Kleče and Brest. For the end-member concentration, long-term data collected at private households at the Kleče and Brest wellfield were used as no simultaneous sampling of source water was provided [45].

3. Results and discussion

The results are presented as electronic supplementary material (Tables S2 and S3) and summarized graphically in Figures 2 and 3. The descriptive statistics of all hydrogeochemical parameters are presented in Table 1.

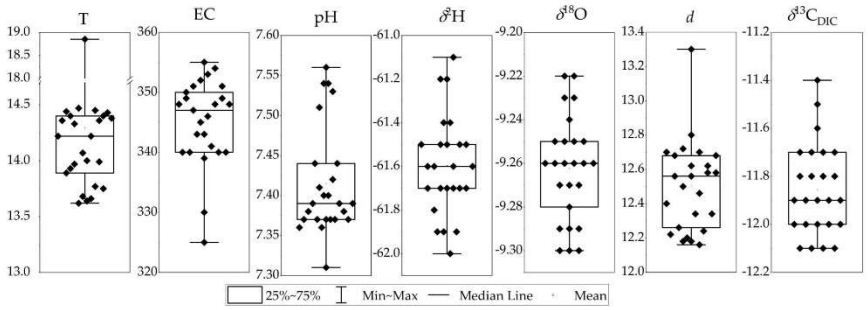

Figure 2. Boxplots of T [°C], EC [µS/cm], pH, δ^2H [‰], δ^{18}O [‰], *d* [‰], and $\delta^{13}C_{DIC}$ [‰] for all tap water samples.

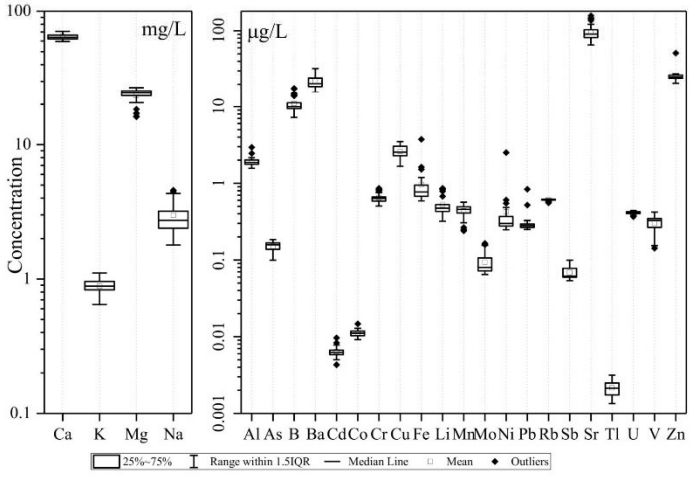

Figure 3. Boxplots of element concentrations (major and trace elements) in all tap water samples.

Differences observed over the 24 h sampling period were relatively small (Table 1), but a more detailed inspection reveals variations in particular parameters. For instance, after stabilization, the temperature varied between 13.5 °C to 14.5 °C, however the initial reading after one minute was 18.9 °C. The pH ranged from 7.10 to 7.61 (Table 1) and is in the range required for drinking water in Slovenia, i.e., between ≥6.5 and ≤9.5 [20], which is similar to the European standards [21,46] (Table 1). The EC values were between 325 µS/cm and 355 µS/cm and were below the official standard for drinking water of 2500 µS/cm (Table 1). Based on EC classification [48], tap water at the JSI sampled has a low mineral concentration and is homogenous.

Table 1. Summary of basic statistics and SI, EU, US EPA, and WHO guidelines for tap water.

	Mean	SD	Min	Max	Range	CV (%)	SI [1]	EU [2]	US EPA [3]	WHO [4]
T [°C]	14.1	0.59	13.5	18.9	5.4	7.0	n.d.	n.d.	n.d.	n.d.
EC [µS/cm]	344	7.0	325	355	30	2.1	2500	2500	n.d.	n.d.
pH	7.43	0.09	7.10	7.61	0.51	0.9	6.5–9.5	6.5–9.5	6.5–8.5	n.d.
δ^2H [‰]	−61.6	0.2	−62.0	−61.1	0.9					
δ^{18}O [‰]	−9.26	0.02	−9.30	−9.22	0.08					
d [‰]	12.5	0.3	12.2	13.3	1.1					
$\delta^{13}C_{DIC}$ [‰]	−11.9	0.2	−12.1	−11.4	0.7					
Ca [mg/L]	64.4	3.11	59.5	70.7	11.2	4.8	n.d.	n.d.	n.d.	n.d.
K [mg/L]	0.884	0.125	0.645	1.11	0.465	14.2	n.d.	n.d.	n.d.	n.d.
Mg [mg/L]	23.3	3.48	16.1	26.9	10.8	15.0	n.d.	n.d.	n.d.	n.d.
Na [mg/L]	2.98	0.836	1.79	4.58	2.79	28.1	200	200	n.d.	n.d.
Al [µg/L]	1.93	0.283	1.56	2.94	1.38	14.7	200	200	50–200	100–200
As [µg/L]	0.150	0.025	0.099	0.184	0.085	16.4	10	10	10	10
B [µg/L]	10.9	2.84	7.20	17.7	10.5	26.0	1000	1000	n.d.	2400
Ba [µg/L]	22.1	4.99	15.7	32.0	16.3	22.6	n.d.	n.d.	2000	1300
Cd [µg/L]	0.0064	0.0012	0.0043	0.0096	0.0053	18.6	5	5	5	3
Co [µg/L]	0.0111	0.0013	0.0091	0.0147	0.0111	12.0	n.d.	n.d.	n.d.	n.d.
Cr [µg/L]	0.651	0.096	0.504	0.859	0.355	14.7	50	50	100	50
Cu [µg/L]	2.60	0.486	1.67	3.49	1.82	18.7	2000	2000	1300	2000
Fe [µg/L]	0.970	0.631	0.588	3.73	3.14	65.1	200	200	300	n.d.
Li [µg/L]	0.528	0.171	0.320	0.857	0.537	32.4	n.d.	n.d.	n.d.	n.d.
Mn [µg/L]	0.437	0.093	0.240	0.566	0.326	21.3	50	50	50	n.d.
Mo [µg/L]	0.093	0.031	0.065	0.165	0.100	33.5	n.d.	n.d.	n.d.	70
Ni [µg/L]	0.424	0.445	0.247	2.51	2.26	104.8	20	20	n.d.	70
Pb [µg/L]	0.310	0.121	0.249	0.834	0.585	39.0	10	10	15	10
Rb [µg/L]	0.606	0.019	0.555	0.624	0.069	3.1	n.d.	n.d.	n.d.	n.d.
Sb [µg/L]	0.068	0.014	0.054	0.099	0.045	20.2	5	5	6	20
Sr [µg/L]	98.1	27.2	65.2	157	91.8	27.7	n.d.	n.d.	n.d.	n.d.
Tl [µg/L]	0.0021	0.0005	0.0013	0.0031	0.0018	22.7	n.d.	n.d.	2	n.d.
U [µg/L]	0.411	0.017	0.367	0.442	0.075	4.0	n.d.	n.d.	n.d.	30
V [µg/L]	0.301	0.079	0.142	0.420	0.278	26.4	n.d.	n.d.	n.d.	n.d.
Zn [µg/L]	25.7	5.61	20.7	51.1	30.4	21.8	n.d.	n.d.	5000	n.d.

