



University of Zagreb

Faculty of Geotechnical Engineering

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**WATER SUPPLY SYSTEM  
MANAGEMENT BY MEANS OF  
HYDROCHEMICAL AND ISOTOPE  
PARAMETERS**

DOCTORAL DISSERTATION

Varaždin, 2026





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Supervisors:

Professor Ivan Kovač, PhD

Scientific Adviser Tamara Marković, PhD

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Sveučilište u Zagrebu

Geotehnički fakultet

Nikolina Novotni-Horčička

**UPRAVLJANJE VODOOPSKRBNIM  
SUSTAVOM POMOĆU  
HIDROKEMIJSKIH I IZOTOPNIH  
PARAMETARA**

DOKTORSKI RAD

Mentori:

Prof.dr.sc. Ivan Kovač

Dr.sc. Tamara Marković, znanstvena savjetnica u trajnom  
izboru

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## SUPERVISORS

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**Professor Ivan Kovač** began his career at the construction company *Niskogradnja*, Pregrada, where he worked as a quarry manager from 1989 to 1990. Since 1990, he has been employed at the Faculty of Geotechnical Engineering, University of Zagreb, where he teaches courses ranging from undergraduate to doctoral levels, including *Applied Statistics*, *Geostatistics in Environmental Protection*, *Groundwater Exploitation*, *Environmental Risk Assessment*, and *Ecological Modeling*.

He earned his **Master of Science** degree in 1995 with the thesis *Contribution to Reserve Calculation and Production Planning at Smaller Ore Deposits*, under the supervision of Professor Uroš Bajželj and Professor Franc Žerdin at the University of Ljubljana. In 2004, he obtained his **PhD** from the Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, with the dissertation *Statistical-Variographic Analysis of Groundwater Chemical Composition in the Varaždin Region*, supervised by Professor Emeritus Darko Mayer and Professor Pero Marijanović.

From the beginning of the 2011/2012 academic year until the end of 2014/2015, he served as **Vice-Dean for Teaching**. Between 1 April 2017 and 30 September 2018, he was **Head of the Department of Environmental Engineering**. He was promoted to **Associate Professor** in 2019 and to **Full Professor** in 2024.

His research focuses on modeling in mining and environmental engineering, monitoring of groundwater quality, and the application of statistical and geostatistical methods.

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**Dr. Tamara Marković** is a Scientific Advisor at the Department of Hydrogeology and Engineering Geology, Croatian Geological Survey in Zagreb. She holds a PhD in Geological Sciences from the University of Zagreb (2007), where she focused on geochemical modeling of the unsaturated zone. She previously earned her MSc (2003) researching contaminant mobility in karst systems, and her BSc in Geology (1999). Her research spans karst and alluvial hydrogeology, isotope hydrology, and environmental geochemistry, with a focus on groundwater recharge, water quality, and pollutant dynamics. She applies tracer methods, stable isotope analysis, and hydrochemical modeling in assessing aquifer vulnerability. More recently, she has worked on nitrate pollution and geothermal aquifer hydrochemistry, using multi-proxy approaches. Her studies contribute to sustainable water resource management and support evidence-based environmental policy. She has participated in international training programs, including those at Joanneum Research (Austria), Hydroisotop (Germany), and several IAEA-led workshops (2020–2022) on isotope hydrology and noble gases in hydrological studies. She regularly collaborates with European partners on fieldwork, data modeling, and laboratory-based analyses, strengthening cross-border expertise in water science. She currently leads the IAEA-funded project on convective rain impacts on groundwater recharge (2022–2026), and previously led the TRANITAL (2017–2021) and HRZZ ESF doctoral training (2018–2022) projects. She is also a collaborator on EU COST Action WATSON, H2020 GeoTwinn, and other international initiatives on water resource resilience and climate adaptation. These projects involve interdisciplinary cooperation and integrate hydrological, chemical, and ecological datasets. Dr. Marković has published over 60 peer-reviewed articles and contributed to more than 90 scientific conferences. Her work has received over 500 citations (h-index 14). She regularly reviews for leading journals and evaluates projects for Croatian (HRZZ), Slovenian (ARIS), and Hungarian (NKFI) research agencies. She has also participated in lab assessments at Ruder Bošković Institute. She served as guest editor for *Water and Geologia Croatica*, and participates in national science committees. She has supervised three PhD theses and co-supervised several master's theses, actively supporting early-career scientists in hydrogeology and environmental geoscience. Her mentorship emphasizes applied skills in field investigations, isotope analysis, and groundwater modeling. She is a dedicated educator and advocate for interdisciplinary approaches to groundwater protection. She regularly presents her findings at international symposia and publishes in journals spanning geology, hydrology, and environmental science.

## Abstract

Public water supply is a complex system whose main goal is to supply consumers with water that is safe for human consumption. Management of this system is mainly carried out by remote monitoring and control by regulating mechanical and hydraulic parameters. Most public suppliers monitor water quality using their own laboratory. In this work, the collected results of routine water analyses were used to improve water supply management. In addition, hydrochemical and isotopic measurements within the system and various geochemical modeling were carried out in order to determine the flow directions, the proportion of water from different sources and the retention time of water in the network. Likewise, on the example of the smallest spring, measurements of noble gases and isotopes  $^3\text{H}$ ,  $\delta^{13}\text{C}$  and  $^{222}\text{Rn}$  were carried out in order to define the recharge of the spring, the risk of pollution, and relate it to the reaction time in the water supply. The main goal of the work is to show how routine chemical analyses and geochemical modeling can help in the management of the water supply system (WSS).

This study focuses on the WSS of the Varaždin County, Croatia, a complex network sourcing water from two alluvial aquifer wellfields (Bartolovec and Vinokovščak) and one karstic spring (Belski Dol).

A one-year sampling campaign was conducted to assess key chemical parameters, including major cations and anions, as well as stable water isotopes ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ). Supplementary measurements of noble gases,  $^3\text{H}$ ,  $\delta^{13}\text{C}$ , and  $^{222}\text{Rn}$  at the Belski Dol spring provided insights into spring recharge dynamics, pollution risk, and response times within the WSS. Results from geochemical and isotopic analyses revealed minor compositional changes throughout the WSS, all within the prescribed Maximum Contaminant Levels (MCL) for drinking water. However, factors such as water retention time, calcium carbonate precipitation, pH variability, and microbial activity were identified as potential factors influencing water quality.

Statistical analysis confirmed significant spatial variation in water quality parameters, reflecting the influence of mixing patterns among different sources. The Piper diagram and geochemical modeling approaches, particularly inverse modeling, proved effective in distinguishing source contributions and identifying regional mixing behaviors. It was observed that the western, southwestern, and northern zones receive water from all three sources, whereas the eastern and southeastern sectors depend more heavily on the Bartolovec aquifer, indicating zones of increased vulnerability.

This study underscores the value of integrating routine monitoring with advanced geochemical tools to improve the understanding and management of WSSs. The findings highlight the importance of proactive risk assessment and modeling for safeguarding water quality and ensuring system resilience.

**Keywords:** water supply system, geochemical modeling, water retention time, isotopes, chemical composition, vulnerability of groundwater and water supply system, TIN approach, Varaždin County

## Extended abstract

Water intended for public supply enters the water supply system (WSS) in accordance with the prescribed standards for water intended for human consumption (Directive (EU) 2020/2184, 2020). Prior to this, it undergoes varying degrees of treatment, depending on the quality of the source water, to meet these standards, and is disinfected before entering the WSS. Nevertheless, once within the distribution network, the water remains subject to various physical, chemical, and biological processes that can degrade its quality and affect its organoleptic properties perceived by consumers. Public utilities continuously monitor water quality within the system through internal or accredited external laboratories, collecting data that provide insight into compliance with regulatory requirements.

In this study, routine monitoring results were complemented by experimental data obtained during a one-year sampling campaign aimed at assessing major cations, anions, and stable isotopes of water. The study area comprised the public water supply system managed by Varkom d.o.o. in Varaždin County, northwestern Croatia. Using these datasets, the statistical significance of variations in fundamental water quality parameters among different WSS locations was evaluated, along with the estimation of water residence time within the system. The results revealed only minor variations in water chemistry throughout the WSS, remaining below the Maximum Contaminant Level (MCL) for human consumption. However, factors such as water retention time, calcium carbonate scaling, pH variability, and microbial growth may influence overall water suitability, highlighting the need for further research into potential risks affecting water quality.

Effective management of WSS is essential to ensure the provision of safe drinking water. To achieve a comprehensive characterization of the system, the collected data were integrated with geochemical modeling. The water mixing processes within the WSS were evaluated using three complementary approaches:

i) mass balance (MB); ii) inverse geochemical modeling using PHREEQC software (IM); and iii) forward geochemical modeling via NETPATH software, based on end-member mixing (FM).

Inverse modeling proved to be more reliable than both forward and mass balance approaches. The results indicated that the western, southwestern, and northern sectors of the WSS receive water from all three sources, while the eastern and southeastern sections primarily rely on the deeper Bartolovec wellfield aquifer, indicating potential vulnerability. Rigorous validation criteria ensured the robustness of the findings, demonstrating the efficiency and applicability of geochemical modeling for water security and management planning.

Groundwater and distribution systems are increasingly susceptible to contamination, yet most assessments address either hydrogeological or infrastructural risks. This study introduces the **Total Integrated Network (TIN)** approach, a comprehensive framework designed to evaluate vulnerability from source to tap. Field investigations were conducted in Varaždin County, Croatia, focusing on the Belski Dol spring, Briška reservoir, and pumping station (PS) Filipići. Hydrochemical analyses, stable isotopes of water ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ), tritium, noble gases, and radon concentrations were monitored and combined with system-level evaluations.

The results indicate that the Belski Dol spring exhibits high stability and low vulnerability, with a TIN index of approximately 25%, supported by long groundwater residence times and stable water quality. PS Filipići shows moderate vulnerability (35%), whereas the Briška reservoir records the highest index (53%), linked to elevated radon and nitrate concentrations and infrastructure-related risks. These findings suggest that natural hydrogeological protection alone cannot guarantee safe drinking water. The TIN framework emphasizes the necessity of integrating aquifer characteristics with distribution system performance to identify critical control points and prioritize mitigation measures.

In summary, the results demonstrate effective and improved management of the water supply system using routine daily water analyses, supplemented by isotopic analyses through geochemical modeling and system vulnerability assessment using the TIN methodology. This approach provides a more realistic basis for water supply security management, supporting proactive measures to improve system resilience and protect public health.

**Keywords:** water supply system, geochemical modeling, water retention time, isotopes, chemical composition, vulnerability of groundwater and water supply system, TIN approach, Varaždin County

## Prošireni sažetak

Voda namijenjena javnoj vodoopskrbi ulazi u javni vodoopskrbni sustav (VS) u skladu s propisanim standardima za vodu namijenjenu ljudskoj potrošnji (Diretiva (EU) 2020/2184, 2020). Prije toga prolazi kroz različite stupnjeve obrade, ovisno o kvaliteti izvorišne vode, kako bi zadovoljila te standarde te se dezinficira prije ulaska u sustav. Ipak, i unutar samog distributivnog sustava voda je podložna različitim fizikalnim, kemijskim i biološkim procesima koji mogu utjecati na njezinu kvalitetu i organoleptička svojstva koja primjećuju potrošači. Javni isporučitelji kontinuirano prate kvalitetu vode u sustavu putem vlastitih ili akreditiranih vanjskih laboratorija, prikupljajući podatke koji omogućuju uvid u usklađenost vode s propisanim zahtjevima.

U ovom istraživanju rutinski rezultati praćenja nadopunjeni su eksperimentalnim podacima prikupljenima tijekom jednogodišnje kampanje uzorkovanja, s ciljem procjene glavnih kationa, aniona i stabilnih izotopa vode. Istraživano područje obuhvaća javni vodoopskrbni sustav kojim upravlja Varkom d.o.o. u Varaždinskoj županiji, sjeverozapadna Hrvatska. Na temelju ovih podataka procijenjena je statistička značajnost razlika u osnovnim parametrima kvalitete vode između različitih lokacija u sustavu, kao i vrijeme zadržavanja vode u mreži. Rezultati su pokazali tek manje promjene u kemijskom sastavu vode unutar sustava, koje su ostale ispod maksimalno dopuštenih koncentracija (MDK) za ljudsku potrošnju. Ipak, čimbenici poput vremena zadržavanja vode, stvaranja naslaga kalcijeva karbonata, promjena pH vrijednosti i mikrobiološkog rasta mogu utjecati na prikladnost vode, što ukazuje na potrebu za daljnjim istraživanjima mogućih rizika koji utječu na njezinu kvalitetu.

Učinkovito upravljanje sustavom javne vodoopskrbe ključno je za osiguranje sigurne vode za piće. Kako bi se postigla cjelovita karakterizacija sustava, prikupljeni podaci integrirani su s geokemijskim modeliranjem. Proces miješanja vode u sustavu procijenjen je pomoću triju pristupa:

i) modelom masene ravnoteže (MB); ii) inverznim geokemijskim modeliranjem pomoću softvera PHREEQC (IM); te iii) direktnim (forward) geokemijskim modeliranjem pomoću softvera NETPATH, koji se temelji na pristupu modeliranja krajnjih članova (FM).

Inverzno modeliranje pokazalo se pouzdanijim u odnosu na izravno modeliranje i model masene ravnoteže. Rezultati su pokazali da zapadni, jugozapadni i sjeverni dijelovi sustava primaju vodu iz sva tri izvora, dok se istočni, jugoistočni i sjeverni dijelovi uglavnom oslanjaju na dublji vodonosnik crpilišta Bartolovec, što ukazuje na potencijalnu ranjivost. Strogi kriteriji validacije osigurali su pouzdanost rezultata, potvrđujući učinkovitost i primjenjivost geokemijskog modeliranja u planiranju sigurnosti i upravljanja opskrbom vodom.

Podzemne vode i vodoopskrbni sustavi sve su osjetljiviji na onečišćenje, no većina procjena razmatra hidrogeološke ili infrastrukturne rizike zasebno. Ovo istraživanje uvodi **Total Integrated Network (TIN)** pristup, sveobuhvatan okvir osmišljen za procjenu ranjivosti od izvora do slavine. Terenska istraživanja provedena su u Varaždinskoj županiji, s fokusom na izvor Belski Dol, vodospremu Briška i precrpnu stanicu Filipići. Provedene su hidrokemijske analize, određivanje stabilnih izotopa vode ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ), tricija, plemenitih plinova i koncentracija radona, u kombinaciji s procjenama na razini sustava.

Rezultati su pokazali da izvor Belski Dol karakterizira visoka stabilnost i niska ranjivost, s TIN indeksom od približno 25 %, što je povezano s dugim vremenom zadržavanja podzemne vode i stabilnom kvalitetom. Precrpnna stanica Filipići pokazala je umjerenu ranjivost (35 %), dok je vodosprema Briška imala najviši indeks (53 %), što se povezuje s povišenim koncentracijama radona i nitrata te infrastrukturnim rizicima. Ovi rezultati ukazuju da prirodna hidrogeološka zaštita sama po sebi ne može osigurati sigurnu vodu za piće. TIN pristup naglašava važnost integracije uvjeta u vodonosniku s učinkom distribucijskog sustava kako bi se identificirale ključne kontrolne točke i odredili prioriteta za intervencije.

Ukratko, rezultati prikazuju učinkovito i poboljšano upravljanje vodoopskrbnim sustavom korištenjem svakodnevnih rutinskih analiza vode, dopunjenih izotopnim analizama kroz geokemijsko modeliranje i procjenu ranjivosti sustava TIN metodologijom. Na taj način je dobivena realnija osnova za upravljanje sigurnošću vodoopskrbe, podupirući proaktivne mjere za poboljšanje otpornosti sustava i zaštitu javnog zdravlja.

**Ključne riječi:** vodoopskrbni sustav, geokemijsko modeliranje, vrijeme zadržavanja vode, izotopi, kemijski sastav, ranjivost, TIN pristup, Varaždinska županija

## **Author's publications included in the doctoral dissertation:**

### **Publication No. 1:**

**Novotni-Horčička, N.**, Marković, T., Kovač, I., & Karlović, I. (2024). Exploring endogenous processes in water supply systems: Insights from statistical methods and  $\delta^{18}\text{O}$  analysis. *Water*, 16(10), 1425. <https://doi.org/10.3390/w16101425>

### **Publication No. 2:**

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### **Publication No. 3:**

Marković, T., **Novotni-Horčička, N.**, Palcsu, L., & Karlović, I. (2025). Assessment of groundwater vulnerability from source to tap using TIN approach. *Water*, 17 (23), 3341. <https://doi.org/10.3390/w17233341>

# Introduction

## Importance of drinking water supply system

One of the fundamental human rights is the right to water, which was established by the United Nations Resolution (UNGA, 2010; UN 2015), and it arose from the historic UN Conference in Dublin, which established four basic principles on water (UN, 1992):

- Water has economic and social values
- Water management must be participatory
- Women have a key role in water management.
- Water is a limited and vulnerable resource.

*The key principles common to legislation in the world came from several basic principles that are repeated in international documents, conventions and guidelines: the UN human rights framework (UNGA, 2010), the Sustainable Development Goals (UN, 2015), the UNECE Water Convention (1992), the EU Water Framework Directive (2000/60/EC), and supporting guidance from WHO (2023a), OECD (2021), GWP (2020), and the Dublin Statement on Water and Sustainable Development (1992).*

Key Principles Common to Water Legislation Worldwide:

1. Human Right to Water – Access to safe and affordable drinking water is recognized as a fundamental human right (UNGA, 2010; UN, 2015). States are responsible for ensuring universal and equitable access without discrimination.
2. Sustainable and Integrated Water Management – Modern legislation adopts an Integrated Water Resources Management (IWRM) approach, emphasizing ecological balance, basin-level planning, and intersectoral coordination (GWP, 2020; UNECE, 1992; EU, 2000).
3. Source-to-Tap Risk Management – Protection of water resources “from catchment to consumer” is a key regulatory requirement ensuring both preventive and corrective actions (WHO, 2023a; EU, 2000).
4. Transparency and Public Participation – Access to water-related information and public involvement in decision-making are essential components of accountable governance (OECD, 2021; UNECE 1992; EU, 2000).
5. Economic and Social Sustainability – Legislative frameworks promote cost recovery and efficiency while maintaining affordability and equity, especially for vulnerable groups (UN, 2015; OECD, 2021; GWP, 2020).

6. Water as a Public Good and Essential Service – Water supply is defined as a public service of general interest that must be provided under state oversight to guarantee public health and social stability (UN, 1992; UNGA, 2010; WHO, 2023).

Back in 2015, the UN adopted the Sustainable Development Goals (SDGs) to be achieved by 2030 of which SDG 6 is clean water and sanitation for all (UN, 2015). According to the 2021 update, 26% (2 billion) of the world's population still lacks a safe drinking water supply, and as many as 46% lack safe sanitation (UN-Water, 2021). In light of all of the above, water and public water supply are more important than ever before.

In Croatia, water management and supply of water intended for human consumption is regulated through national regulations (OG, 2019; OG, 2023) that were adopted by the implementation of European Union directives (EU Directive, 2000; EU, 2020; Council of EC, 1991a; Council of EC, 1991b; EU Parliament and Council of EU, 2006). According to the State Audit Office of the Republic of Croatia (2024), approximately 93.4% of the population has access to public water supply networks, while 86.9% are actually connected. (State Audit Office of the Republic of Croatia, 2024). Although data for Croatia show that the vast majority of the population has safe access to drinking water, there is still room for improvement. In addition, high standards have been set for public suppliers, mandating that they provide water that is safe, hygienic and always available in adequate quantities.

Ensuring continuous and equitable access to potable water has become increasingly complex and costly as a result of population growth, the expanding distance between available water sources and urban centers, heightened contamination risks, and the effects of climate change (Gleick, 2003). Addressing these challenges requires a combination of technological innovation, systematic management, and adherence to regulatory frameworks.

Public water suppliers employ various technological and operational strategies to ensure that the water supplied to consumers meets both quality and quantity requirements (Tipple et al., 2017a). Due to the increasing impact of climate change on the environment, emissions that disrupt the natural balance, increasing costs and the requirements to achieve sustainable development goals, water supply management strategies are becoming increasingly important (Mian et al., 2023). The World Health Organization advocates an approach to water supply management through Water Safety Plans, which are now recognized as best practices for ensuring safe water supply - from source to consumer (WHO, 2023b). They are based on the principle of risk identification, prevention and multiple barriers of protection that help prevent the occurrence of water-borne epidemics and increase the reliability of water supply. Therefore, the effective protection and management of both water resources and distribution infrastructure

are of paramount importance. Sound management practices not only minimize water losses, thus ensuring adequate supply, but also prevent contamination within the network. These practices form the foundation of sustainable water supply management and contribute directly to the reliability and safety of the delivered water.

Water distribution systems represent complex and extensive networks composed of pipelines, valves, and reservoirs through which water is transported to end-users. Throughout this process, a range of physical, chemical, and biological factors can influence water quality and consequently affect consumer satisfaction and public health.

A comprehensive understanding of system operation is essential for water utilities to effectively respond to incidents such as pipeline ruptures, contamination events, or consumer complaints. Such understanding facilitates the identification of root causes and the implementation of corrective and preventive measures to mitigate risks and restore system functionality.

Continuous monitoring of drinking water quality is essential to verify compliance with the standards established by WHO through guidelines which are incorporated in national and regional regulatory frameworks such as Directive on the quality of water intended for human consumption (Directive (EU) 2020/2184, 2020). Accordingly, water utilities, using their own laboratories and through authorized laboratories, continuously monitor the quality of water in the inflow area, water resources and in the WSS.

This study investigated the possibility of using these data not only for the assessment of water conformity, but also for improving the management of WSS, which would enhance response in accident situations. This was particularly useful in WSS where several sources were used for supply, so the delivered water was usually a mixture of pumped water. Isotopes  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ,  $^3\text{H}$ , noble gases, and  $^{222}\text{Rn}$  have proven to be useful natural tracers for defining the recharge area and water temperature at the time of aquifer recharge, as well as for determining groundwater residence time and interactions between water and the aquifer matrix. Here, their application within the WSS itself was investigated through the introduction of the novel Total Integrated Network (TIN) approach, a framework designed to evaluate vulnerability from source to tap.

## **Previous research on water supply system management**

Before entering the water supply system (WSS), raw water typically undergoes a series of conditioning and disinfection processes, depending on the quality of the source. However, once water enters th

e distribution network, it is subjected to various physical, chemical, and biological processes that can affect both regulatory compliance and organoleptic properties (Liu, G. et al., 2015).

The most common causes of water quality deterioration within WSSs include pipeline failures, sudden or intermittent changes in flow conditions (Weston, 2021), water stagnation (Fuertes-Miguel, 2022; Nisar et al., 2020), and prolonged water retention resulting from reduced consumption or long distances between the source and end users (Wang et al., 2025). According to the US EPA (2002), water retention time, commonly referred to as water age, is the primary factor influencing water quality degradation in distribution systems. Reduced consumption or over-dimensioning the system to meet fire flow requirements often leads to extended residence times in pipes and reservoirs. As a result, disinfectant concentrations decline, promoting microbial regrowth, pH fluctuations, increases in water temperature particularly during warmer periods, and a range of physicochemical reactions involving pipe materials and accumulated sediments.

Additional processes contributing to water quality degradation include corrosion of metallic surfaces, accumulation and subsequent release of deposits from pipe walls, and the formation of disinfection by-products (DBPs). DBPs arise from reactions between disinfectants and natural organic matter (Prest et al., 2016a; Fish et al., 2017; Ainsworth, 2004; Liu J. et al., 2015; Boulay et al., 2001; Gonzales et al., 2013), as a product of decomposition of disinfectant (Driljo, 2015), as well as from reactions between bromide and oxidizing agents, leading to bromate formation (Garcia-Villanova et al., 2010; Wang et al., 2022).

Biofilms are ubiquitous in water distribution pipelines (Douterelo et al., 2016; Fish et al., 2017), and sediments are present in all systems, even those with highly effective treatment processes (Vreeburg & Boxall, 2007; Husband & Boxall, 2011). Sudden hydraulic disturbances can mobilize these deposits, resulting in water quality deterioration. Such events may cause increased turbidity and microbiological contamination, as well as the release of metals, elevated concentrations of nitrogen, phosphorus, and organic matter, and changes in colour, taste, and odour (Vreeburg, 2010; Wang et al., 2025).

These considerations clearly demonstrate that water quality monitoring exclusively at the entry point of the WSS cannot guarantee equivalent quality at the consumer's tap. Consequently, continuous monitoring at multiple points within the distribution network is essential.

In addition to water quality, ensuring adequate water quantity and pressure throughout the WSS is of critical importance. Water quantity assessments commonly rely on deterministic or probabilistic hydraulic analyses to evaluate flow rates, pressures, and other network parameters (Puust et al., 2010; Mutikanga et al., 2013; Tipple et al., 2017a). Although these methods are

well established, they are computationally intensive and often constrained by insufficient field data, which complicates model calibration and validation (Waldrip et al., 2016).

To ensure the continuous delivery of safe drinking water, water utilities implement systematic monitoring programs that include routine chemical and microbiological analyses. The frequency and scope of these analyses depend on the size of the population served or the volume of distributed water and are defined within water safety and sampling plans (WHO, 2023a; OG 88/2023). Operational monitoring typically includes daily measurements of temperature, turbidity, disinfectant concentration ( $\text{ClO}_2$ ,  $\text{Cl}_2$ ), electrical conductivity (EC), pH, major anions and cations, and microbiological indicators such as coliform bacteria, enterococci, *Escherichia coli*, and total bacterial counts. While the primary purpose of these measurements is to assess current water quality at sampling locations, long-term datasets also provide substantial added value when analysed using appropriate statistical and modeling approaches.

Continuous data collection and evaluation enable water suppliers to identify spatial and temporal variations in water quality, support informed operational decision-making, improve system efficiency, and ensure compliance with national and European regulations (Directive (EU) 2020/2184; OG, 2023a; OG, 2023b). Furthermore, accumulated datasets form the basis for statistical and predictive analyses aimed at detecting trends and forecasting potential short- and long-term water quality deterioration (Nemčić-Jurec et al., 2022a; Ruk et al., 2022; Mohammed et al., 2022a; Maiolo, S. et al., 2021). Such predictive capabilities are essential for proactive system management and long-term sustainability.

When non-compliance is identified within a section of the WSS, determining the origin of the supplied water is crucial. In systems supplied by multiple sources, identifying water origin based solely on hydraulic indicators is often challenging. In this context, hydrochemical analyses, combined with historical data and water mixing models, represent a valuable tool for identifying the causes of non-compliance. Geochemical modeling has been widely applied to identify hydrogeochemical processes and to evaluate mixing relationships among different water types (Karlović et al., 2022b; Ezzeldin & Bahr, 2023; Arya et al., 2021; Marković et al., 2013), particularly within recharge areas. The application of mixing models directly within WSSs, using alternative modeling tools, has also been explored in several studies (Jameel et al., 2016; Nagode et al., 2021). Stable isotopes of water, specifically  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , have proven to be reliable tracers for identifying water flow patterns within distribution networks and for linking distributed water to its sources (Nagode et al., 2021; Jameel et al., 2016; Grimmeisen et al., 2017). The use of stable isotopes and geochemical parameters as natural tracers is well established in hydrological and hydrogeological studies (Froelich et al., 2002; Dotiska et al.,

2010; Gross et al., 2019; Vreča & Kern, 2020). In several studies, isotopic and geochemical approaches have demonstrated greater reliability than simplified deterministic or probabilistic network analyses (Tipple et al., 2017b; Mutikanga et al., 2013).

In this study, three complementary approaches were applied to quantify water mixing ratios. The first approach is based on mass balance (MB) calculations, a widely used method (Vázquez-Suñé et al., 2010; Eberts et al., 2013; Hepburn et al., 2020), in which the proportions of two end-members in a mixed sample are estimated using conservative tracers, namely  $\text{Cl}^-$  and  $\delta^{18}\text{O}$ . The remaining two approaches employ geochemical modeling software to infer the physical and chemical processes controlling water chemistry along flow paths, specifically within the water supply network (pipelines and reservoirs), and to quantify reactions occurring within this system. Inverse geochemical modeling (IM) was conducted using the PHREEQC software (Parkhurst & Appelo, 2013). The software applies a mole-balance approach to calculate phase transfers (i.e., the amounts of minerals and gases entering or leaving solution) to explain the observed compositional differences between initial and final water along a defined flow path, in this case within the WSS. The third approach involved forward geochemical modeling (FM) using NETPATH-WIN software (Plummer et al., 1994; El-Kadi et al., 2010).

Water residence time within WSSs can be estimated using chemical tracers, mathematical models, or integrated approaches, each with specific advantages and limitations (US EPA, 2002; Smith et al., 2001; Monteiro et al., 2021; Gross et al., 2019; Burkhart & Janke, 2023; Zhou et al., 2021). In recent years, naturally occurring radioactive and stable isotopes have increasingly been applied for this purpose (Waples et al., 2015). Stable isotopes of water ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) provide additional insight into water residence time and related chemical processes (Kralik, 2015; de Wet et al., 2020; Leslie et al., 2014; Nagode et al., 2022; Sanchez-Murillo et al., 2020; Marković et al., 2020).

Protecting the environment and maintaining the quality of groundwater used for human consumption require a thorough assessment of groundwater vulnerability. However, as evidenced by the discussion above, vulnerability assessment is needed not only at the catchment scale but also within the WSS itself. Numerous methods have been developed to evaluate groundwater vulnerability in support of aquifer protection (Aller et al., 1987; Foster, 1987; Civita & De Maio, 2004; Ribeiro, 2000). Among the most commonly applied index-based approaches are DRASTIC, GOD, SI, and SINTACS, which differ in methodological complexity, applicability, and data requirements (Aller et al., 1987; Foster, 1987; Civita & De Maio, 2004; Ribeiro, 2000). Integrating or comparing multiple vulnerability indices has been

widely recommended to improve the robustness and reliability of groundwater vulnerability assessments and to better inform policy and management decisions related to aquifer protection (Civita & De Maio, 2004; Kazakis et al., 2011; Anane et al., 2013; Ghouili et al., 2021).

Water supply system vulnerability refers to the susceptibility of water infrastructure and its operation to hazards that may compromise water quality or the continuity of supply (EPA, 2002; Murray et al., 2010). Such hazards include physical infrastructure failures, contamination incidents, cyber-attacks, natural disasters, and operational deficiencies (Lence et al., 2001). Assessing WSS vulnerability involves identifying weaknesses in infrastructure, operational procedures, or management practices that could lead to water quality degradation, service interruption, or system failure (ASCE, 2010). Several assessment frameworks have been developed for this purpose, depending on system characteristics and data availability, including the All-Hazards Approach (USACHPPM, 2005), Risk-Based Asset Assessment (ASCE, 2010), Water Safety Plans (WSP) (WHO, 2023b), and Climate Change Vulnerability Assessment (USEPA, 2014).

Despite substantial advances in both groundwater and WSS vulnerability assessments to date, no widely accepted or operational framework exist that comprehensively evaluate the sensitivity of both the aquifer system and the water supply infrastructure using a unified set of parameters. Traditionally, vulnerability analyses have been conducted independently, focusing either on the intrinsic susceptibility of aquifers to surface-derived contamination (Aller et al., 1987; Foster, 1987) or on the vulnerability of water supply infrastructure, such as abstraction works, pipelines, reservoirs, and treatment facilities, using risk- or failure-based assessment frameworks (ASCE, 2010). Groundwater vulnerability methods such as DRASTIC, GOD, and SI generally emphasize aquifer-scale conditions and evaluate sensitivity at the catchment or source protection area level, rather than at the scale of individual abstraction points (Aller et al., 1987; Ribeiro, 2000). This represents a critical limitation, as these approaches implicitly assume homogeneous vulnerability within a given aquifer and therefore overlook local-scale heterogeneity that can strongly influence the actual vulnerability of a specific spring or well (Hamza et al., 2010; Ghazavi & Ebrahimi, 2015).

In reality, hydrogeological heterogeneity, including spatial variations in permeability, porosity, structural features, and unsaturated zone thickness, means that wells located within the same aquifer can exhibit markedly different vulnerability levels. For example, one abstraction point may be effectively protected by a thick, low-permeability overburden, while a nearby well may be highly exposed due to thin or fractured protective layers (Civita & De Maio, 2004; Gogu & Dassargues, 2000).

Furthermore, WSS vulnerability assessments often begin downstream of the abstraction point, implicitly assuming that the water source is either adequately protected or uniformly vulnerable. This neglects source-specific risks that may critically affect overall system resilience. Consequently, there is a clear need for integrated methodologies that jointly evaluate the vulnerability of the source aquifer unit and the abstraction infrastructure using harmonized parameters, such as recharge conditions, land use, geological media, well construction characteristics, and system redundancy (Anane et al., 2013).