n.d.—not defined. SI [1] (Regulation about drinking water, Slovenian Gazette 19/2004 [20]), EU [2] (Council Directive 98/83/EC (1998) [21]), US EPA [3] (Safe Drinking Water Act (2019) [46]) and WHO [4] (Guidelines for Drinking-water Quality (2008) [47]).

3.1. δ^2H and $\delta^{18}O$ in the Tap Water

The diurnal variations of stable isotope ratios in tap water are presented in Figure 4 and, as a whole, show only slight statistically nonsignificant variations. The δ^2H and δ^{18}O vary from −62.0‰ to −61.1‰ and from −9.30‰ to −9.26‰ (Table 1), respectively, standard deviations for hourly δ^2H and δ^{18}O are 0.2‰ and 0.02‰, respectively. The highest and the lowest δ^2H appeared at 05:00 and 21:00 (Figure 4a). The highest δ^{18}O appeared at 09:01 and 08:00, and the lowest at 15:00, 23:00, and 05:00 (Figure 4b). Also, there was no significant difference between the average values in tap water during the daytime (09:01–20:00) and night-time (21:00–09:00) [49]. However, there is a slight difference between the average isotope values during morning hours (09:01–11:00 and 07:00–09:00) and the rest of the day/night time (12:00–06:00). The difference for δ^2H and δ^{18}O is 0.13‰ and 0.04‰. However, the variability is still small and is in the range of measurement uncertainty. It also shows that the sources of tap water from Kleče and Brest have similar

isotope compositions, which prevents the differentiation of tap water origin solely using stable isotope ratios (Figure 4).

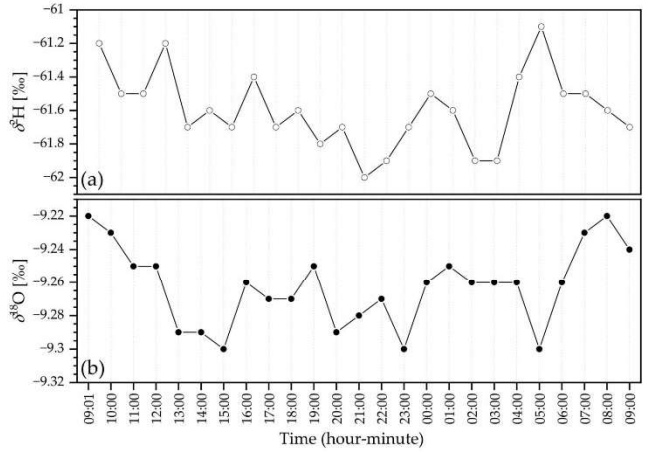

Figure 4. Diurnal variations of stable isotope ratios in tap water: (**a**) δ^2H, (**b**) δ^{18}O.

No correlation (r = 0.3) was observed between δ^2H and δ^{18}O since the source water does not change in such a short period (24 h). Moreover, as the water moves through the soil, the groundwater signal is attenuated resulting in small differences between aquifers. The values obtained are typical for the source water, i.e., groundwater from shallow aquifers of Ljubljansko polje and Ljubljansko barje [25].

All values fall close to the Global Meteoric Water Line (GMWL) and the Local Meteoric Water Line for Ljubljana [50], confirming that groundwater from the Ljubljansko polje aquifer originates primarily from infiltration of local precipitation and water from the River Sava [18] and at the Ljubljansko barje aquifer from precipitation and surface streams [33]. Deuterium excess (*d*) was also relatively constant, with an average of 12.5‰, and ranging between 12.2‰ and 13.3‰. Therefore, it could not be used as an indicator of different water sources.

3.2. $\delta^{13}C_{DIC}$ in the Tap Water

The 24 h δ^{13}C variability of tap water ranged from −12.1‰ to −11.4‰ (Table 1). The lowest $\delta^{13}C_{DIC}$ of −12.1‰ was observed at 14:00, 15:00, 17:00, and 3:00, while the highest value of −11.4‰ occurred at 08:00. Samples with lower $\delta^{13}C_{DIC}$ are more characteristic for Brest, while samples with higher $\delta^{13}C_{DIC}$ are characteristic for Kleče [26]. All values in tap water indicate both biogeochemical processes: CO_2 produced during organic matter decomposition and carbonate dissolution.

3.3. Concentrations of Major and Trace Elements in the Tap Water

The largest variation in major elements was observed for Na (CV = 28.1%; Figure 5a) followed by K (CV = 14.2%) and Mg (15.0%; Figure 5b) (Table 1). Generally, higher values were observed for Ca and Na at the beginning and at the end of the experiment and opposite for Mg and K that had lower values at the start and end of the experiment (Figure 5a,b). However, data for K show much higher fluctuations during the 24 h experiment. There is no numerical Slovenian drinking water quality guideline for Ca, Mg, and K (Table 1). Trace elements were detected in all water samples, but were below the limits set by the Slovenian regulation and the EU Drinking Water Directive [20–22,46,47].