An integrated assessment framework would bridge hydrogeological and WSS vulnerability analyses and support more accurate risk-based zoning, resource allocation, and emergency planning, particularly in complex or fractured aquifer systems where assumptions of uniform vulnerability are misleading. Although the literature increasingly highlights the need for such integration, a comprehensive and operational framework has yet to be established (Goyal et al., 2021; Yazdani & Jeffrey, 2011).

In this study, we propose the Total Integrated Network (TIN) vulnerability approach as a comprehensive methodology for assessing water quality risks from the groundwater source, through the entire water supply system, to the point of use. The TIN approach addresses both natural and anthropogenic factors influencing water vulnerability along the source-to-tap pathway. By integrating aquifer sensitivity with infrastructure and operational vulnerabilities, TIN provides a more realistic and location-specific characterization of risk. This, in turn, enables water utilities and decision-makers to prioritize interventions, optimize resource allocation, and implement targeted protection and monitoring measures. Ultimately, the TIN approach supports proactive and adaptive water supply management, enhances system resilience, and contributes to the protection of public health.

## **Previous Research on Water Supply System Management in Croatia**

Research on WSS management in Croatia has primarily focused on water losses and the reduction of non-revenue water, issues that have been addressed by the national water sector reform (World Bank, 2023). Considering that nearly half of abstracted water is lost before reaching consumers, minimizing leaks in WSS is of critical importance for economic efficiency, public health, environmental protection, and climate resilience.

Studies on water quality in Croatian WSSs indicate that the country generally possesses high-quality water sources and sufficient water availability. Challenges in water supply are mostly

associated with turbidity, occasional microbiological contamination, and, more recently, the presence of pesticides in catchment areas (Croatian Institute of Public Health [CIPH], 2025). The CIPH has also conducted studies on WSS processes, providing recommendations and guidance for improved system management (CIPH, 2022).

Recent research demonstrates a growing scientific interest in monitoring and managing changes within WSS, particularly regarding disinfection by-products (Kurajica et al., 2020; Gregov et al., 2022), the development of bacterial communities, and their dependence on disinfection type (Štiglić et al., 2023). Earlier studies focused on changes in catchment areas and their impacts on water quality at the source (Nemčić-Jurec et al., 2022b; Ruk et al., 2022). To date, the approach of determining water transport and mixing within distribution networks has not been widely applied in Croatia. Only recently have studies begun to explore the effects of changing water sources on the quality of drinking water in WSS (Kurajica et al., 2021, 2022). Furthermore, stable isotopes have been extensively applied to determine groundwater age, identify contamination sources, and analyse surface–groundwater interactions (Horvatinčić et al., 2007; Buškulić et al., 2023; Cukrov et al., 2012; Mance et al., 2022).

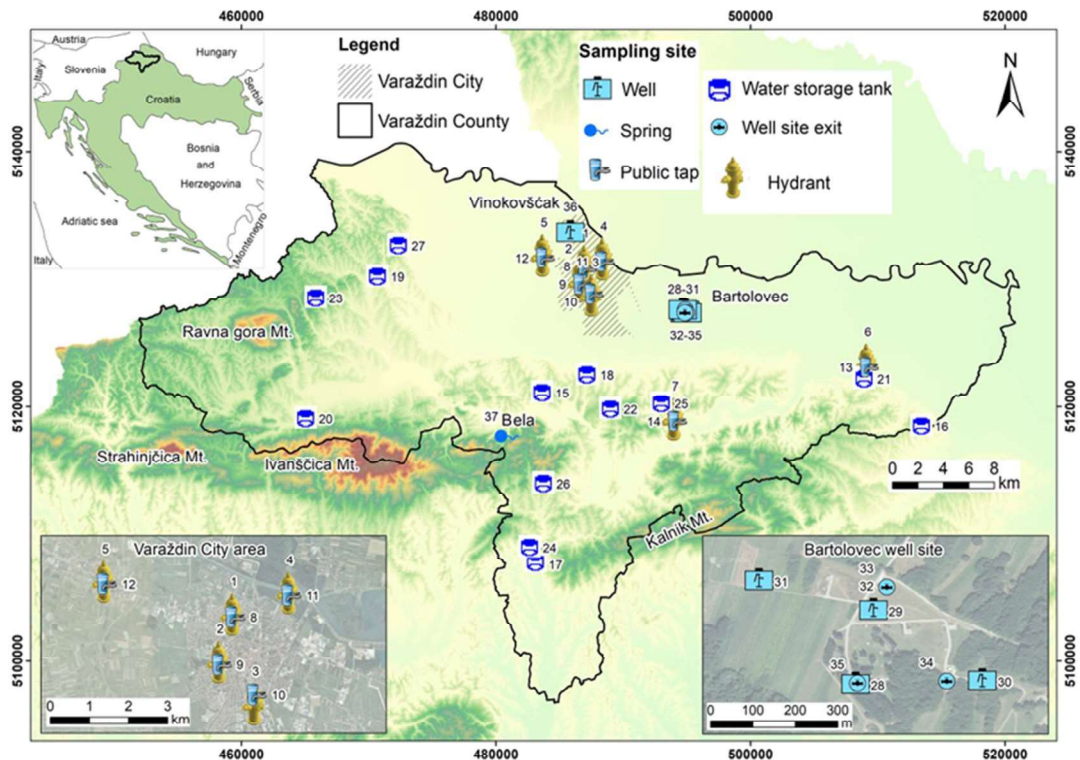
The public water supply of Varaždin County is almost entirely based on groundwater abstraction from the Drava River alluvial aquifer, a critical strategic resource for northwestern Croatia. Hydrogeological studies describe the aquifer as highly permeable, composed mainly of gravel and sand, with significant hydraulic connectivity to surface waters, particularly the Drava River and its tributaries (Karlović et al., 2021a, 2021b). This connectivity allows relatively rapid aquifer recharge, but simultaneously increases its vulnerability to surface water changes and anthropogenic impacts.

Recharge studies confirm that aquifer replenishment occurs through rainfall infiltration and inflow from surface water bodies, with spatially and temporally variable hydraulic conditions (Karlović et al., 2022a). Due to the shallow groundwater table and limited natural protective layers, the Varaždin aquifer is classified as highly vulnerable to contamination, particularly in areas of intensive agricultural activity (Larva et al., 2023).

Numerical modeling of groundwater flow and nitrate transport further confirms that agricultural sources are the primary contributors to elevated nitrate concentrations in certain parts of the aquifer, representing a long-term challenge for maintaining safe drinking water quality (Karlović et al., 2022b). These findings underscore the importance of integrated water resources management, stricter protection of water sources, and continuous monitoring to ensure a sustainable and safe water supply for Varaždin County.

## Study area

This study focused on the Varaždin area in NW Croatia, where potable water is distributed by the public water supplier Varkom d.o.o. ( Paper 2, Figure 1). The main source of potable water is groundwater extracted from the Varaždin aquifer at two wellfield sites, Bartolovec and Vinokovščak, as well as a spring in Belski Dol. Water from these three sources is, after disinfection with chlorine, transported to consumers via a 1670 km long distribution network. The Bartolovec wellfield site, situated approximately 7 km east of Varaždin town in the village of Bartolovec, serves as the primary water source for the majority of consumers in the Varaždin County, meeting around 70% of the water needs for human consumption in the regional WSS. The annual average rate of pumped water was 264 L/s (data for 2022) from 9 wells (B1-B9), of which 5 capture water from the upper aquifer (depth up to 45 m), and 4 from the lower aquifer (depth up to 120 m). The alluvial aquifer in this area is divided by a 5 m thick silty-clay aquitard between the shallow aquifer (SA) and the deeper aquifer (DA) (Urumović et al., 1990). This aquitard protects the DA from pollution from the surface, due to its poor permeability. Pumped groundwater from wells is disinfected and mixed in a ring-shaped pipeline system with five exits designated for distribution: Varaždin, Ludbreg, Novakovec, Doljan, and Tonimir (Paper 2, Figure 2). Because water mixes in a ring-shaped pipeline, it is hard to know the specific source and quantity of water distributed in each direction. This information is especially important in case of incidents, when potential deterioration of water quality in the water supply network could occur.



**Figure 1.** Schematic map of sampled points. See Table 1 for description (Paper 2).

The Vinokovščak wellfield site is located approximately 3 km NW of Varaždin, where groundwater is pumped from 4 wells (ZV1-ZV4), with an average annual rate of 82 L/s (data for 2022, Paper 2, Figure 1). Due to the thinner alluvial aquifer in this area, the wells draw water from a maximum depth of 45 m. Screens in wells are installed along the depth of wells, facilitating the mixing of water from SA and DA during pumping. After disinfection, the pumped groundwater from wells is distributed to one pipeline towards the north part of the Varaždin town and the NW part of the Varaždin County.

Spring water from Belski Dol is captured at an average rate of 30 L/s (Paper 2, Figure 1). It is located in the village of Bela at the foot of the Ivanščica Mountain, 20 km SW from the town of Varaždin. This water source gravitationally flows through the pipeline to the pumping station Filipiči, where it is disinfected and distributed into the water supply network. The Belski Dol spring represents the smallest groundwater source within the WSS, covering 8% of the region's water needs. Unlike the previously described groundwater sources, the catchment area of the spring Belski Dol consists of carbonate-fissured rocks, mainly dolomite of the Triassic age (Crnogaj et al., 1997).

# Hypothesis, Research Objectives, and Expected Scientific Contribution

Effective and economically efficient management of a WSS is based on an integrated approach that combines technical tools, high-quality and reliable data, risk management, financial sustainability, and institutional capacity. Such an approach enables the reduction of water losses, preservation of drinking water quality, and long-term security of water supply. A fundamental prerequisite for effective management is the accurate and continuous availability of data on abstracted water volumes, pressures and flows within the distribution network, water losses, as well as water quality throughout the system.

This study investigated additional opportunities for improving WSS management through the application of hydrochemical and physical water quality parameters that were continuously monitored as part of routine operational monitoring. These data were further complemented by an interdisciplinary methodological approach. The methodology included hydrochemical and isotopic analyses of water, statistical data processing, geochemical modeling, calculation of vulnerability indices, and estimation of water retention times within the system.

The main objective of this study was to demonstrate how routine chemical analyses, combined with geochemical modeling, could support informed decision-making and enhance the management of WSS. The research was conducted on the public water supply system of Varaždin County, which is operated by the public water utility Varkom d.o.o.

The selection of research objectives was carefully defined and was based on three research hypotheses, which constituted the conceptual framework of this study. These research hypotheses were as follows:

1. Routine measurements of chemical indicators and monitoring of isotopic indicators in WSS can help in its management.
2. Using  $\delta^{18}\text{O}$ , it was possible to determine the retention time of water in WSS and, together with statistical analyses, to observe changes in water quality.
3. Geochemical modeling was a useful tool for determining the proportion of water from individual sources in mixed WSS.

To confirm or reject the established hypotheses, the following objectives were defined:

1. To determine the applicability of routine measurements of water quality and isotopic parameters to WSS management.

2. To apply geochemical modeling to determine the proportion of water from individual sources in mixed WSS.
3. To determine the applicability of  $\delta^{18}\text{O}$  content for calculating water retention time in the system.
4. To define the conditions under which statistical processing of chemical indicators is applicable and whether it can indicate changes in water quality.

The expected scientific contributions of the proposed research were:

1. The development of a methodology to improve WSS management, especially in incident situations, using routine water analyses.
2. The determination of water retention time in WSS using  $\delta^{18}\text{O}$  isotopic measurements.
3. The development and validation of a methodology for determining the proportion of water from individual sources in WSS.
4. The definition of the origin and age of water in the Belski Dol spring, as well as the assessment of contamination risk for this source and the part of the WSS it supplies.

The research addressing the above-stated objectives has been published in three scientific papers (Paper 1, Paper 2, Paper 3). The results, presented below, are discussed in the context of testing the proposed hypotheses.

## Discussion

### **Hypothesis #1: Routine measurements of chemical indicators and monitoring of isotopic indicators in WSS can help in its management**

The study area used for testing this hypothesis encompassed the entire WSS managed by Varkom d.o.o. in Varaždin County. The system is of a mixed type and relies on three water abstraction sites: Bartolovec, comprising nine wells; Vinokovščak, comprising four wells; and the Belski Dol spring, with two catchments (Paper 2). The water is of groundwater origin, and no water treatment was applied, except for activated carbon filtration at one well. Prior to distribution, the water was disinfected with chlorine. The supplier's internal laboratory routinely performed water quality monitoring in the catchment inflow area, in raw water samples from wells and the spring source, and across the distribution network (reservoirs, hydrants, and public taps), in accordance with a weekly sampling program (Paper 1, Paper 3). Annually, approximately 2,100 samples were analysed, providing a robust dataset of chemical and microbiological parameters relevant to drinking water quality assessment and regulatory compliance. In order to test the hypothesis and the given objective (1), the research included additional indicators: major cations and anions, stable water isotopes  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , and, in Paper 3, also tritium, radon, and noble gases.

The results of water analyses showed that water quality differences were already present at the very beginning of the WSS, even among individual wells within the same wellfield, as indicated by the Piper diagram (Paper 2, Figure 3). These findings were consistent with operational monitoring data from Varkom d.o.o. The Bartolovec wellfield exploits two aquifers, SA and DA, separated by a clay–silt layer that strongly controls groundwater residence time and limits the downward migration of contaminants (Kovač et al., 2017; Karlović et al., 2022).

Significantly higher concentrations and stronger seasonal variability of nitrate, chloride, and EC in SA compared to DA confirmed the greater vulnerability of the shallow aquifer (Paper 1, Table 1; Paper 2, Figure 2). Vertical hydrochemical heterogeneity was further evidenced by differences between wells B1 and Zp-7, which capture the same aquifer at different depths. Elevated nitrate concentrations in SA were attributed to intensive agricultural activity and a thin surface layer, whereas consistently low nitrate levels in well Zd-4 indicated longer groundwater transit times and effective protection of the deep aquifer.

Additional geochemical contrasts between SA and DA were reflected in higher concentrations of major ions in SA. Nevertheless, groundwater from both aquifers belongs to the CaMg–HCO<sub>3</sub> hydrochemical type, indicating that carbonate and silicate mineral dissolution is the dominant geochemical process in the aquifer system.

However, even in the Piper diagram (Paper 2, Figure 3), differences between waters were visible. In addition to the aforementioned parameters, monthly measurements of stable oxygen and hydrogen isotopes in water also revealed differences between SA and DA, especially in the warmer part of the year (Paper 2, Figure 4). In SA,  $\delta^{18}\text{O}$  values ranged from -10.69 to -9.55 ‰ and  $\delta^2\text{H}$  from -74.5 to -67.8 ‰, while in DA,  $\delta^{18}\text{O}$  ranged from -10.69 to -10.1 ‰ and  $\delta^2\text{H}$  from -73.6 to -70.6 ‰ (Paper 2, Figure 4, Table S1). Variations between wells B-1 and Zp-7, although they captured the same aquifer, mirrored the patterns observed in temperature, chloride, and nitrate concentrations. This phenomenon underscored the heterogeneous nature of SA. All these differences provided valuable insights for developing mixing models.

At the Vinokovščak wellfield, one of the four existing wells was selected for sampling in the context of this study, as historical data from the Varkom internal laboratory indicated the absence of significant differences in water quality among the wells. This similarity in groundwater quality can be attributed to the fact that the wells abstract water from both aquifer layers, while the intervening low-permeability clay layer separating them is relatively thin.

The measured groundwater values at the Vinokovščak wellfield indicated generally stable hydrochemical conditions throughout the monitoring period. While chloride (7.6–10.9 mg/L) and nitrate (16.1–25.5 mg/L) concentrations did not exhibit pronounced temporal oscillations, a slight decreasing trend was observed. This trend was attributed to the exceptionally dry hydrological year and the strong hydraulic connection between the aquifer and the Drava River during periods of low groundwater levels. Given the relatively low chloride and nitrate concentrations in the Drava River, an increased river contribution likely resulted in dilution of these constituents in groundwater toward the hydrological minimum.

Hydrochemical classification based on the Piper diagram indicated a CaMg–HCO<sub>3</sub> water type, reflecting dominant water–rock interaction processes, primarily the dissolution of carbonate and silicate minerals forming the aquifer (Paper 2, Figure 3). Although the Ca<sup>2+</sup>/Mg<sup>2+</sup> ratio was comparable to that observed in groundwater from the deep well Zd-4 at the Bartolovec wellfield, higher chloride and sulfate concentrations at Vinokovščak suggested different geochemical conditions within the aquifer system.

Stable isotope compositions ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) closely resembled those reported for the Bartolovec wellfield (Paper 2, Figure 4), with observed variations largely within analytical uncertainty

( $\pm 0.2$  ‰ for  $\delta^{18}\text{O}$  and  $\pm 1$  ‰ for  $\delta^2\text{H}$ ). This limited variability indicated that  $\delta^{18}\text{O}$  was not a suitable tracer for mixing modeling in this setting. Furthermore, several samples, particularly from wells DA and ZV-4, plotted above the local meteoric water line, pointing to specific hydrological processes that have been discussed in detail in previous studies (Marković et al., 2020).

All measured hydrochemical parameters at the Belski Dol groundwater source were a consequence of the long residence time of groundwater (Marković & Larva, 2013). Higher oscillations were observed in chloride, nitrate, and sulphate concentrations (Paper 2, Figure 7, Table S1), which were attributed to the influence of surface water. The spring is situated along the Varaždin–Podrute road and is separated from it by a stream. During high-water periods, surface runoff into the spring occurred. Compared to the other two groundwater sources, the spring water contained higher concentrations of  $\text{Mg}^{2+}$  (22.9–26.5 mg/L) due to dolomite dissolution in the catchment area. According to the Piper diagram, the spring water belongs to the CaMg– $\text{HCO}_3$  hydrochemical type, noticeably different from the other two sources (Paper 2, Figure 3).

The measured  $\delta^{18}\text{O}$  values ranged from -10.67 to -10.29 ‰, and  $\delta^2\text{H}$  ranged from -72.20 to -70.80 ‰ (Paper 2, Table S1). These values were the most negative among all investigated groundwater sources and were shifted relative to the LMWL for Varaždin (Paper 2, Figure 6). This discrepancy was attributed to several factors. Firstly, the catchment area of the spring is situated at a higher elevation (averaging about 700 m a.s.l.), with the highest peak exceeding 1000 m a.s.l., resulting in more negative  $\delta^{18}\text{O}$  values in spring water. Secondly, the transit time in such aquifer types is long, exceeding 50 years (Marković & Larva, 2013). During this period, winters were colder, with high amounts of snow (Zaninović et al., 2008) serving as the major source of recharge.

Geochemical and isotopic characteristics of water from water supply network showed wide range of measured values. In reservoir water, high oscillation of basic cations and anions was observed due to the mixing of different groundwater sources. An important finding was that none of the measured concentrations exceeded those measured in the groundwater source, indicating no significant impact (contamination) within the network. Similar to the reservoirs, the geochemical parameters of sampled waters from public taps and hydrants showed variability, but concentrations did not exceed the maximum values of groundwater sources.

Preliminary stable isotope results for reservoirs, public taps, and hydrants were plotted against LMWL (according to Marković et al., 2020) (Paper 2, Figure 8). It was observed that the summer sampling campaign for reservoirs and public taps differs from the winter sampling

(reservoirs and hydrants). This discrepancy can be attributed to different factors such as water temperature variations, fractionations within pipes, different pumping regimes, etc. Regardless of all these influences, it was observed that values are distributed within the elliptical shapes, which represent their origin. Moreover, one reservoir in both sampling campaigns showed the same origin (reservoir R1-Briška and the Belski Dol source). Consistent with the geochemical parameters, there were no outliers observed, confirming no contamination within the water supply network.

Based on the presented data, it is evident that the observed WSS is a mixed system that delivers potable water composed of a mixture of waters from different source areas. Knowledge of water provenance in each part of the WSS enables more efficient system management, particularly in incident situations such as water contamination, pipeline failures, or consumer complaints.

In this study (Paper 2), a geochemical modeling approach was applied to determine water origin, as will be explained in detail in Hypothesis #3. A simple Piper diagram showed at a glance that only one reservoir (R1 - Briška) during both sampling campaigns was filled from only one groundwater source, Belski Dol. However, all other network sampling points demonstrated a mixing of different sources (Paper 2, Figure 9).

It is important to emphasize that previously described analytical results were used as input data for the mixing model calculations, with water samples from the wellfields serving as end-member (source) waters, and samples from the water supply network (hydrants, reservoirs, and public fountains) representing the mixed waters.

Furthermore, routine water quality monitoring data within the WSS were applied in an approach for assessing system vulnerability that accounts for the condition of both the aquifer and the distribution network (Paper 3). This research was conducted on a smaller segment of the WSS, encompassing the Belski Dol spring and the portion of the water supply network it supplies, including the Filipiči pumping station and the Briška reservoir.

A novel methodology, termed the Total Integrated Network Vulnerability Approach (TIN), was proposed. By tracing water and its quality changes from recharge zones, through abstraction and conveyance, storage, and distribution, the TIN approach identifies and quantifies cumulative and segment specific risks. This holistic methodology enables: spatial mapping of vulnerability hot spots across both the aquifer and WSS infrastructure; temporal assessment of changes in vulnerability due to natural processes (e.g., recharge variability) and operational factors (e.g., system maintenance, leakage); identification of critical control points (CCPs) where interventions can most effectively reduce overall risk.

The proposed approach utilizes 10 parameters, half of which are routinely monitored by all water supply companies in accordance with the obligations of the Drinking Water Directive (EU) 2020/2184 (Directive (EU) 2020/2184, 2020). These parameters include EC, T, pH,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , the stable isotopes  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , and  $^{222}\text{Rn}$ . For the source spring Belski Dol, the same eight parameters were considered, but the analysis was extended to include tritium and noble gases, as these provide additional information on groundwater residence time and recharge conditions. Table 1 and 2 (Paper 3) provide an overview of the relevance of each parameter and what changes in their values can indicate for both the groundwater system and the WSS.

The methodology followed the approach described in the TIN framework, in which each parameter is assigned a vulnerability score ranging from 1 (low) to 5 (high) presented in Table 3 (Paper 3). The scoring was based on the degree of deviation from reference conditions. For the WSS locations, the reference baseline was the values measured at Belski Dol spring on the same sampling date, thus representing the natural source water quality. In contrast, for Belski Dol itself, the reference was defined as the mean of its own values over the monitoring period, so that the index reflects temporal variability of the spring rather than spatial differences. For most parameters, the score was assigned according to the percentage deviation from the baseline: values within  $\pm 10\%$  correspond to a score of 1, deviations of 10–20% to a score of 2, 20–30% to 3, 30–50% to 4, and  $>50\%$  to 5. In addition, regulatory thresholds were applied as overriding conditions: nitrate concentrations above 50 mg  $\text{NO}_3^-/\text{L}$ , pH values below 6.5 or above 9.5, and temperatures exceeding 25 °C automatically receive the highest score of 5. For stable isotopes, absolute differences relative to the baseline were used instead of percentages, with threshold bands defined in per mil (‰). The  $\delta^{18}\text{O}$  values received scores of 1 for differences  $<0.10\text{‰}$ , 2 for 0.10–0.20‰, 3 for 0.20–0.30‰, 4 for 0.30–0.50‰, and 5 for  $>0.50\text{‰}$ . For  $\delta^2\text{H}$ , the thresholds were set at 1, 2, 3, and 5‰ for scores 1 to 4, with values above 5‰ receiving a score of 5.

Once all parameters had been scored, the TIN vulnerability index for each site and date was calculated as the arithmetic mean of the scores, normalized to a percentage of the maximum possible value. For Belski Dol, an additional adjustment was applied to account for the evidence of long groundwater residence time provided by tritium and noble gas measurements, which indicate a mean residence time of about 25 years and recharge under cold climatic conditions. This information implies a higher degree of natural protection of the source.

The results show that Belski Dol spring consistently exhibits the lowest TIN vulnerability, with an overall index of 25.5%, placing it in the category of low vulnerability. PS Filipiči has a somewhat higher index of 35%, reflecting moderate deviations from the source conditions. The

Briška reservoir displays the highest-values, with an average index of 52.5%, corresponding to moderate vulnerability (Figure 6). This higher vulnerability is primarily associated with greater deviations in radon, nitrate, and conductivity compared to the Belski Dol baseline. The unusually high  $^{222}\text{Rn}$  concentration observed in the Briška reservoir compared to the source Belski Dol can be explained by the cumulative effects of soil-rock radon emanation coupled with aged distribution infrastructure. Belski Dol, being close to the source, exhibits relatively modest radon levels (12.6–13.3 Bq/L) and is less exposed to external contamination. However, at Briška reservoir, water travels through older pipelines and possibly through soils or fractured bedrock that allow radon to diffuse or emanate into the water column, which together with microleaks and pipe joint degradation may boost radon levels. Such phenomena were observed by Özden et al. (2022), demonstrating how soil properties such as porosity, moisture, and radium content strongly influence radon release from the ground. In addition, Sukanya & Sabu (2023) outline how aquifer-rock contact and aged pathways (via fractures or disturbed soil) enhance radon concentration in downstream water. Taken together, these findings provide a coherent explanation for the higher  $^{222}\text{Rn}$  levels observed in the Briška reservoir relative to the Belski Dol spring.

Overall, the analysis demonstrates that the natural spring Belski Dol is well protected and chemically stable, while the WSS sites show increased vulnerability, with Briška reservoir being the most affected (Paper 3, Figure 6).

The integrated evaluation confirmed that hydrogeological protection alone is not sufficient to ensure water safety. Instead, continuous monitoring across both natural and engineered components is essential. By incorporating hydrochemical, isotopic, and radiological parameters, the TIN method allowed identification of critical control points where interventions would be most effective, such as targeted monitoring at the Briška reservoir and maintenance of distribution infrastructure.

The proposed TIN approach allows application specifically for each observed area, with threshold values to be determined according to available data. Each parameter is assigned a weighting factor reflecting its relative importance or diagnostic value in assessing system vulnerability. These weights can be uniform or adapted based on expert judgment, sensitivity analysis, or system-specific relevance. In this paper, a general scoring framework is proposed. The interpretation of our results reflects the scope of the available data set, and the limited sampling frequency for certain parameters is a factor in the baseline uncertainty.

**Hypothesis #2: With the help of  $\delta^{18}\text{O}$ , it is possible to determine the retention time of water in WSS and, together with statistical analyses, observe changes in water quality.**

In order to test and verify this hypothesis, the study was published in Paper 1. For this study a small segment of WSS was selected due to its well-defined traceability, allowing tracking the water flow from pumped well through pipelines to the reservoir, without mixing water from other wells. This approach enabled monitoring of changes in chemical parameters throughout the distribution. Specifically, the study centered around well B1 at the Bartolovec wellfield, from which water is drawn and sent through pipelines to the Tonimir (T) and Golo Brdo (GB) water reservoirs. The water from the Tonimir reservoir was directed for consumption, while a flow rate of 4.2 L/s filled the Rukljevina (R) water reservoir (Paper 1, Figure 2).

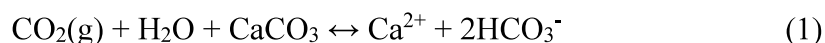
Water samples were taken from well B1 and reservoirs T, GB and R by two different campaigns, employing different sampling frequencies.

The first data set is a part of water sampling campaigns from well B1 and reservoirs T, GB and R as part of operational monitoring of Varkom d.o.o., the public supplier. The dynamics of sampling was once per week during 2021 and 2022. The monitored water quality parameters included pH, EC,  $\text{Cl}^-$  and  $\text{NO}_3^-$ . These parameters were chosen because they are part of regular analysis and show certain spatial and temporal fluctuations. During this monitoring, additional parameters such as  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , temperature, turbidity, free residual chlorine and microbiological indicators were also measured. However, they are not included in this study due to specific reasons:  $\text{NO}_2^-$  and  $\text{NH}_4^+$  are consistently below detection limits, while the remaining parameters depend on external influences.

The second data set was obtained from three sampling campaigns in July and November 2022 (well B1 and reservoir T) and February 2023 (well B1 and reservoirs T, R and GB) performed by Croatian Geological Survey within the scopes of TRANITAL and WATSON projects. Prior to sampling, pH, EC, T, dissolved oxygen (DO) and redox potential (ORP) were measured using a WTW multi meter. Concentrations of basic anions and cations were analyzed by ion chromatography, while alkalinity was determined by titration. Stable isotopes  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  were determined by using Picarro L2130i instrument (Santa Clara, USA) using CRDS (Cavity Ring-Down Spectroscopy) technology, and the results were expressed according to the international standard.

According to major ion composition, both reservoirs' waters and well B1 waters had the same hydrochemical type, characterized as CaMg-HCO<sub>3</sub>, without pronounced differences on the Piper diagram (Paper 1, Figure 3). However, observing the relationship between pH, logpCO<sub>2</sub> pressure, and calcium saturation index (SI<sub>calcite</sub>), differences were noticed (Paper 1, Figure 4a, b). The well water exhibited lower pH value and SI<sub>calcite</sub>, but higher logpCO<sub>2</sub>. On the other hand, reservoir waters displayed higher pH value and SI<sub>calcite</sub>, but lower logpCO<sub>2</sub> (Paper 1, Figure 8a, b). In addition, it was observed that in the reservoir farthest from the well, where water retention time was the longest, the pH tended to be higher (Paper 1, Figure 4a).

In a geochemical context, reservoirs represent open systems where gas exchange between air and water occurs (as there is space above the water filled with air), and groundwater from well B1 is oversaturated with CO<sub>2</sub>. These changes are a consequence of CO<sub>2</sub> degassing from water and shifting carbonate mass balance towards the left side of the well-known equation:



With calcium saturation index above 0, precipitation of calcium in the water is induced, leading to formation of calcium crust on the water surface in reservoirs. This reaction results in a decrease in alkalinity, as well as an increase in pH due to precipitation of calcium carbonate, which further contributes to the decrease in EC.

All measured values for δ<sup>2</sup>H and δ<sup>18</sup>O in reservoirs and well indicated that the water had a meteoric origin (Paper 1, Figure 5), as they were scattered around the local meteoric water line (LMWL) for the study area (Marković et al., 2020). Isotope values ranged from -9.98 (well B1) to -9.72‰ (reservoirs T and R) for δ<sup>18</sup>O and from -69.3 (reservoir T) to -68.6‰ (well B1) for δ<sup>2</sup>H. Based on the measured δ<sup>2</sup>H and δ<sup>18</sup>O values in waters from reservoirs, there was no evaporation effect during the sampling campaigns, indicating a short retention time of water. Consequently, the retention time was not long enough for seasonal temperature changes, that could potentially affect water temperature in reservoirs and thus isotope fractionation.

### **Water retention time in the Tonimir reservoir**

The water retention time of water in the Tonimir reservoir was calculated using oxygen-18 measurements in well and reservoirs. The calculation utilized a simplified model (Kralik, 2015) which is applied to estimate the residence time of water in the ground:

$$t = (1/2 \pi) \times \sqrt{1 / (b/a)^2 - 1} \text{ [yrs]} \quad (2)$$

where  $t$  is the estimated residence time,  $b$  is the maximal amplitude of the groundwater isotopic data, and  $a$  is the maximal amplitude of the precipitation isotopic data over several years. This formula was adapted for our specific context, where  $t$  represents the estimated retention time of water in the system,  $b$  is the maximal amplitude of the water in reservoir, and  $a$  is the maximal amplitude of the water isotopic data from well B-1 over two-year monthly measurements. Water retention time in two other reservoirs was not calculated due to stable isotopes being measured only once. To verify the calculated result, water retention time was estimated using an algorithm that considers input parameters such as diameters and length of pipes, reservoir dimensions, and water flux within the pipes.

According to the Eq. 2, water retention time in the Tonimir reservoir was estimated to be approximately 17 hours using stable isotopes  $\delta^{18}\text{O}$ . A similar estimate of around 16.2 hours was obtained when applying the methodology that accounts for the technical characteristics of the WSS. The consistency between the results from both methods indicates that oxygen-18 can be useful and reliable tool to gather information about the system, especially when WSS managers encounter situations where their understanding of the system's operation is limited.

### Findings of statistical data processing

For each parameter at every location, the number of data ( $n$ ), average concentration ( $\bar{x}$ ), corresponding variance ( $\sigma^2$ ) and its estimate ( $s^2$ ) were determined:

$$s_i^2 = \frac{n_i}{n_i-1} \sigma_i^2 \quad (3)$$

In order to determine the statistical significance of the difference between the concentrations at the locations  $L_i$  and  $L_j$ , it was necessary to apply the t-test:

$$t = \frac{\bar{x}_i - \bar{x}_j}{s_d} \quad (4)$$

whereby:

$$s_d^2 = \frac{(n_i-1)s_i^2 + (n_j-1)s_j^2}{n_i+n_j-2} \cdot \frac{n_i+n_j}{n_i n_j} \quad (5)$$

The obtained  $t$ -value was compared with the critical value ( $t_\alpha$ ), which was determined for a significance level of 5% and based on the number of degrees of freedom:

$$k = n_i + n_j - 2 \quad (6)$$

Statistical data processing was conducted using the MS Excel tool.