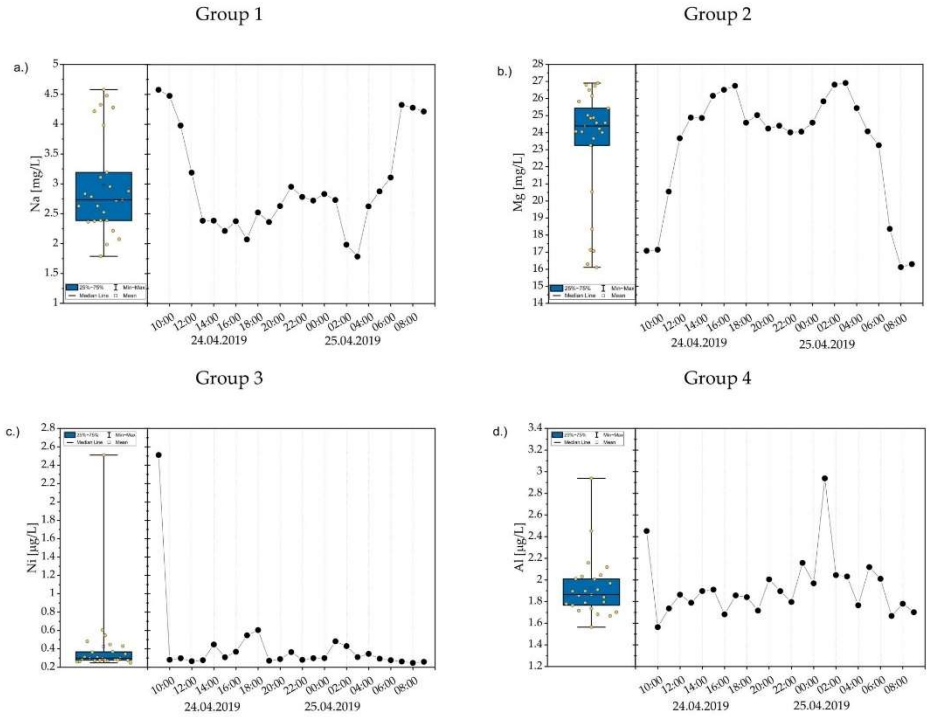

Figure 5. The most representative boxplots and hourly variability of concentrations based on visual observation for Group 1 (**a**), Group 2 (**b**), Group 3 (**c**) and Group 4 (**d**).

Based on the visual examination of the data, we can distinguish four different groups:

(1) Group 1 (Figure 5a): higher values in the beginning and at the end and lower in between (i.e., δ18O, δ13CDIC, Ca, Na, B, Ba, Cr, Li, Sr);
(2) Group 2 (Figure 5b): lower values in the beginning and at the end and higher in between (i.e., K, Mg, As, Mn, V);
(3) Group 3 (Figure 5c): higher values at the beginning of the experiment (i.e., T, Cd, Co, Fe, Ni, Pb, Sb, Zn) with a subgroup showing exponential decrease with time (i.e., Mo, Sb, Tl);
(4) Group 4 (Figure 5d): no specific pattern; (i.e., EC, pH, δ2H, d, Al, Cu, Rb, U).

Drinking water in the central WSS has been subject to periodic monitoring of different parameters. In the period 2016 to 2019, measured Ca and Mg concentrations [45] from an average wellfield were 70.8 mg/L (1.77 mM) and 16.5 mg/L (0.68 mM) in Kleče, and 62.0 mg/L (1.55 mM) and 29.7 mg/L (1.23) from the Brest wellfield respectively. The average Mg^{2+}/Ca^{2+} ratio for Kleče is 0.38 and for Brest 0.79 (Figure 6). Carbonate dissolution plays an important role: in Brest, dolomite dissolution prevails, whereas in Kleče, limestone dissolution is more important. The Mg^{2+}/Ca^{2+} ratio during the 24 h experiment shows that most samples have a Mg^{2+}/Ca^{2+} ratio between 0.5 and 0.75, which indicates that the dominant water source is Brest. In contrast, samples below the 0.5 line (09:01, 10:00 and 11:00 on 24 April 19 and 07:00, 08:00 and 09:00 on 25 April 19) suggest that water from Kleče predominates (Figure 6).

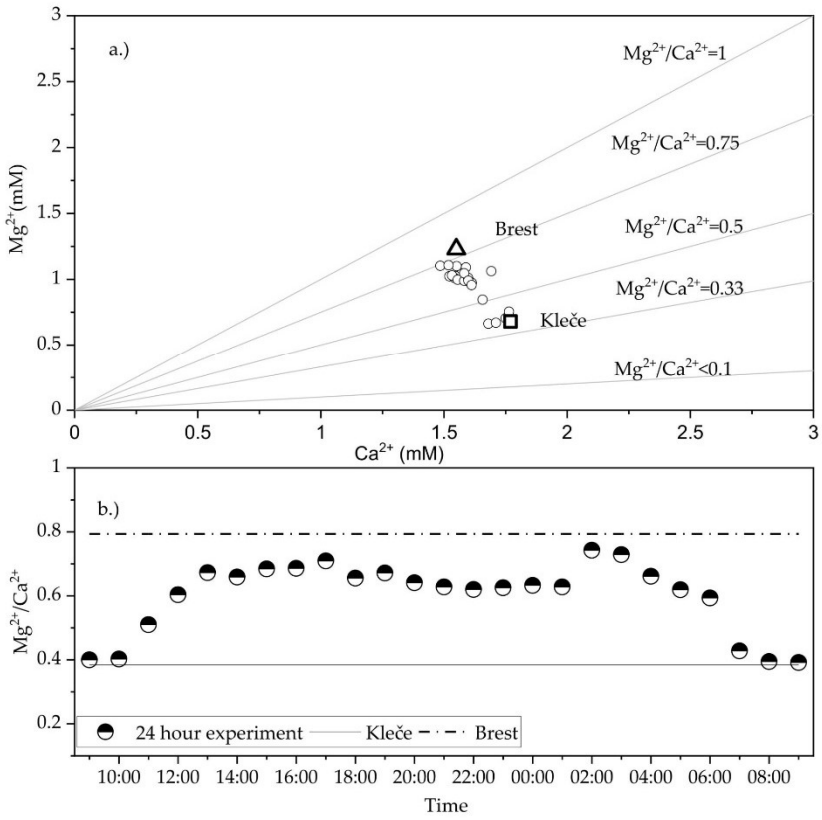

Figure 6. (**a**) Mg^{2+} versus Ca^{2+} concentration in tap water samples collected during the 24 h experiment. For comparison, average concentrations for wellfields Kleče (calcite prevails) and Brest (dolomite prevails) are shown. (**b**) Temporal changes in Mg^{2+}/Ca^{2+} values in tap water during the 24 h experiment.

3.4. Sr/^{86}Sr Isotope Ratio

The $^{87}Sr/^{86}Sr$ values are presented in Supplementary Table S3. The Rb concentration in the samples was 0.558 to 0.614 µg/L, with the lowest values at 10:00 and 08:00. The Sr concentration was in the range of 65.2 µg/L to 147 µg/L. The water collected during morning hours (at 10:00 and 08:00) had a lower Rb/Sr ratio than the samples collected at 17:00, 00:00, and 03:00. The hours when the Rb/Sr ratio corresponds to the low Mg^{2+}/Ca^{2+} ratios (chapter 3.4) allow us to conclude that the samples collected in the morning belong to the water from Kleče, while higher ratios indicate the prevailing water from Brest [27].

3.5. Multivariate Statistical Analysis

The multivariate statistical analysis was performed using SCA, HCA, and PCA. The SCA results are summarized in Supplementary Figure S1, HCA is presented in Figure 7 and Supplementary Table S4, while PCA results are presented in Supplementary Table S5. The final dataset used for multivariate statistical analysis is a data matrix of 25 samples (observations) by 32 parameters (variables) for SCA, while for the PCA and HCA, only

25 parameters, i.e., major and trace elements, were used (Table 1). The distribution of most chemical parameters is positively (Al, B, Ba, Cr, Fe, Li, Mo, Ni, Pb, Sb, Sr, Zn) or negatively (Mg, Mn, As, Rb, V) skewed and only a few are close to a normal distribution (Ca, K, Na, Cd, Co, Cu, Tl, U). Chemical parameters that were positively or negatively skewed were log-transformed. Finally, standardization was applied to 16 lognormal data and 12 normal distributions to ensure that each variable is weighted equally.

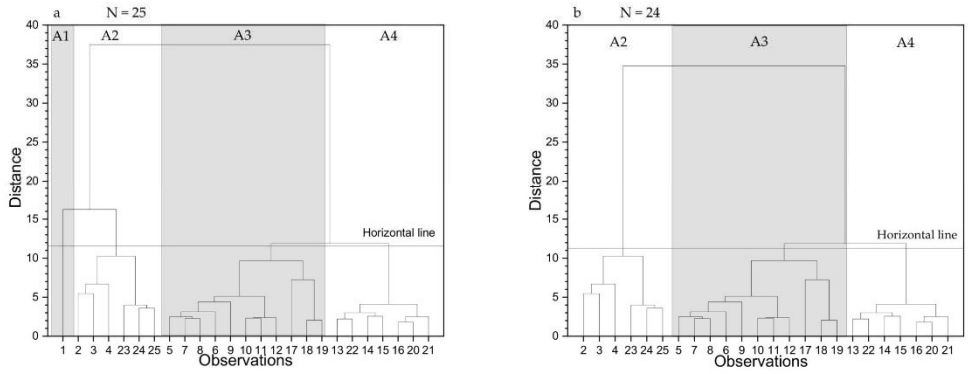

Figure 7. Dendrogram for the tap water samples, showing: (**a**) the division into four clusters; (**b**) the division into three clusters.

Based on the results of the SCA (Figure S1), all the parameters were divided into three groups regarding the number of significant correlations with other parameters:

(1) Parameters with ≤10 correlations (T, EC, *d*, Al, Co, Cu, Fe, Mo, Pb, Rb, Sb, and Tl);
(2) Parameters with 11 to 19 correlations (pH, δ^2H, δ^{18}O, $\delta^{13}C_{DIC}$, Ca, K, As, Li, Ni, and U);
(3) Parameters with 20 and 21 correlations (Mg, Na, B, Ba, Cd, Cr, Mn, Sr, V, and Zn).

δ^2H, δ^{18}O, $\delta^{13}C_{DIC}$ showed a significant correlation with 12, 15, and 18 other parameters, respectively, and can therefore be used as possible indicators for determining water origin and changes in the WSS. A significant positive Spearman correlation (r_s = 0.9) exists between Ca and Na, B, Ba, Cr, Li, and Sr, suggesting a common water origin. It also shows a high negative correlation ($r_s \geq -0.7$) with As, Mg, Mn, and V, resulting in a possible different origin of the water.