It is clear from expression (2) that the  $t$ -value is proportional to the difference between the average concentrations at locations  $L_i$  and  $L_j$ . If the  $t$ -value is less than the critical one, the null

hypothesis ( $H_0$ ) is accepted, indicating that the observed difference is not statistically significant. Otherwise, the alternative hypothesis ( $H_1$ ) is accepted:

$$t \leq t_{\alpha} \rightarrow H_0: \bar{x}_i = \bar{x}_j \quad (7)$$

$$t > t_{\alpha} \rightarrow H_1: \bar{x}_i \neq \bar{x}_j \quad (8)$$

If the  $t$ -value is greater than the critical one, the difference between the average concentrations is considered statistically significant, which indicates an endogenous process in the water between locations  $L_i$  and  $L_j$  within the water supply system.

Using the data from Table 1 (Paper 1), the statistical significance of the differences in concentrations of the measured indicators was determined by comparing the locations on the network (reservoirs T, GB and R) with the data at the starting sampling point - well B1 at the wellfield. The calculated  $t$ -values were then compared with  $t_{\alpha}$ , which, for the given number of data points, is 1.984. The results of these comparisons are summarized in Tables 3a and 3b (Paper 1). Consistent with hypotheses (7) and (8), the obtained results show that in 2021, negative  $t$ -values increased with the distance from well B1 for pH and  $\text{NO}_3^-$ , with significant difference observed for  $\text{NO}_3^-$  in water reservoirs GB and R (Paper 1, Table 3a). For EC, positive  $t$ -values increased with distance from well B1, but did not demonstrate significant difference as for chloride concentration.

In 2022, the analysis revealed an increase in negative  $t$ -values with distance for pH and  $\text{NO}_3^-$ , whereas for EC, it decreased in the more distant water reservoirs GB and R (Paper 1, Table 3b). Conversely, the  $t$ -value for  $\text{Cl}^-$  was positive and it was increasing. For the parameter pH,  $\text{Cl}^-$  and  $\text{NO}_3^-$ , a significant difference was observed between the water samples from B1 and reservoirs GB and R, as all  $t$ -values were greater than the critical  $t_{\alpha}$ .

In both monitored years, differences were noted in the  $t$ -values for pH, but more significant for 2022, as a result of  $\text{CO}_2$  degassing from water, as explained earlier. However, since reservoir systems are very dynamic (as they are filled with fresh water and undergo aeration during regular maintenance), pH of water within reservoirs would not reach the critical value for human consumption of 9.5. Hypothetically, considering reservoir T as an example: if the reservoir were sealed, without inflow or outflow occurring, the pH would gradually increase until reaching equilibrium between  $\text{CO}_2$  in water and air.

The significant decrease of chloride could be attributed to chlorine degassing. Even ORP decreases and in WSS, ORP and chlorine concentrations are very well connected (James et al., 2004). However, looking at the mean, minimum and maximum measured values and considering the measuring error of  $\pm 10\%$ , it is evident that all of them fall within a similar

range. The same issue appears when analyzing nitrate concentrations. While bacteria from biofilm in pipes could potentially reduce nitrate into nitrite or ammonium, all measured values for these two parameters are consistently below detection limit which is  $<0.01$  mg/L. In these two cases, statistical data processing led to unreliable conclusions.

Despite the occurrence of precipitation of calcium carbonate and degassing of chlorine, their impact on reservoir waters is not significant.

The study elaborated the advantages and disadvantages of employing oxygen-18 isotopes, geochemical modeling, and statistical data processing to determine water retention time in WSSs, how retention time influence water quality within the system and significance of processes that are occurring.

Statistical data processing indicated the significance of certain changes within the WSS, though careful interpretation is required to prevent misleading conclusions. Electrical conductivity declines with increasing distance from the well due to calcium carbonate precipitation. At the Tonimir reservoir, the short water retention time prevents water quality deterioration within the system. While pH changes are occurring, the WSS's dynamic status characterized by a short water retention time, prevents it from reaching the MCL of pH 9.5. Overall, stable isotope analysis has proven useful for calculating water retention time in the system and can serve as a complementary tool for WSS management.

### **Hypothesis #3: Geochemical modeling is a useful tool for determining the proportion of water from individual sources in mixed WSS**

The discussion under Hypothesis #1 demonstrated how water quality data collected through routine monitoring, supplemented by isotopic measurements, can contribute to improved management of WSS. One of the specific objectives was to determine the origin of water within a mixed system, such as the investigated public WSS in northwestern Croatia operated by Varkom d.o.o. Input data were collected during a one-year monitoring campaign at the locations described in Table 1 (Paper 2). The measured parameters included physicochemical indicators, major anions and cations, and stable isotopes of water (Paper 2, Table S1). This study employed three approaches, i.e., mixing models, to calculate the water mixing ratios. The first approach involved the application of mass balance calculations (MB), a commonly used method (Vazquez-Sune et al., 2010; Eberts et al., 2013; Hepburn et al., 2020) in which proportions of

two-end members in the observed sample were calculated using simple formulas based on conservative tracers  $\text{Cl}^-$  and  $\delta^{18}\text{O}$ .

Specifically, the calculations were performed using the following two equations:

$$f_{S1} = \frac{\text{Cl}_{\text{sample}}^- - \text{Cl}_{s2}^-}{\text{Cl}_{s1}^- - \text{Cl}_{s2}^-} \quad (9)$$

$$f_{S1} = \frac{\delta^{18}\text{O}_{\text{sample}} - \delta^{18}\text{O}_{s2}}{\delta^{18}\text{O}_{s1} - \delta^{18}\text{O}_{s2}} \quad (10)$$

where  $f_{S1}$  represents the fraction (between 0 and 1) of source water 1 estimated in a sample of mixed origin. The  $\text{Cl}_{\text{sample}}^-$  and  $\delta^{18}\text{O}_{\text{sample}}$  represent concentrations in waters from reservoirs, public taps, exits, and hydrants;  $\text{Cl}_{s1}^-$ ,  $\delta^{18}\text{O}_{s1}$ ,  $\text{Cl}_{s2}^-$ , and  $\delta^{18}\text{O}_{s2}$  represent concentrations in different groundwater sources.

The other two models were implemented using geochemical modeling software, which uses geochemical parameters to infer the physical and chemical processes that control water chemistry along flow paths, specifically within the water supply network (pipeline, reservoirs), and to quantify reactions occurring within this network. The inverse geochemical modeling (IM) was performed using the PHREEQC software, version 3-A (Parkhurst & Appelo, 2013). It is based on a geochemical mole-balance program that calculates the phase mole transfers (the moles of minerals and gases that enter or leave a solution) to account for the differences observed between initial and final water composition along the flow path, in our case, within the network. The third approach involved using the NETPATH-WIN software for forward geochemical modeling (FM) (Plummer et al., 1994; El-Kadi et al., 2010). In all three models, EC,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\delta^{18}\text{O}$  were used as constraints. The accuracy of the results was controlled according to the saturation index data for calcite and dolomite, which were compared with the actual values.

At the Bartolovec source, mixing models were performed in two steps because the mixing of SA and DA occurs at the source prior to water reaching the water supply network. The first step was to calculate the mixing proportions of groundwater from SA (represented by B-1 and Zp-7) and DA (represented by Zd-4) in the final waters of the wellfield, which are the exits (E1-E5). For the groundwater sources Vinokovščak and Belski Dol, this step was unnecessary due to the presence of only one exit into the network. In the second step, mixing within the network (reservoirs, hydrants, and public taps) was calculated, where exits from all water sources (E1-E5, ZV-4, and Belski Dol) represented initial waters, and samples from the network (H1-H7, PT1-PT7, and R1-R13) represented final waters. The modeling results are presented as percentage ratios of the initial waters in the final ones (ranging from 0 to 100%).

The validation of all three mixing models was performed by calculating sulfate concentrations in end-members and comparing them with measured values. Sulfate concentration was selected due to its conservative nature, its inability to precipitate or be added during disinfection, and its was not used as a tracer in the calculations. Considering a 5% measurement error for IC, all values below 0.5 mg/L were considered reliable, while values exceeding this threshold were classified as poor results

### **Origin of Water at Exits at the Bartolovec Wellfield**

In the Bartolovec wellfield, mixing modeling was conducted on four of the five exits, as exit Tonimir exclusively receives water from well B-1 (SA). Also, it was observed that modeling with  $\delta^{18}\text{O}$  as constraints did not show satisfactory matches in most calculations, so these results were not considered. Chloride emerged as the most effective constraint in the majority of MB model calculations, with a generally better fit observed in the IM and FM models compared to MB models (Paper 2, Table 2).

Nevertheless, all three models showed that at exit Doljan, depending on the pumping regime, more than 50% and up to 77% of water is pumped from the DA and distributed towards the southern part of the network. On the other hand, exit Ludbreg primarily supplies the eastern part of the network with DA water, ranging from 92 to 100% (Paper 2, Table 2). At the exit Varaždin, up until April 2022, water was mainly pumped from the DA, between 93 to 99% of the supply. After that, the regime of pumping changed, favoring SA water from 62 to 72%, before reverting back to dominantly DA water (Paper 2, Table 2). At the exit, Novakovec primarily supplies the eastern part of the network with the SA water, ranging from 92 to 100% (Paper 2, Table 2).

### **Reservoirs, Public Taps and Hydrants**

Similar to the exits, the best fit obtained by MB models was achieved using chloride as a constraint, while IM and FM models generally showed a better fit than MB. After validation, IM models yielded the most reliable results and are therefore discussed further. Despite some increased complexity at this level, most results showed a good agreement, indicating that this modeling approach is robust but requires further refinement. Differences arise due to the variable chemical and isotopic composition of multiple wells, which are alternately integrated into the water supply system. More accurate results would likely be obtained by sampling all wells at pumping stations rather than only representative ones. Additionally, the chemical composition of water changes during storage in reservoirs. During warmer months, evaporation

affects  $\delta^{18}\text{O}$  composition, while stagnant conditions promote carbonate precipitation, affecting EC. Furthermore, free chlorine concentrations decrease, while bacterial activity that can influence nitrification increases. Chlorination may also slightly affect chloride concentrations, potentially influencing model results. Each of these processes may affect modeling outcomes. Incorporating additional water quality indicators (anions and cations), as well as expanding sampling locations, would likely improve model accuracy. In the western part of the network, reservoirs predominantly contain a mixture of waters from Bartolovec (exits E1 and E4) and Belski Dol sources (Paper 2, Figure 10c). Sampling was not conducted in this area due to the absence of public taps. In the northern part of the network, mixing between Vinokovščak and Bartolovec sources was observed (Paper 2, Figure 10c). Hydrants and taps closer to the Vinokovščak source showed higher proportions, although some values were unexpected. Seasonal differences between summer and winter periods were also evident. The southern and eastern parts of the network are predominantly supplied with water from Bartolovec (exits E2 and E3) and B-1 (Paper 2, Figure 10a–c). Mixing ratios indicate that Bartolovec is the dominant groundwater source, with a significant contribution from DA. Analysis of pumping volumes during sampling dates confirmed the modeled results.

## Conclusion

Water supply systems are “living” and dynamic systems that represent a major achievement of civilization and play a crucial role in the life of both the community and the individuals. In contemporary society, social and economic development is inconceivable without meeting fundamental human needs such as the right to safe drinking water and sanitation. The management of WSSs is a complex and demanding task, as it involves numerous interconnected hydraulic and hydrotechnical structures that must function as an integrated whole. In addition to delivering water to every consumer, the supplied water must comply with strict public health standards.

For these reasons, the presented dissertation represents a significant advancement in the field of WSS management by demonstrating the potential application of hydrochemical and isotopic parameters. Such an approach has not previously been applied in Croatia, nor has it been widely implemented worldwide. The conducted research resulted in numerous insights, which are presented through three published scientific papers. The most important findings and conclusions are summarized below:

- The quality of water in the investigated WSS operated by Varkom d.o.o. is fully compliant with public health regulations, despite certain variations identified through statistical data analysis. By calculating *t*-values and comparing selected indicators of raw (inlet) water and distributed network water, statistically significant differences were identified for pH, EC, nitrate, and chloride concentrations. The pH value increases with distance from the source, while EC decreases, which can be attributed to CO<sub>2</sub> degassing and CaCO<sub>3</sub> precipitation. However, these differences are minor, and the system exhibits constant hydraulic dynamics with continuous inflow of fresh water; therefore, it is not expected that pH values will reach the critical threshold of 9.5.
- The relationship between pH, logarithmic partial pressure of CO<sub>2</sub> (log pCO<sub>2</sub>), and the calcium carbonate saturation index (SI<sub>calcite</sub>) shows clear differences between water types. Well water is characterized by lower pH values and SI<sub>calcite</sub>, but higher log pCO<sub>2</sub>. In contrast, reservoir waters exhibit higher pH values and SI<sub>calcite</sub>, accompanied by lower log pCO<sub>2</sub>. Furthermore, in the reservoir located farthest from the well, where water retention time is longest, a tendency toward higher pH values was observed.
- The statistically significant decrease in chloride concentration may be attributed to chlorine degassing. A simultaneous decrease in ORP was also observed; in water supply systems, ORP and chlorine concentrations are known to be closely related. However,

when mean, minimum, and maximum measured values are considered together with the measurement uncertainty of  $\pm 10\%$ , all values fall within a comparable range. A similar issue arises in the analysis of nitrate concentrations. Although biofilm-associated bacteria within pipes could theoretically reduce nitrate to nitrite or ammonium, all measured values of these parameters were consistently below the detection limit ( $< 0.01$  mg/L). In both cases, statistical data processing led to conclusions that must be regarded as unreliable.

- Despite the occurrence of calcium carbonate precipitation and chlorine degassing, their overall impact on reservoir water quality is negligible.
- Water retention time in the Tonimir reservoir was estimated to be approximately 17 hours using stable isotope  $\delta^{18}\text{O}$  analysis, which is consistent with the value obtained using conventional methods based on the technical characteristics of the WSS (16.2 hours).
- Stable isotopes have proven to be a valuable tool for estimating water retention time in WSSs and represent a useful complement to conventional management approaches.
- Based on the major ion composition and the Piper diagram, water from all sources (Bartolovec, Vinokovščak, and Belski Dol) is of the Ca–Mg– $\text{HCO}_3$  type. The Belski Dol source contains higher magnesium concentrations due to dolomite dissolution.
- The isotopic composition of water from the Bartolovec and Vinokovščak sources is very similar, with differences within the range of analytical uncertainty; therefore,  $\delta^{18}\text{O}$  was not suitable for mixing-model calculations.
- The Belski Dol source exhibits a distinct isotopic composition. The measured values are the most negative among all analyzed samples and are shifted relative to the LMWL for Varaždin. This is most likely due to recharge at higher elevations and longer residence times in the aquifer, corresponding to periods with colder winters and higher snowfall.
- The results of hydrochemical and isotopic indicators measured within the WSS show a range that reflects the input waters from the sources. Measured concentrations did not exceed those observed in the groundwater sources, confirming that no significant changes or secondary contamination occur within the WSS.
- A seasonal variation in the isotopic composition of water within the WSS was observed. This discrepancy can be attributed to factors such as water temperature variations, fractionation processes within pipelines, and different pumping regimes. Despite these influences, the values are distributed within fields that represent their source waters. Moreover, one reservoir showed the same origin during both sampling campaigns

(reservoir R1 and the Belski Dol source). In agreement with the geochemical parameters, no outliers were detected, confirming the absence of contamination within the water supply network.

- The origin of water within the WSS was determined using three mixing-modeling approaches: the mass balance model (MB), forward modeling (FM) using the NETPATH-WIN geochemical modeling software, and inverse modeling (IM) using PHREEQC version 3-A. At the Bartolovec wellfield, mixing of water from individual wells occurs prior to distribution into the network; therefore, mixing was calculated as an initial step at this site. At the other two wellfields, no mixing occurs, and this step was omitted.
- Validation of all three mixing models was performed by calculating sulfate concentrations in the end members and comparing them with measured values. Sulfate was selected due to its conservative behavior, lack of precipitation, absence of addition during disinfection, and it was not used as a tracer. Considering a 5% measurement error for ion chromatography (IC), values below 0.5 mg/L were considered reliable, whereas values exceeding this threshold were regarded as poor results.
- Although all three modeling approaches yielded satisfactory results, inverse modeling (IM) proved to be more reliable than forward modeling (FM) and mass balance modeling (MB). Mixing models indicated contributions from all three sources in the western, southwestern, and northern parts of the water supply network. In contrast, the eastern and southeastern parts of the network rely predominantly on DA water from the Bartolovec groundwater source, indicating high vulnerability of these areas in the event of an emergency at that source. This should be taken into account during water supply risk assessment and when defining control measures to enhance system resilience. Such measures include enabling supply from alternative sources, increasing water storage capacity in vulnerable areas, and, as a short-term measure, supplying water via mobile water tanks.
- Although  $\delta^{18}\text{O}$  did not provide reliable mixing results due to fractionation processes within pipelines, it indicated that water in the reservoirs is in isotopic equilibrium with air, with no evidence of evaporation. This confirms that the reservoirs are well sealed and impermeable.
- The results demonstrate that geochemical modeling can be effectively applied in water security management plans. The proposed methodology is globally applicable to a wide

range of WSS configurations, particularly in systems with significant water losses, for example due to leaking pipelines.

- Validation of mixing models using selected chemical parameters measured in initial and end-member waters enables estimation of the reliability of mixing-model results and provides a practical tool for managing complex water distribution networks.
- A new Total Integrated Network (TIN) approach is presented. By tracing water and quality changes from recharge zones through abstraction, storage, and distribution, it identifies cumulative and segment-specific risks. The approach enables spatial identification of vulnerability hotspots, temporal assessment of natural and operational influences, and identification of critical control points (CCPs). It is based on ten parameters: five routinely monitored under the EU Drinking Water Directive (2020/2184) and five additional tracers, including stable water isotopes, tritium, radon, and noble gases at the sources.
- Recharge temperature was derived from noble gas concentrations, which provide an independent proxy for past recharge conditions in the Belski Dol catchment area. The calculated recharge temperature of  $\sim 8$  °C indicates recharge at higher elevations compared to lowland mean temperatures (10.5 °C). The mean residence time derived from the  $^3\text{H}/^3\text{He}$  method is approximately 25 years.
- Elevated  $^{222}\text{Rn}$  concentrations in the Briška reservoir, relative to the Belski Dol spring, are attributed to radon emanation from soils and rocks combined with aged distribution infrastructure. While radon levels at Belski Dol remain low (12.6–13.3 Bq/L), water transport through older pipelines and fractured media toward the Briška reservoir likely enhances radon input, consistent with findings reported in previous studies.
- The TIN concept extends conventional groundwater vulnerability assessments by explicitly integrating the entire water supply network, thereby supporting more effective risk management. Results indicate that the Belski Dol spring exhibits high hydrochemical stability, long residence times, low vulnerability, and minimal diffuse nitrate risk, confirming its reliability as a naturally protected drinking water source. In contrast, system components (Briška reservoir and PS Filipiće) show increased vulnerability due to elevated radon, nitrate concentrations, and electrical conductivity. The Briška reservoir exhibits the highest vulnerability index, indicating issues related to aged pipelines, potential radon pathways, and increased susceptibility to future contamination.

- The integrated evaluation confirmed that hydrogeological protection alone is not sufficient to ensure water safety. Instead, continuous monitoring across both natural and engineered components is essential. By incorporating hydrochemical, isotopic, and radiological parameters, the TIN approach enables identification of critical control points where interventions would be most effective, such as targeted monitoring at the Briška reservoir and maintenance of distribution infrastructure.

This dissertation has resulted in several scientific contributions: the development of a methodology that improves WSS management, particularly in incident situations, using routine water quality analyses; estimation of water residence time within the system using  $\delta^{18}\text{O}$  isotopic measurements; development of a methodology for quantifying the contribution of individual sources to the WSS, including the introduction of a new validation approach; determination of the origin and age of water at the Belski Dol spring; and presentation of a novel Total Integrated Network (TIN) approach for risk assessment from source to tap.

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# Apendices

## Scientific papers

### Paper 1

**Novotni-Horčička, N.**, Marković, T., Kovač, I., & Karlović, I. (2024). Exploring endogenous processes in water supply systems: Insights from statistical methods and  $\delta^{18}\text{O}$  analysis. *Water*, 16(10), 1425. <https://doi.org/10.3390/w16101425>



## Article

# Exploring Endogenous Processes in Water Supply Systems: Insights from Statistical Methods and $\delta^{18}\text{O}$ Analysis

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**Abstract:** Water used for water supply undergoes numerous changes that affect its composition prior to entering the water supply system (WSS). Once it enters the WSS, it is subject to numerous influences altering its physical and chemical composition, redox potential, and microbial quality. Observations of water quality parameters at different locations within the WSS indicate that it is justified to assume that these processes take place from the source to the end user. In this study, we used the results of routine everyday analyses (EC, T, pH, ORP, chloride, nitrate, nitrite, ammonium, and bacteria) supplemented by experimental data from a one-year sampling campaign assessing the main cations and anions and stable isotopes  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ . Through these data, the statistical significance of the differences between the concentrations of the basic water quality parameters among different WSS locations was determined, together with the water retention time in the system. The results indicate minor changes in water chemical composition within the observed WSS, remaining below the prescribed Maximum Contaminant Level (MCL) for human consumption. However, factors such as water retention time,  $\text{CaCO}_3$  deposition, pH fluctuations, and bacterial growth may influence its suitability, which necessitates further investigation into potential risks affecting water quality.

**Keywords:** water supply system; major cations and anions; stable isotopes; water retention time



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## 1. Introduction

Water entering the water supply system (WSS) must be in accordance with the prescribed requirements for human consumption [1,2]. Before reaching the WSS, it undergoes disinfection processes and/or other conditioning procedures, depending on the quality of the water at the sources. However, the system itself is subjected to the influence of various processes that may affect its regulatory compliance, as well as organoleptic acceptability by consumers. The water supply system is a complex network consisting of pipes with different diameters and lengths, along with tanks, pumps, valves, and other plumbing devices made of various materials, all of which can have an impact on the processes within the system. The potentially occurring process is the formation of biofilms due to microbial growth in the presence of nutrients, such as natural organic matter, iron, nitrogen, phosphorus, manganese, sulfates, and humic substances, that are originally present or have entered the system after processing [3]. Additional processes include the formation and release of deposits in pipes, corrosion, and the formation of harmful disinfection byproducts due to interaction between the disinfectant and organic matter in water, etc. [4–9]. All these processes could have a significant impact on water quality and acceptability [4–7].

The water supply system is dynamic, as hydraulic conditions fluctuate continuously over a 24 h period due to consumption needs and malfunctions within the system (pipe burst, maintenance activities, etc.). This dynamic nature leads to changes in the water flow direction, pressure, and temperature, which can influence the water retention time within the system, cause changes in pH, influence the solubility of metals present in the system, etc. [8,9].

Water suppliers are obligated to control the quality of delivered water to consumers. Water quality monitoring is carried out within the framework of conducting basic and extended chemical and microbiological analyses on a daily, weekly, and monthly basis depending on the number of consumers and amount of water pumped. By systematically collecting this data, water suppliers gain insights into the water quality within their system, allowing them to improve guidelines for managing the WSS [10,11]. The collected data can be used as a base for statistical analysis in order to predict whether water quality will deteriorate in the near or distant future [12–15]. The stable water isotopes  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  serve as very useful tools in the analysis of the water cycle, providing essential information about water retention time (residence time), identification of chemical processes, etc. [16–20]. According to the US EPA [21], water retention time is the main factor affecting the deterioration of water quality in WSSs. It often happens that, due to less consumption or over-dimensioning of the system for fire flow requirements, water stays in pipes or reservoirs for a longer time, which leads to a decrease in disinfectant concentration. This further facilitates microbial growth, changes in pH levels, particularly during warmer months due to increases in water temperature, and various reactions between materials or sediments. Methods for determining water retention time in WSSs include chemical tracers, mathematical models, or their combined use, each with its own set of advantages and disadvantages [22,23]. Recently, naturally occurring radioactive and stable isotopes in water have been utilized for the determination of the water retention time in distribution systems [24].

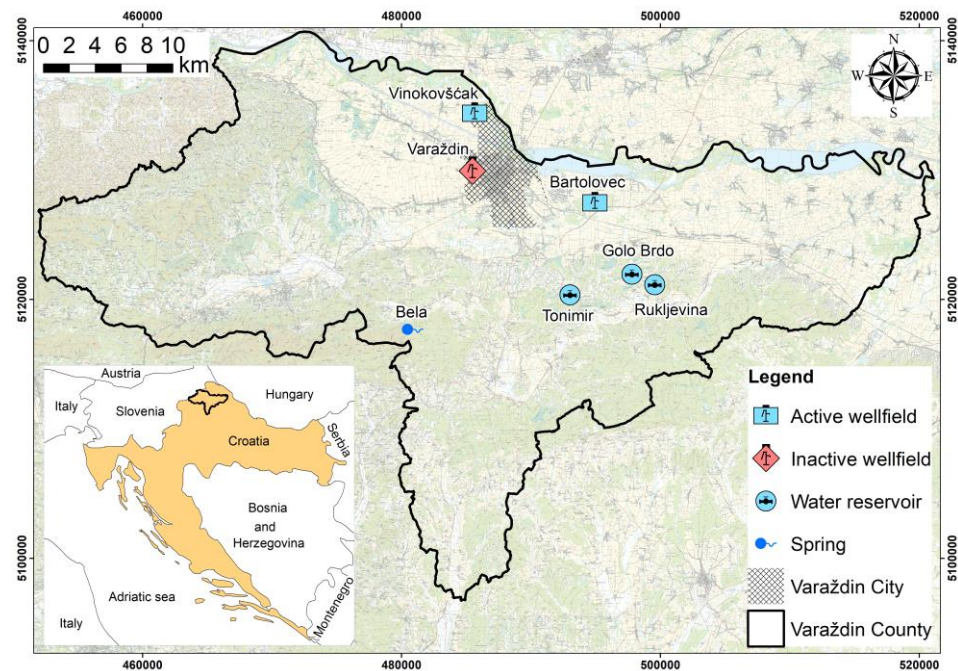
This paper explores the application of  $\delta^{18}\text{O}$  and statistical data processing on selected chemical parameters within a small part of the water supply network managed by Varkom Inc., Croatia. The objectives of the study were the following: (i) to characterize the water from the source to the tap by analyzing hydrochemical parameters; (ii) to statistically analyze selected water quality parameters: chloride, nitrate, pH, electrical conductivity (EC) and temperature (T) over a two-year period, aiming to detect any significant changes that would potentially impact the compliance of the drinking water standards; (iii) to verify the reliability of basic statistical analysis results through geochemical modeling; (iv) to calculate the water retention time in the WSS by using  $\delta^{18}\text{O}$  and an algorithm based on technical WSS information, and compare the obtained results. All this work is carried out to ensure sustainable management of the WSS, not only within the studied system but also to validate its applicability for WSSs worldwide.

## 2. Materials and Methods

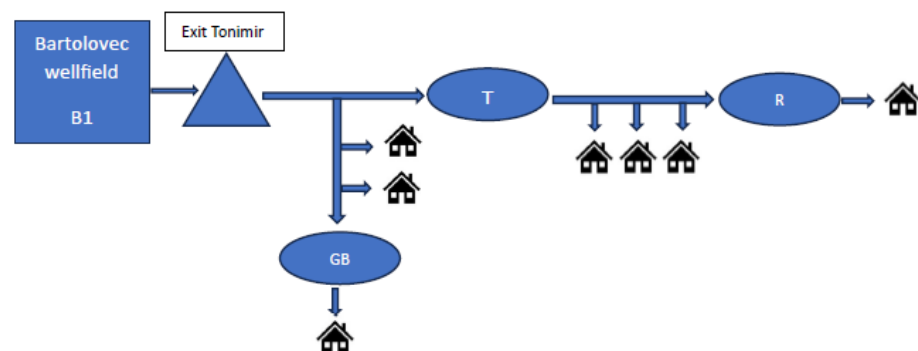
### 2.1. Research Area

This research focused on a small segment of the WSS operated by Varkom Inc. in Varaždin County, northwestern Croatia (Figure 1). The whole WSS spans approximately 1600 km, comprising 20 reservoirs with a total volume of 19,500 m<sup>3</sup>, and supplies about 120,000 inhabitants [25]. Generally, there is no water treatment (except for one well that is filtered through activated carbon, but it is not situated in the study area).

The entire WSS is mixed and very complex, drawing water from three groundwater sources (Bartolovec and Vinokovščak wellfields, and Bela spring). For this study, a small segment of the WSS was selected due to its well-defined traceability, allowing tracking of the water flow from the pumped well through pipelines to the reservoir, without mixing water from other wells. This approach enables us to monitor changes in chemical parameters throughout the distribution. Specifically, this study centered around well B-1 at the Bartolovec wellfield, from which water is drawn and sent through pipelines to the Tonimir (T) and Golo Brdo (GB) water reservoirs, which have volumes of 500 m<sup>3</sup> and 100 m<sup>3</sup>. The water from the Tonimir reservoir is directed for consumption, while a flow rate of 4.2 L/s fills the 100 m<sup>3</sup> large Rukljevina (R) water reservoir (Figure 2).



**Figure 1.** Geographical position of the study area presenting the main groundwater sources and the selected water reservoirs investigated within this study.



**Figure 2.** Schematic illustration of the selected segment of the WSS (B1—well; Tonimir—exit from the wellfield towards reservoirs (T—Tonimir, R—Rukljevina, GB—Golo Brdo)).

## 2.2. Water Sampling and Analysis

Water samples were taken from well B-1 and reservoirs T, GB, and R by two different companies employing different sampling frequencies.

The first data set is a part of the water sampling campaigns from well B-1 and reservoirs T, GB, and R as part of the operational monitoring of the Varkom Inc. supplier from Varaždin, Croatia. Samples were collected in accordance with HRN ISO 5667-5:2011: Water quality—Sampling—Part 5: Guidance on sampling of drinking water from treatment works and piped distribution systems (ISO 5667-5:2006) and analyzed in its own laboratory. The dynamics of the sampling were once a week throughout 2021 and 2022. The monitored water quality parameters include pH, electrical conductivity (EC), chloride ( $\text{Cl}^-$ ), and nitrate ( $\text{NO}_3^-$ ). These parameters were chosen because they are part of regular analysis and show certain spatial and temporal fluctuations. During this monitoring, additional parameters, such as  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , temperature, turbidity, free residual chlorine, and microbiological indicators, were also measured. However, they are not included in this study due to the following specific reasons: nitrite ( $\text{NO}_2^-$ ) and ammonium ( $\text{NH}_4^+$ ) are consistently below detection limits, while the remaining parameters depend on external influences. In addition, heavy metals were not considered because of the following: they

are not included in the everyday routine analysis and concentrations are very low, mostly below the detection limit in wells and WSS waters. The pH and EC parameters were measured using a multimeter (Multimeter HQ40d, HACH, Ames, IA, USA); chlorides were determined by titration (Stand. Meth. 22nd Ed., 4500-Cl-B), and nitrates were determined spectrophotometrically (St. Meth. 22nd Ed., 4500-NO<sub>3</sub>-B) on a UV-VIS spectrophotometer (Camspec, M509T, Leeds, UK). The precision and accuracy of analytical methods were below 10%, as determined by repeated measurement of standard solutions of known concentration (CertiPUR, Merck, VWR Chemicals, Radnor, PA, USA).

The second data set was obtained from three sampling campaigns in July and November 2022 (well B-1 and reservoir T) and February 2023 (well B-1 and reservoirs T, R, and GB) performed by the Hydrochemical Laboratory of Croatian Geological Survey, Zagreb, Croatia within the scopes of the TRANITAL and WATSON projects. Prior to sampling, pH, EC, T, dissolved oxygen (DO), and redox potential (ORP) were measured using a WTW multimeter. Concentrations of basic anions and cations were analyzed on Ion Chromatograph Dionex ICS 6000, while alkalinity was determined by titration with 1.6 N H<sub>2</sub>SO<sub>4</sub> with phenolphthalein and bromocresol green-methyl indicators, and then converted into equivalent concentrations of HCO<sub>3</sub><sup>-</sup>. The precision of the measurements was determined based on the charge balance of the main ions, as quantified by Ion Balance Error (IBE), which was less than 5%.

Ratios of the stable isotopes δ<sup>18</sup>O and δ<sup>2</sup>H were determined using a Picarro L2130i device (Santa Clara, CA, USA) using CRDS (Cavity Ring-Down Spectroscopy) technology [25], and the results were expressed according to the international standard. USGS standards were used to control measurements, which were periodically checked according to the IAEA international standards: Vienna Standard Mean Ocean Water 2 (VSMOW2) and Standard Light Antarctic Precipitation 2 (SLAP2). For δ<sup>18</sup>O, the measurement precision was ±0.2‰, while for δ<sup>2</sup>H, it was ±0.9‰.