HCA was first performed on the whole set of data (Figure 7a; N = 25), and then on the results after removing the first observation (sample: 09:01; Figure 7b; N = 24). In this study, a horizontal line is drawn across both dendrograms at a linkage distance of about 12. Three distinct clusters were identified: A2 (N = 6), A3 (N = 11), and A4 (N = 7), while cluster A1 (Figure 7a) represents only the first sample. Observation of the dendrogram reveals some similarities between clusters; however, the clusters A1 (only in the left dendrogram) and A2 are less similar as they have high linking similarity clusters A3 and A4. To describe the characteristics of each cluster, Table S4 presents the median values of geochemical data. To the group A1 belongs sample collected at 09:01, to group A2 belong samples collected from 10:00 to 12:00 and from 07:00 to 09:00 and can be attributed to water from Kleče. On contrary, to A3 belong samples collected during the hours when majority of water was coming from Brest (from 13:00 to 20:00 and 01:00 to 03:00). To the group A4 belong samples collected from 21:00 to 00:00 and from 04:00 to 06:00 and represents hours in between the origin change. For cluster A1, we can see that the elevated median values of Fe, Ni, Pb, and Zn indicate the leaching of elements from the WSS collected at the beginning of the experiment and can be linked to the visual classified Group 3. The second

dendrogram shows that the clusters include the same tap water samples as in the first dendrogram; however, the representative median concentrations changed (Table S2). The most representative elements for the A2 cluster of the second dendrogram are Ca, Na, B, Ba, Cr, Fe, Li, Mo, Sb, and Sr, while for the A3 cluster, higher values of K, Mg, As, Cd, Co, Ni, Rb, Tl, V, and Zn are characteristic. Most elements (Ca, Na, B, Ba, Cr, Li, and Sr) representative of A2 belongs to Group 1 (Fe, Mo, and Sb belong to Group 3), while elements K, Mg, As, V and Cd, Co, Ni, Tl, Zn belong to visually divided Group 2 and Group 3, respectively (Figure 5b,c). For A4, the most representative elements are Al, Cu, and U that belong to Group 4 (Figure 5d) and confirm the mixing of water, presented in Figure 6.

In 2018, the multi-elemental analysis was performed on water samples from one well in Brest and one well in Kleče. The results showed higher values of B, Ba, Li, and Sr in Kleče, whereas in Brest, higher Mg, As, and V values were detected [27]. Based on all results, we can conclude that the tap water samples in the cluster A2 represent water from Kleče and those in A3 from Brest.

The first two principal components account for 72.7% of the total variance in the dataset; the principal component loadings are presented in Table S5 (left). Loadings that represent the most important variables for the components are bolded for values greater than 0.25. PC1 explains the greatest amount of the variance and is characterized by positive loadings in Ca, Na, B, Ba, Cr, Li, and Sr (Table S5), and belongs to Group 1 (Figure 5a) and can be attributed to the wellfield Kleče. Component 2 is characterized by positive loadings in Al, Cd, Co, Fe, Ni, Pb, and Zn, were all but Al represent Group 3 (Figure 5c).

Further, the first sample was excluded, and the analysis was performed for 24 samples. The results are presented in Table S5 (right). The first two components account for 70.2% of the total variance in the dataset. Component 1 is characterized by positive loadings in Mg, Mn, and V, representing Group 2 (Figure 5b, Table S5), while component 2 is characterized by positive loadings in Mo, Sb, and Tl. The latter elements belong to subgroup 3. The most significant loadings belong to elements related to the leaching from the pipes within the WSS.

3.6. Mixing of Water

Tap water can involve two or more discrete end-members and is easy to observe and calculate. It is important to demonstrate that the tracers of mixing behave conservatively and not react with other solutes, solids, or gases. For the source partitioning, Na was selected for SLMM. Also, Cr and As were used since they represent common contaminants in groundwater [51]. It is known that Ljubljansko polje is higher in Cr, while higher As values are characteristic of Ljubljansko barje. Also, Cr and As are highly correlated with Na and can be used for SLMM. Data of Na concentrations were gathered from 2016 to 2019 in periodical sampling of drinking water [45] with an average value of 4.9 mg/L (min = 3.3 mg/L, max = 7.7 mg/L) for Kleče and 1.6 mg/L (min = 0.99 mg/L, max = 4.4 mg/L) for Brest. By comparing these results with this study's data, all tap water samples fall in the mixing area between Kleče and Brest. Using equation 2.3.5 and average Na concentration data for end members, the proportion of water from Kleče was calculated. Results show that over 24 h the mixing ratio changed from 7% to 90%. When using Cr and As as end-members and long-term data from private users [45], it gave estimates of 23% to 74% and 0.1% to 100%, respectively. Moreover, based on the high positive correlation between Na and, e.g., Mg, Li, Mn, Sr, and V these elements could also be used for the source determination if the end-member concentration would be known.

4. Conclusions

This study is, to the best of our knowledge, the first to look at the variability of stable isotopes and elemental composition during a 24 h analysis of tap water. It involved in-situ monitoring of T, EC, and pH. Samples were collected for multi-elemental and stable isotope analyses (δ^2H, δ^{18}O and $\delta^{13}C_{DIC}$) every hour over 24 h in tap water at a location where water from Kleče and Brest wellfields is mixed.

Using the isotope composition (δ^2H, δ^{18}O, and $\delta^{13}C_{DIC}$) to determine the mixing ratios remains inconclusive given the isotope similarity between the two sources waters. Concentrations of elements, although low, did carry more information. Based on the visual observation of temporal differences, four groups were identified. The characteristics of these were: higher values in the beginning and at the end and lower between; lower values in the beginning and at the end and higher in between; higher values at the beginning of the experiment; and a group with no specific pattern. While the isotopes can help us to understand the sources and dynamics of flows in urban areas, the use of additional hydrogeochemical parameter in the SCA, HCA, and PCA analyses helps with testing and identifying hourly variability and the origin of tap water at given time. Based on SCA we divided the investigated parameters into three groups based on the number of significant correlations: parameters that have 10 or less significant correlations (i.e., *d*), parameters with 11 to 19 significant correlations (i.e., δ^{18}O) and parameters with 20 or 21 significant correlations (i.e., Ca). Stable isotopes are weakly but significantly correlated with different parameters. Considering HCA for all samples collected, samples were linked together based on the time of sampling: the tap water was divided into four clusters (A1, A2, A3, and A4), however when removing the first sample, samples were grouped into three groups (A2, A3, and A4). The cluster A1 (also part of the third visual observed pattern), indicates the influence of the leaching of specific elements (e.g., Fe, Ni, Pb, Zn), probably due to leaching from the water pipe of the internal WSS at the beginning of the experiment, when drinking water starts flowing. The latter was also confirmed with elevated PCA loadings.