### 2.3. Data Analysis

For each parameter at every location, the number of data points ( $n$ ), average concentration ( $\bar{x}$ ), corresponding variance ( $\sigma^2$ ), and its estimate ( $s^2$ ) were determined:

$$s_i^2 = \frac{n_i}{n_i - 1} \sigma_i^2 \quad (1)$$

In order to determine the statistical significance of the difference between the concentrations at the locations  $L_i$  and  $L_j$ , it is necessary to apply the  $t$ -test:

$$t = \frac{\bar{x}_i - \bar{x}_j}{s_d} \quad (2)$$

whereby:

$$s_d^2 = \frac{(n_i - 1)s_i^2 + (n_j - 1)s_j^2}{n_i + n_j - 2} \cdot \frac{n_i + n_j}{n_i \cdot n_j} \quad (3)$$

The obtained  $t$ -value was compared with the critical value ( $t_\alpha$ ), which was determined for a significance level of 5% and based on the number of degrees of freedom:

$$k = n_i + n_j - 2 \quad (4)$$

Statistical data processing was conducted using the MS Excel tool.

### Hypothesis

It is clear from expression (2) that the  $t$ -value is proportional to the difference between the average concentrations at locations  $L_i$  and  $L_j$ . If the  $t$ -value is less than the critical

one, the null hypothesis ( $H_0$ ) is accepted, indicating that the observed difference is not statistically significant. Otherwise, the alternative hypothesis ( $H_1$ ) is accepted:

$$t \leq t_\alpha \rightarrow H_0 : \bar{x}_i = \bar{x}_j \quad (5)$$

$$t > t_\alpha \rightarrow H_1 : \bar{x}_i \neq \bar{x}_j \quad (6)$$

If the  $t$ -value is greater than the critical one, the difference between the average concentrations is considered statistically significant, which indicates an endogenous process in the water between locations  $L_i$  and  $L_j$  within the water supply system.

#### 2.4. Water Retention Time (Water Age)

The calculation of water retention time of water in the Tonimir reservoir was performed by using  $\delta^{18}\text{O}$  measurements in well and reservoirs. The calculation utilized a simplified model by [25], which was applied to estimate the residence time of water in the ground:

$$t = (1/2 \pi) \times \sqrt{1 / (b/a)^2 - 1} \text{ [years]} \quad (7)$$

where  $t$  is the estimated residence time,  $b$  is the maximal amplitude of the groundwater isotopic data, and  $a$  is the maximal amplitude of the precipitation isotopic data over several years. This formula was adapted for our specific context, where  $t$  represents the estimated retention time of water in the system,  $b$  is the maximal amplitude of the water in the reservoir, and  $a$  is the maximal amplitude of the water isotopic data from well B-1 over two-year monthly measurements. Water retention time in two other reservoirs was not calculated due to stable isotopes being measured only once. To verify the calculated result, water retention time was estimated using an algorithm that takes into account input parameters such as the diameters and length of pipes, reservoir dimensions, and water flux within the pipes.

The PHREEQC version 3 software was used to determine saturation indices and  $\text{CO}_2$  pressure as calculations of carbonate balance within the reservoir system [26].

### 3. Results and Discussion

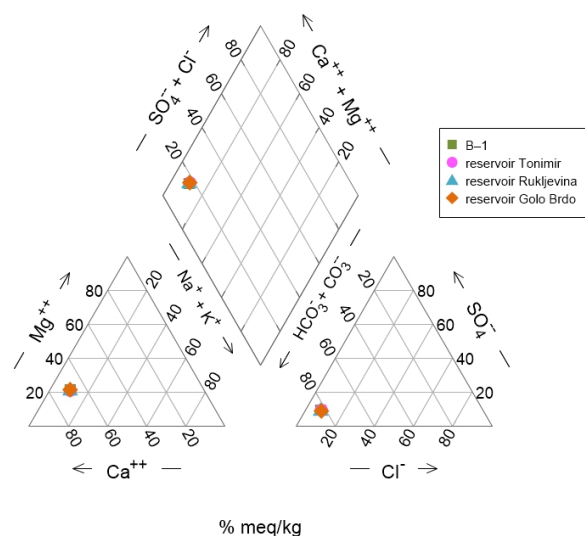
#### 3.1. Hydrochemical Characteristics of Sampled Water

From Tables 1 and 2, it is observed across all sampling campaigns that the EC values are higher in the well water than in reservoirs, ranging from 584 to 680  $\mu\text{S}/\text{cm}$  for wells and from 481 to 674  $\mu\text{S}/\text{cm}$  for reservoirs. pH values displayed oscillations in well and reservoir waters, with the highest oscillation noted during the year 2022. Furthermore, pH values are higher in reservoir waters than in well waters. Both average  $\text{Cl}^-$  and  $\text{NO}_3^-$  concentrations are similar in 2021 and 2022. However, oscillations were observed in minimum and maximum concentrations during this period. By comparing both years, a slight increase in the pH value at all locations and a decrease in chloride and nitrate concentrations, and, consequently, electrical conductivity, at all locations were observed. DO concentrations and ORP were lower in well water in comparison to reservoir waters. Additionally, it is observed that the ORP is the highest in T reservoirs (first in the row after chlorination) and gradually decreases in more distant reservoirs (Table 2). Samples taken from wells represent raw water, meaning that DO concentrations and ORP reflect the natural status of the water within the aquifer. At the T reservoir, water is coming directly after chlorination, so the ORP is higher here than in reservoirs GB and R. This suggests that water travels faster towards reservoir T, followed by reservoir GB, and takes the longest time to reach reservoir R. During this transit, chlorine degassing occurs, leading to a decrease in ORP. The alkalinity ( $\text{HCO}_3^-$ ) was the highest in the well water, while the lowest concentration was measured in the most distant reservoirs (R and GB) from the well (Table 2).

**Table 1.** Minimum, maximum, and mean concentrations of selected parameters for the years 2021 and 2022, measured in the supplier laboratory.

Year		2021					2022				
Location	n	pH	Cl <sup>-</sup> (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	EC (μS/cm)	n	pH	Cl <sup>-</sup> (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	EC (μS/cm)	
B-1	min	6.68	17	13.55	584	52	7.19	19.45	16.6	570	
	max	8.06	29.3	30.7	681		7.92	29.3	22.0	663	
	mean	7.37	23.2	26.5	631		7.46	23.2	19.8	600	
GB	min	6.82	17.0	22.0	596	50	7.09	15.6	18.3	582	
	max	7.74	31.0	33.0	640		7.86	24.9	22.5	622	
	mean	7.42	23.2	27.9	628		7.52	22.2	20.5	603	
R	min	6.84	16.3	22.6	471	49	7.13	18.4	17.4	544	
	max	7.84	30.7	33.6	643		8.04	25.2	22.5	619	
	mean	7.43	22.9	27.8	625		7.65	22.4	20.5	601	
T	min	7.02	15.6	22.1	604	50	7.10	17.9	17.1	577	
	max	7.73	29.3	34.9	650		7.79	25.8	22.4	660	
	mean	7.41	23.1	27.4	629		7.47	22.6	20.2	603	

According to major ion composition, both reservoir waters and well B-1 waters have the same hydrochemical type, characterized as CaMg-HCO<sub>3</sub>, without pronounced differences on the Piper diagram (Figure 3).



**Figure 3.** Piper diagram of sampled waters.

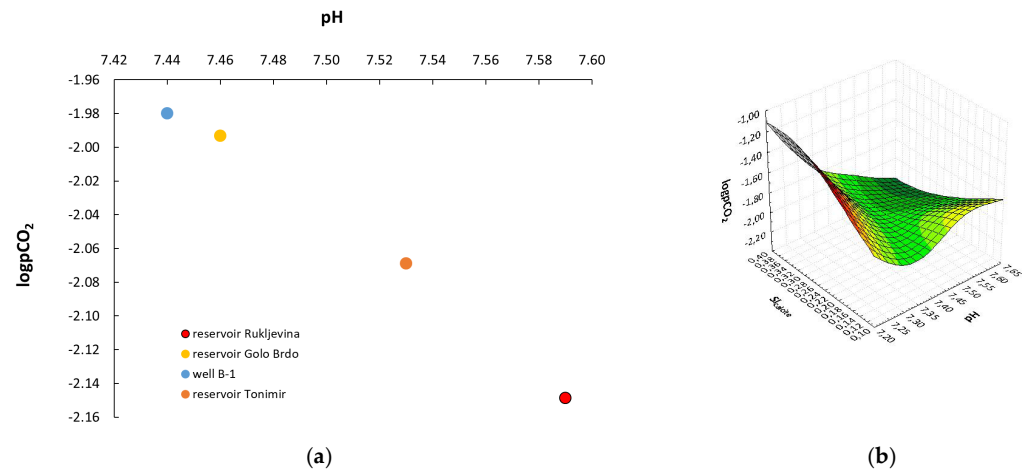
However, when observing the relationship between the pH, logpCO<sub>2</sub> pressure, and calcium saturation index (SI<sub>calcite</sub>), differences are noticed (Figure 4a,b). The well water exhibits a lower pH value and SI<sub>calcite</sub>, but higher logpCO<sub>2</sub>. On the other hand, reservoir waters display higher values of pH and SI<sub>calcite</sub>, but lower logpCO<sub>2</sub> (Figure 4b). In addition, it was observed that in the reservoir farthest from the well, where water retention time is the longest, the pH tended to be higher (Figure 4a).

Given that reservoirs, in a geochemical context, represent open systems where the exchange of gasses between air and water occurs (as there is space above the water filled with air), groundwater from well B-1 is oversaturated with CO<sub>2</sub>. When well water reaches reservoirs, degassing of CO<sub>2</sub> occurs and, as a consequence, the shifting of the carbonate mass balance towards the left side of the well-known equation occurs:



**Table 2.** Results of measurements in Hydrochemical Laboratory of Croatian Geological Survey.

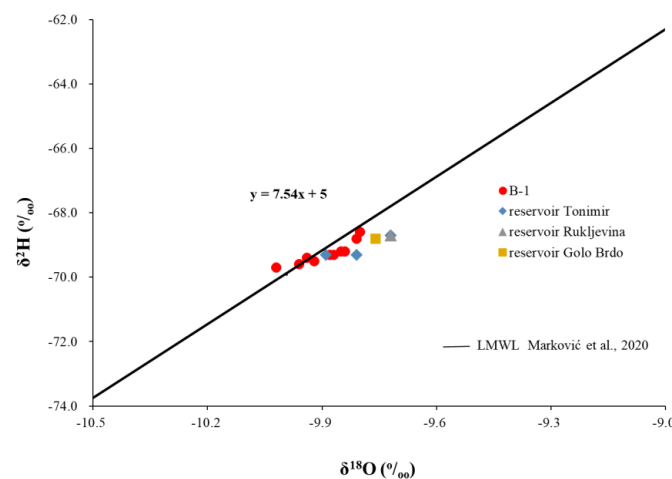
Location	Date	EC ( $\mu\text{S/cm}$ )	T ( $^{\circ}\text{C}$ )	pH	DO (mg/L)	ORP (mV)	$\text{HCO}_3^-$ (mg/L)	$\text{Cl}^-$ (mg/L)	$\text{SO}_4^{2-}$ (mg/L)	$\text{NO}_3^-$ (mg/L)	$\text{Ca}^{2+}$ (mg/L)	$\text{Mg}^{2+}$ (mg/L)	$\text{Na}^+$ (mg/L)	$\text{K}^+$ (mg/L)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
B-1	26 July 2022	661	14.6	7.25	0.9	184	342	22.2	31.5	18.3	96.5	17.8	15	4.5	−9.85	−69.2
T	26 July 2022	660	14.2	7.3	0.8	139	307	22.4	31.5	18.4	96.8	17.8	14.9	4.5	−9.98	−69.3
B-1	30 November 2022	680	13	7.44	1.5	160	340	22.8	32.4	21.7	92.9	17.4	14.5	4.2	−9.8	−68.6
T	29 November 2022	674	12.6	7.52	4.4	162	348	22.3	32.4	21.4	93.9	17.8	14.5	4.3	−9.81	−69.3
B-1	1 February 2023	670	12.7	7.46	2.1	130	375	21.4	31.8	19.7	100	18.7	15	4.3	−9.73	−68.7
T	2 February 2023	603	9.7	7.53	3.2	280	372	22.9	31.7	20.3	100.6	18.6	15.2	4.7	−9.72	−68.7
R	2 February 2023	578	5.7	7.59	8.9	240	371	21.8	31.8	20.5	100.2	18.6	15	4.3	−9.72	−68.7
GB	2 February 2023	586	6.7	7.44	7.6	273	371	22.4	31.4	20.1	100.2	18.6	15	4.3	−9.76	−68.8



**Figure 4.** (a) Relationship between pH vs. logpCO<sub>2</sub>; (b) relationship between pH vs. SI<sub>calcite</sub> vs. logpCO<sub>2</sub> in reservoir and well waters. Red colored part of floating chart represents well water while yellow and green colored parts represent reservoir waters.

With a calcium saturation index above 0, precipitation of calcium in the water is induced, leading to the formation of a calcium crust on the water surface in reservoirs. This reaction results in a decrease in alkalinity, as well as an increase in pH due to precipitation of calcium carbonate, which further contributes to the decrease in EC.

All measured values for δ<sup>2</sup>H and δ<sup>18</sup>O in reservoirs and wells indicate that the water has a meteoric origin (Figure 5), as they are scattered around the local meteoric water line (LMWL) of the study area [20]. Values of isotopes ranged from −9.98 (well B-1) to −9.72‰ (reservoirs T and R) for δ<sup>18</sup>O, and from −69.3 (reservoir T) to 68.6‰ (well B-1) for δ<sup>2</sup>H. According to the measured δ<sup>2</sup>H and δ<sup>18</sup>O values in the water from reservoirs, there was no evaporation effect during the sampling campaigns, indicating a short water retention time. Consequently, the retention time is not long enough to be affected by seasonal temperature changes, which could potentially affect water temperature in reservoirs and thus isotope fractionation.



**Figure 5.** Relationship between δ<sup>18</sup>O and δ<sup>2</sup>H in sampled waters [20].

### 3.2. Water Retention Time in the Tonimir Reservoir

According to Equation (7), water retention time in the Tonimir reservoir is estimated to be approximately 17 h using the stable isotope δ<sup>18</sup>O. Employing the methodology that takes into account the technical characteristics of the water supply system yields a similar estimate of around 16.2 h. The consistency between the results obtained from both methods indicates that δ<sup>18</sup>O could be a useful and reliable tool to gather information about the

system, especially when WSS managers encounter situations where their understanding of the system's operation is limited.

### 3.3. Findings of Statistical Data Processing

Using the data from Table 1, the statistical significance of the differences in concentrations of the measured indicators was determined by comparing the locations on the network (reservoirs T, GB, and R) with the data at the starting sampling point—well B-1 at the wellfield. The calculated  $t$ -values were then compared with  $t_{\alpha}$ , which, for the given number of data points, is 1.984 [27]. The results of these comparisons are summarized in Table 3a,b.

Consistent with hypotheses (5) and (6), the obtained results show that, in 2021, negative  $t$ -values increased with the distance from well B-1 for pH and  $\text{NO}_3^-$ , with significant difference observed for  $\text{NO}_3^-$  in water reservoirs GB and R (Table 3a). For EC, positive  $t$ -values increased with distance from well B-1 but did not demonstrate a significant difference in chloride concentration.

In 2022, the analysis revealed an increase in negative  $t$ -values with distance for pH and  $\text{NO}_3^-$ , whereas, for EC, it decreased in the more distant water reservoirs GB and R (Table 3b). Conversely, the  $t$ -value for  $\text{Cl}^-$  is positive and it is increasing. For the parameters pH,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ , a significant difference was observed between the water samples from B-1 and reservoirs GB and R, as all  $t$ -values are greater than the critical  $t_{\alpha}$ .

In both monitored years, differences were noted in the  $t$ -values for pH, but these differences were more significant for 2022, as a result of  $\text{CO}_2$  degassing from water, as explained in Section 3.1. However, since reservoir systems are very dynamic (filling with fresh water and undergoing aeration during regular maintenance), the pH of water within reservoirs would not reach the critical value for human consumption of 9.5. Hypothetically, considering reservoir T as an example, if the reservoir were sealed, without inflow or outflow occurring, the pH would gradually increase until reaching an equilibrium between  $\text{CO}_2$  in the water and air.