Altogether, the results indicate that, as expected, the proportion of water from Kleče and Brest changed throughout the day. However, since no simultaneous data from the sources were provided, the long-term average concentration of Na was considered for SLMM. The proportion of water from Kleče changed from 7% to 90% over the 24 h experiment. Moreover, Cr and As show similar mixing ratios. The results show that at the beginning and the end of the experiment, a higher proportion of the water was from Kleče, whereas between 12:00 and 18:00, most water was from Brest. It should be emphasized that the water managers know the WSS, namely the exact information of the capacity at which wells operate, measured in 15 min intervals. However, by performing this experiment we confirmed their assumptions about the mixing of water in the investigated area with application of elemental composition of tap water. The results, which positively reflect assumptions, show that during the day, when water consumption is high, Brest wellfield contributes a larger share of water. During the night, the Brest wellfield contribution is low and the Kleče wellfield contribution pushes the watershed between the wellfields to the south of the city.

Within this study we can conclude that elemental composition of some elements (i.e., N and As) could be used to provide good proxies of water mixing from two different reservoirs. We must acknowledge that shallow aquifers are characterized by the hydrometeorological seasonal variability that affects the water chemistry. At the time of the experiment, data on the chemistry of water from wells had not been acquired, and long-term data of regular monitoring was used. Therefore, long-term multi-parameter monitoring should be established to determine the monthly and seasonal variations. Finally, we planned to repeat the experiment under different conditions in WSS (i.e., during different seasons and the COVID-19 pandemic when water consumption has significantly changed due to lockdowns) to deduce parameters that can help in long-term evaluation of mixing water at the tap.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/w13111451/s1, Figure S1: Pearson correlation matrix for all the analyzed parameters. * $p \leq 0.005$. H, O, and C represents δ^2H, δ^{18}O and $\delta^{13}C_{DIC}$, respectively; Table S1: Metadata information regarding data attributes; Table S2: Basic sampling attributes and results of temperature (T), electrical conductivity (EC) and pH for all measurements; Table S3: Elemental compositions of the analyzed tap water samples collected every full hour; Table S4: Geochemical characteristics of median concentrations: left for four clusters and right for three clusters; Table S5: Principal component loadings and explained variance for the two components.

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Chapter 4

Data and Resource Management

Databases play a crucial role in organizing and managing large volumes of data, making it easier to store, access, and analyse information. In research, they support collaboration by scientists to share data efficiently, improving the reproducibility of experiments and speeding up discoveries. By integrating different types of data, databases allow researchers to perform different analyses that would be difficult with scattered information. They also help ensure data integrity and security, making them indispensable tools for handling the complexities of modern data and driving innovation (Pauli et al., 2017). Different stakeholders from academia, industry, funding agencies and scholarly publishers have endorsed a set of principles names FAIR Data Principles (Findability, Accessibility, Interoperability, and Reusability). The aim is for these principles to serve as a guide for individuals seeking to improve the reusability of their data collections, applying not only to conventional 'data' but also to the algorithms, tools, and workflows used to generate that data (Wilkinson et al., 2016). Different databases have been initiated in the field of isotope investigations i.e. Global Network of Isotopes in Precipitation ('GNIP', 2019), Global Network of Isotopes in Rivers, IsoBank ('IsoBank'), ('GNIR', 2019), and SLONIP (Vreča et al., 2022).

During our investigations in the frame of CRP, various reports (Nagode & Vreča, 2022b, 2022a; Nagode, Vreča, Kanduč, & Zuliani, 2021; Nagode et al., 2022; Nagode, Vreča, Kanduč, Zuliani, et al., 2021; Vreča, Nagode, Kanduč, Zuliani, & Žigon, 2019; Vreča, Nagode, Kanduč, et al., 2019, 2019) were created. To ensure broader accessibility and usability of our data, we published several databases through the Pangaea Data Publisher for Earth & Environmental Science (Vreča et al., 2020; Žagar et al., 2022a, 2022b). Additionally, two databases were included as a supplementary material in a research publication, further enhancing transparency and reproducibility. Moreover, a map of sampling locations titled "Isotope sampling from source to tap" was prepared to assist other researchers and potential users (retrieved from: https://shorturl.at/tWlHW). This map identifies the points where sampling was conducted providing possibilities for future studies and comparative analyses. Alongside the map, metadata was prepared, providing basic information about the sampling locations and details on where the databases and publications are published.

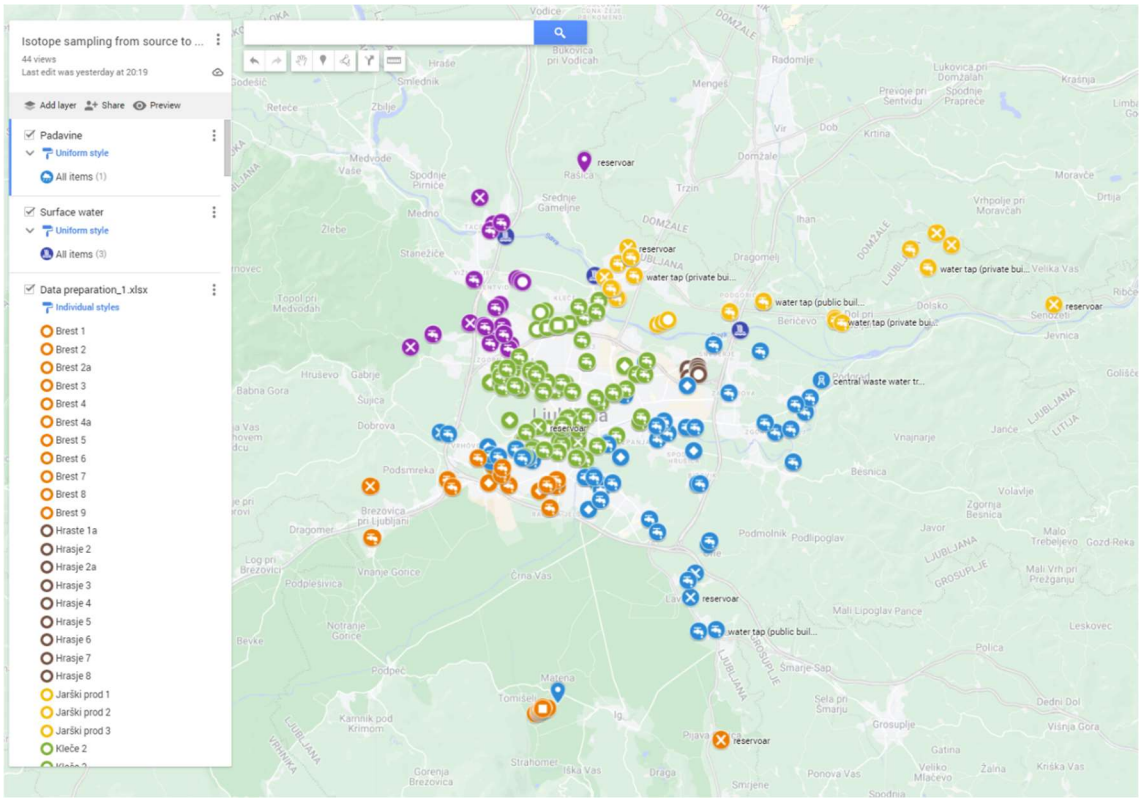

Figure 4.1: Water sampling locations in Ljubljana area, providing visual context for the geographical distribution of our data collection efforts. The metadata offers detailed information on each sampling site, including coordinates, site descriptions, and references to the associated databases and publications.

Chapter 5

Guidelines

In the frame of the CRP a manuscript was prepared by the participants and submitted to Hydrological Processes titled: “Tracing urban drinking water sources: global state of the art and insights from an IAEA-Coordinated Research Project”. In the manuscript, we presented the current research trends and introduce new methodologies for better assessing and managing urban water resources. Different case studies from cities in Canada, the USA, Costa Rica, Ecuador, Morocco, Botswana, Romania, Slovenia, India and Nepal were presented on how isotopic techniques can reveal seasonal and temporal variations in water sources. The findings showed that urban areas rely on a mix of mountain recharge, groundwater extraction, and water transfer from river basins. High-resolution monitoring revealed significant diurnal variations in tropical regions and more uniform variations in areas dependent on groundwater. The study emphasized the potential for isotopic data to improve drinking water treatment and urban water management in response to climate change.

Altogether, these resources not only support the findings presented in this thesis but also contribute to the broader scientific community by offering accessible, well-documented data for further research. Based on the outputs of this study, the guidelines will be prepared for the Slovenian public utility and others interested in the field of the water management using stable water isotopes.

Chapter 6

Conclusions

In urban environments, the heterogenous dynamics of water fluxes, along with the interactions between natural and engineered components of water cycle are often not well understood (Gessner et al., 2014; Pataki et al., 2011). With population growth, urban extensions and climate change, challenges related to water distribution are expected to intensify. Therefore, a deeper comprehension of urban water circulation and the development of adaptive water management strategies are crucial for meeting demand in a sustainable way (Howard & Israfilov, 2002; McGrane, 2016). One promising approach for enhancing the assessment of water sources and flow paths in urban areas is the use of isotope tracers (Ehleringer et al., 2016; Jameel et al., 2016; Kuhlemann et al., 2020). The provision of water for domestic supply usually involves many source (i.e. groundwater surface water) with different isotopic signals. Despite the potential of this method, the number of studies employing isotopes in urban contexts is limited, making it a significant frontier in research (Ehleringer et al., 2016; Kuhlemann et al., 2020).

To address this research gap, this thesis uses stable isotopes of water, in addition to other physico-chemical properties, meteorological data and hydrological data, to evaluate and understand the water sources for domestic supply in urban areas. The study focusses on two aquifers in Ljubljana: Ljubljansko polje and Ljubljansko barje between 2019 and 2021. We started with summary of previous investigations of water source in the Ljubljana area (Chapter 3.1). It includes a preliminary investigation tracing water from source to tap (Chapter 3.2), an analysis of the dynamics and partitioning of water sources (Chapter 3.3), and an examination of tap water samples collected from various locations around Ljubljana across three different seasons (Chapter 3.4). Additionally, a 24-hour experiment was conducted to gain further insights (Chapter 3.5) and data and resource management strategies are discussed (Chapter 3.6). At the end (Chapter 3.7), guidelines are presented. This research complements the activities performed under the IAEA CRP F33024.

The review of previous isotope investigations of the Ljubljansko polje and Ljubljansko barje aquifers showed that sampling was performed at multiple sites capturing spatial and temporal variations. However, many studies were short-term and intermittent, highlighting the need for continuous, long-term monitoring programs. The sampling network, particularly in wellfields and other parts of water supply system, was insufficient. One of the main gaps identified is also lacking of detailed information on sampling times, locations, and methods, making reproducibility and data comparison difficult. Therefore, the study design was prepared in order to answer the specific goals and hypotheses of this dissertation.

The conclusions drawn from this research confirm that the properties of water can change significantly from the source (precipitation and surface water) to the end-user. This change is driven by a combination of natural processes in the aquifer and its recharge area

and anthropogenic influences within the water supply system. These changes are evident in the isotopic composition of hydrogen and oxygen and physico-chemical properties of the water (temperature, pH, electrical conductivity), providing valuable insights into the behaviour of water sources, the dynamics within a complex water supply system, and the impacts of human activities and climate change on freshwater resources.

The dissertation also validated three sub-hypotheses.

1.) Stable water isotopes can be used in the urban water supply systems and assess changes in the water cycle.

The use of stable water isotopes in urban water supply systems has been proven to be an effective method for tracing urban water dynamics and assessing changes in the water cycle. In our study, this approach involved collecting samples over large temporal and spatial scales to gain an understanding of city-wide water fluxes. In the case of Ljubljana, a relatively small city, the isotope composition from different sources exhibited a narrow range. Despite this, some statistical significance was observed. The δ^{2}H and δ^{18}O signatures of precipitation showed seasonal variation, but such seasonality was not evident in the water supply system (WSS). Surface water sampling points revealed a strongly dampened isotope signal with almost no observed seasonality. At the Ljubljansko polje, the groundwater isotope signals varied depending on the well's location and the contributions from precipitation and the Sava River. In contrast, at the Ljubljansko barje, deeper wells exhibited more negative isotope signals with no observed seasonality compared to shallower wells. This signal further diminished when entering the water supply system. The isotopic signal range of tap water was narrow; however, variations were observed, i.e. more positive signals in the Šentvid water supply area and more negative signals in the Brest WSA.

One major limitation observed during the study was the small range of isotope signals of sources and therefore also from various objects of the water supply system. This is due to the limited size of the Ljubljana catchment, highlighting the need for measurements of additional parameters. Similarly, monthly sampling can obscure temporal variability; thus, higher-resolution sampling over more extended periods would likely reveal more complex dynamics. For example, water temperature data collected within the water supply system showed the smallest temperature range for wells compared to other objects within the WSS.

2.) Changes in the source contribution can be observed in the study area by determining the isotopic composition and other hydro-chemical parameters

The study demonstrates that changes in the source contributions to groundwater can be effectively monitored by determining the isotopic composition and other hydro-chemical parameters. The variations in isotopic signals across different wells and aquifers provide valuable insights into the recharge dynamics and the relative contributions of surface water and local precipitation. In the Kleče wellfield, the contribution of the Sava River to groundwater recharge has increased compared to precipitation. The largest differences were observed in wells of Kleče wellfield K-8a (38 %) and K-11 (33 %), both centrally located within the wellfield. In well H-3 (wellfield Hrastje), the contribution of surface water increased significantly by 47 %, while in other wells like H-1a, the increase was slight. On other hand, surface water contribution decreased in wells Š-2a (−10 %) (wellfield Šentvid) and Jp-3 (−18 %), with no change observed in Jp-1(wellfield Jarški prod). These findings align with previous studies indicating the Sava River's role in supplying and draining the Lp aquifer.

In addition, the isotopic composition in the Brest wellfield and the Iška River indicates that riverbed surface infiltration is a crucial recharge component for the shallower Lb aquifer. However, the more positive isotope signals in shallow wells suggest that precipitation contributes more to groundwater recharge than surface water. The most positive isotope values were observed during the winter months in well B-8, corresponding to the more positive isotope signal of surface water and precipitation during warmer months. The most negative values were observed in deeper wells with minimal temporal variability.

3.) The observed changes in the isotopic composition of water sources in the study area are correlated with climatic variations and trends.

The study supports the hypothesis that climatic variations and trends significantly influence the isotopic composition of water sources in the study area. The Alpine region's contributing to the recharge of the Sava River, projected above-average warming and changing climate patterns (e.g., shorter periods with reduced snow cover, increased winter precipitation, and higher intensity of extreme events) are likely to impact future recharge rates, thus affecting the isotopic composition of the river. Based on the precipitation and surface water, the mean residence time of surface water was determined at the Sava River. The mean residence times of 4.1 and 3.5 years at Brod and Šentjakob were estimated, respectively, suggesting a minimal influence of young water from recent precipitation. The observed longer MRT, likely resulting from sampling during low and semi-low flow conditions, suggests that similar conditions will become more common in the future, also due to projections of higher temperatures. The longer MRT implies that the surface water age estimates derive from older groundwater reservoirs, with ages exceeding the stable isotope discernment limit of four years.

The hypotheses can also be confirmed based on the Iška River, recharging the Ljubljansko polje aquifer. The Iška River's smaller size makes it more vulnerable to warm and dry climatic conditions, as reflected in the positive $\delta^{18}O$ values and lower d-excess observed during the study period, indicating surface evaporation.

When comparing the tap water data gathered during our sampling with the previous investigations in 2014, showed more negative isotopic values, highlighting the impact of climatic conditions on isotopic composition.

Lastly, we emphasize the importance of publishing databases and accompanying metadata. Accessible and well-documented data sets are crucial for ensuring transparency, reproducibility, and collaboration in scientific research. They enable other researchers to verify findings, build upon the existing work, and apply similar methodologies to different contexts or regions.

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Biography

Klara Žagar was born on November 11 1993 in Ljubljana, Slovenia. She completed her primary school education at 8 Talcev in Logatec and graduated from the Diocesan Classical Gymnasium in Ljubljana in 2012. That same year, she enrolled in the Faculty of Natural Sciences and Engineering, Department of Geology, at the University of Ljubljana. She earned her bachelor's degree in geology with a thesis titled "Mineralogical and Geochemical Characteristics of Archaeological Ceramics from the Bukovščica Site." During her undergraduate studies, she worked for a year at the Institute for the Protection of Cultural Heritage. In 2015 she commenced her master's studies in Geoenvironment and Geochemistry at the same faculty, where she defended her thesis titled "The effect of clinkerization process on mineralogical properties of belite-sulfoaluminate clinkers". Her master thesis was prepared at the Slovenian National Building and Civil Engineering Institute and during her six months Erasmus+ exchange traineeship at the Institute for Mineralogy and Crystallography in Vienna, Austria.

Klara began her PhD studies in 2019 at the Jožef Stefan Postgraduate School, Ljubljana, Slovenia, under the supervision of Dr. Polona Vreča. Most of her experimental work for the PhD was carried out at the Department of Environmental Sciences, JSI. Her research primarily focused on isotope hydrology in the urban areas. The work was related to the IAEA CRP (F33024) entitled "Use of Isotope Techniques for the Evaluation of Water Sources for Domestic Supply in Urban Areas". In 2022, she received a three-month internship position at the International Atomic Energy Agency (IAEA) in Vienna, at the Isotope Hydrology Section. Later that year, she received a one-month fellowship scholarship from the same department. In addition, she participated in eight trainings regarding the isotope hydrology, modelling and R language. She also actively participated at domestic and international projects.

Throughout her academic journey, Klara was actively involved in the Student Council and served as the President of the IPSSC Student Conference organizing team. She participated in numerous workshops and attended various national and international conferences. Notably, she received the Best Poster award at the 2nd ISO FOOD conference in 2023, held in Piran, Slovenia.