The significant decrease in chloride could be attributed to chlorine degassing. Even ORP is decreasing and, in WSSs, ORP and chlorine concentrations are very well connected [28]. However, looking at the mean, minimum, and maximum measured values and considering the measuring error of  $\pm 10\%$ , it is evident that all of them fall within a similar range. The same issue appears when analyzing nitrate concentrations. While bacteria from biofilms in pipes could potentially reduce nitrate into nitrite or ammonium. All measured values for these two parameters are consistently below the detection limit, which is  $<0.01$  mg/L. In these two cases, statistical data processing led us to unreliable conclusions.

Despite the occurrence of precipitation of calcium carbonate and degassing of chlorine, their impact on reservoir waters is not significant.

**Table 3.** (a) Hypothesis testing for parameters measured in year 2021. (b) Hypothesis testing for parameters measured in year 2022.

<b>(a)</b>																
YEAR 2021	pH				Cl <sup>-</sup> (mg/L)				NO <sub>3</sub> <sup>-</sup> (mg/L)				EC (μS/cm)			
Statistics	B-1	T	GB	R	B-1	T	GB	R	B-1	T	GB	R	B-1	T	GB	R
Mean ( $\bar{x}$ )	7.37	7.41	7.42	7.43	23.2	23.1	23.2	22.9	26.5	27.4	27.9	27.8	631	629	628	625
Standard Deviation ( $\sigma$ )	0.266	0.160	0.191	0.205	2.25	2.37	2.32	2.56	2.90	2.47	2.45	2.5	18.8	11.1	9.6	23.7
Sample Variance ( $\sigma^2$ )	0.071	0.026	0.036	0.042	5.04	5.63	5.38	6.57	8.42	6.08	6.00	6.3	352.6	123.1	92.0	561.2
$s^2$	0.071	0.026	0.036	0.042	5.04	5.63	5.38	6.57	8.42	6.08	5.84	6.3	352.6	123.1	92.0	561.2
Minimum	6.68	7.02	6.82	6.84	17.00	15.6	17.0	16.3	13.6	22.1	22.0	22.6	584	604	596	471
Maximum	8.06	7.73	7.74	7.84	29.25	29.3	31.0	30.7	30.7	34.9	33.0	33.6	681	650	640	643
$n$	50	52	51	51	50	52	51	51	50	51	51	50	50	52	51	51
$sd^2$		0.00187	0.00211	0.00223		0.209	0.206	0.230		0.287	0.282	0.293		9.24	8.75	18.14
$t$		-0.868	-0.992	-1.260		0.125	-0.033	0.533		-1.640	-2.674	-2.350		0.612	0.887	1.362
$t_\alpha$		1.984	1.984	1.984		1.984	1.984	1.984		1.984	1.984	1.984		1.984	1.984	1.984
Hypothesis		H0	H0	H0		H0	H0	H0		H0	H1	H1		H0	H0	H0
<b>(b)</b>																
YEAR 2022	pH				Cl <sup>-</sup> (mg/L)				NO <sub>3</sub> <sup>-</sup> (mg/L)				EC (μS/cm)			
Statistics	B-1	T	GB	R	B-1	T	GB	R	B-1	T	GB	R	B-1	T	GB	R
Mean ( $\bar{x}$ )	7.46	7.47	7.52	7.65	23.2	22.6	22.2	22.4	19.8	20.2	20.5	20.5	600	603	603	601
Standard Deviation ( $\sigma$ )	0.166	0.137	0.144	0.220	1.81	1.49	1.84	1.47	1.28	1.37	1.26	1.24	14.2	14.6	10.8	12.5
Sample Variance ( $\sigma^2$ )	0.028	0.019	0.021	0.048	3.28	2.23	3.38	2.17	1.65	1.88	1.59	1.53	202.9	213.2	117.5	156.6
$s^2$	0.028	0.019	0.021	0.048	3.28	2.23	3.38	2.17	1.65	1.88	1.59	1.53	202.9	213.2	117.5	156.6
Minimum	7.19	7.1	7.09	7.13	19.5	17.9	15.6	18.4	16.6	17.1	18.3	17.4	570	577	582	544
Maximum	7.92	7.79	7.86	8.04	29.3	25.8	24.9	25.2	22.0	22.4	22.5	22.5	663	660	622	619
$n$	52	50	50	49	52	50	50	49	52	50	50	49	52	50	50	49
$sd^2$		0.00091	0.00095	0.00149		0.108	0.131	0.109		0.0691	0.0636	0.0630		8.16	6.32	7.15
$t$		-0.617	-2.076	-5.106		1.714	2.671	2.288		-1.467	-2.859	-2.693		-1.070	-0.953	-0.268
$t_\alpha$		1.984	1.984	1.984		1.984	1.984	1.984		1.984	1.984	1.984		1.984	1.984	1.984
Hypothesis		H0	H1	H1		H0	H1	H1		H0	H1	H1		H0	H0	H0

#### 4. Conclusions

In this paper, we elaborated on the advantages and disadvantages of employing  $\delta^{18}\text{O}$  isotopes, geochemical modeling, and statistical data processing to determine water retention time in WSSs, and investigated how retention time influences water quality within the system and the significance of the processes that are occurring. The major findings are the following:

- The application of statistical data processing indicated the significance of certain changes within the WSS. However, the results of statistical processing should not be taken easily, because they can lead to wrong conclusions.
- Electrical conductivity decreases with increasing distance from the well due to the precipitation of calcium carbonate.
- In the example of the Tonimir reservoir, the water retention time is not long enough that it could deteriorate the water quality in the system.
- pH change is occurring. However, it will never reach MCL, which is pH 9.5, due to the dynamic status of WSSs—short water retention time.
- Stable isotopes have proven to be useful for calculating water retention time in the system, and they can be a useful complement to the management of WSSs.

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## **Paper 2**

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## Article

# Application of Hydrochemical Parameters as Tool for Sustainable Management of Water Supply Network

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**Abstract:** Effective management of Water Supply Systems (WSSs) is crucial for ensuring safe drinking water. The WSS of Varaždin County is a complex network involving three groundwater sources: Bartolovec and Vinokovščak wellfields (alluvial aquifers) and Bela karstic spring. To achieve a comprehensive characterization of WSSs, routine laboratory data was integrated with stable isotopes and geochemical modeling. Within this study, all measured parameters remain below the Maximum Contaminant Level (MCL), ensuring water safety for human consumption. The Piper diagram identified variations in water sources based on their chemical composition, providing a simplified overview of mixing patterns within WSSs. Among the modeling approaches, inverse modeling (IM) was found to be more reliable than forward modeling (FM) and mass balance modeling (MB). Despite the limited capacity of  $\delta^{18}\text{O}$  to provide accurate mixing results, it was revealed that the reservoir water was in equilibrium with the air (no evaporation effects), indicating well-sealed reservoirs. Mixing modeling showed that the western, southwestern, and northern parts of the WSS mixed all three sources, whereas the eastern and southeastern areas primarily relied on the deeper aquifer of the Bartolovec source, indicating potential vulnerability. Strict validation criteria ensured the reliability of results, demonstrating the effectiveness and applicability of geochemical modeling in water security management plans.

**Keywords:** chemical composition; stable isotopes; geochemical modeling; origin; WSS; Varaždin County



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## 1. Introduction

Water for human consumption is a precious resource that affects the development of civilization. While often taken for granted in developed nations, access to safe drinking water remains a significant challenge in less developed or underdeveloped countries, particularly among marginalized communities. According to the World Health Organization [1], over 2 billion people do not have access to safe water for human consumption. Consequently, ensuring access to drinking water for the population becomes progressively more challenging and expensive due to growing demand, the distance of available water source(s) from urban areas, enhanced contamination risks, and climate change impacts [2]. To address these challenges, municipal water managers rely on numerous technologies to ensure the capacity to deliver water with adequate quality and quantity to their consumers [3]. Water suppliers monitor water to ensure its quality meets the standards according to the EU Directive 2020/2184 on the quality of water intended for human consumption [4]. Therefore, it is necessary to protect and manage not only water resources but also the WSS itself. Effective management of the WSS not only reduces water losses (ensuring quantity) but also protects water from contamination within the system.

Within the WSS, water passes through an intricate network of pipelines, valves, latches, and water reservoirs (storage tanks); before reaching end-users, various changes can affect the water quality and, consequently, customer satisfaction with the delivered water.

Therefore, it is necessary to have a comprehensive understanding of the system to quickly address incidents such as pipeline ruptures, water contamination, or user dissatisfaction. This knowledge enables the identification of causes and the implementation of control measures to mitigate risks to acceptable levels. To evaluate water quantity within a water supply network, suppliers commonly employ deterministic or probabilistic analyses to determine the flow rates and pressures in different sections of the network [3,5,6]. Generally, such analysis is robust; it is computationally intensive due to the lack of unique solutions, and the accuracy of these analyses is difficult to verify due to the lack of field measurements within the networks [7].

The application of stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) and geochemical parameters have been widely used as natural tracers in delineating the hydrological cycle of water to better understand the hydrogeological systems [8–12]. In recent studies, the application of stable isotopes and geochemical parameters was used to determine the status of WSSs because they are methodologically very straightforward and allow data to be uniquely connected to the consumer [13–16]. These parameters were shown to be more reliable compared to simplified deterministic or probabilistic network analyses [3,7]. Furthermore, various types of modeling, including mixing models and both forward and inverse geochemical models utilizing isotopic and geochemical parameters, have been used to obtain information about leaks in the water supply network, sewage permeability, and even correlations with a socioeconomic indicator such as population size and income [13].

To the best of our knowledge, the approach of determining the water transport and mixing within the network has not been used in Croatia. Only in recent years has research been conducted to explore the effects of changing water sources on water quality in the drinking WSS [17,18]. However, the application of stable isotopes has been widely used to determine groundwater age, identify sources of contamination, analyze surface and groundwater interaction, etc. [19–26]. In addition, the validation of mixing models using selected chemical parameters measured in initial and end member waters helps to estimate the reliability of gained values by mixing modeling.

The aim of this paper is to employ a multi-proxy approach that integrates geochemical parameters (major ion chemical data and in-situ physiochemical data), stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ), and different types of mixing models to analyze water flow paths within the network and to determine the origin of water in different sections of the network. In addition, this study compares different mixing models and provides recommendations on which model is best suited for complex systems such as in the Varaždin area. The major novelty of this work is demonstrating that simple tools, specifically geochemical parameters that are routinely measured in water supply laboratories, combined with modeling and stable isotopes, can be useful tools for the management of water supply networks, not just on a local but also on a global scale. Furthermore, this study introduces a novel method for validating mixing models, enhancing the reliability of their results.

## 2. Materials and Methods

### 2.1. Study Area

This study focuses on the Varaždin area in NW Croatia, where potable water is distributed by the public water supplier Varkom d.o.o. (Figure 1). The main source of potable water is groundwater extracted from the Varaždin aquifer at two wellfield sites, Bartolovec and Vinokovščak, as well as a spring in Belski dol situated at the foothill of Mt. Ivanščica. Water from these three sources is, after disinfection with chlorine, transported to consumers via a 1670 km long distribution network.

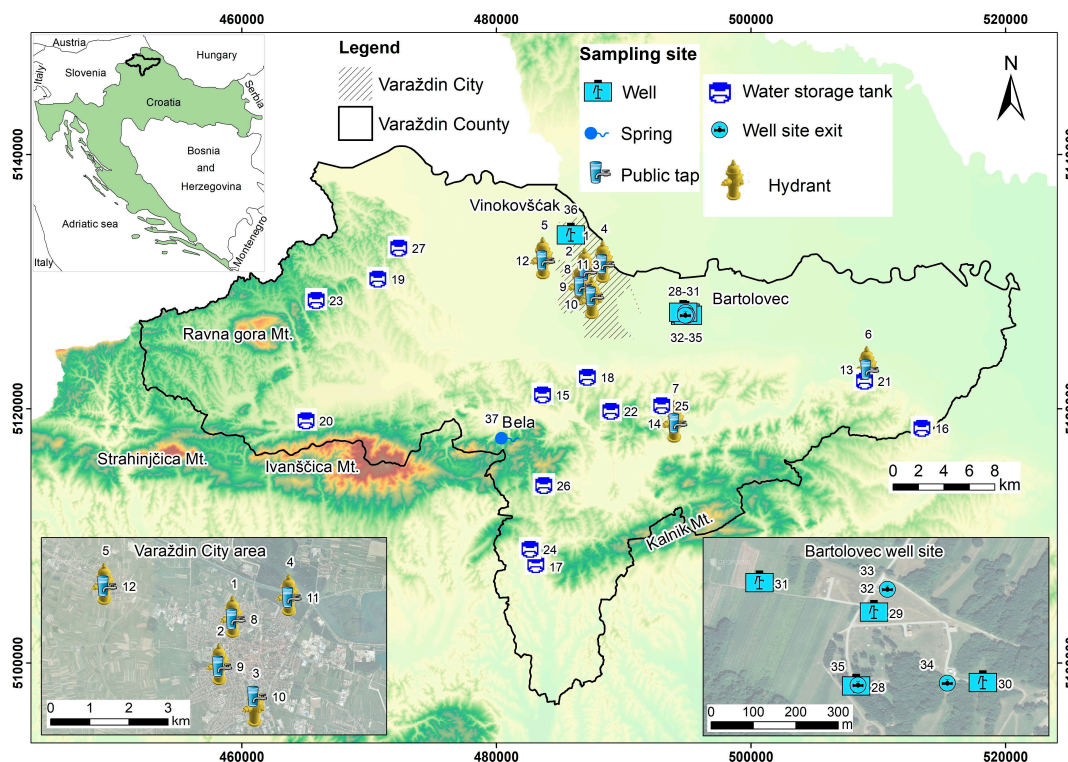


Figure 1. Schematic map of sampled points. See Table 1 for description.

Table 1. Sampling points coordinates and technical data.

Mark on Map (Figure 1)	Code	Description	Longitude (E) (HTRS96/TM)	Latitude (N) (HTRS96/TM)	Elevation (m a.s.l.)	Well Depth (m)	Filter (m)
1	H1	Hydrant AGM	487,061	5,130,938	172.24		
2	H2	Hydrant Perivoj M.Culeja	486,712	5,129,729	171.72		
3	H3	Hydrant S. Vukovića	487,617	5,128,649	170.00		
4	H4	Hydrant Drava	488,490	5,131,493	170.50		
5	H5	Hydrant Sračinec	483,780	5,131,782	175.12		
6	H6	Hydrant Ludbreg	509,239	5,123,187	153.50		
7	H7	Hydrant Varaždinske Toplice	494,099	5,118,929	189.72		
8	PT1	Public tap AGM	487,061	5,130,938	172.24		
9	PT2	Public tap Perivoj M.Culeja	486,712	5,129,729	171.72		
10	PT3	Public tap S. Vukovića	487,609	5,128,958	171.54		
11	PT4	Public tap Drava	488,490	5,131,493	170.50		
12	PT5	Public tap Sračinec	483,780	5,131,782	153.50		
13	PT6	Public tap Ludbreg	509,239	5,123,187	175.12		
14	PT7	Public tap Varaždinske Toplice	494,156	5,118,958	192.23		
15	R1	Reservoir Briška	483,631	5,121,191	331.48		
16	R2	Reservoir Bolfan	513,429	5,118,567	258.52		
17	R3	Reservoir Breznički Hum	483,103	5,107,850	240.00		
18	R4	Reservoir Doljan	487,150	5,122,584	223.13		
19	R5	Reservoir Donja Voća	470,694	5,130,305	275.30		
20	R6	Reservoir Lepoglava	465,054	5,119,159	285.98		
21	R7	Reservoir Ludbreg	508,931	5,122,285	207.58		
22	R8	Reservoir Lužan	489,003	5,119,909	305.41		
23	R9	Reservoir Pintarići	465,842	5,128,636	432.18		
24	R10	Reservoir Ščepanje	482,649	5,109,059	336.34		
25	R11	Reservoir Tonimir	492,999	5,120,354	258.81		
26	R12	Reservoir Topličica	483,721	5,114,068	358.96		
27	R13	Reservoir Vinica	472,327	5,132,738	259.86		
28	B1	Well B-1, Bartolovec well field (BWF), SA	494,829	5,127,376	161.56	32	15–25
29	Zd-4	Well Zd-4, BWF, DA	494,858	5,127,550	162.50	105	62–102
30	Zp-7	Well Zp-7, BWF, SA	495,036	5,127,384	161.35	45	15–42
31	Zp-9	Well Zp-9, BWF, SA	494,671	5,127,620	162.14	45	15–42
32	E1	Exit Varaždin, BWF	494,880	5,127,604	162.13		
33	E2	Exit Ludbreg, BWF	494,880	5,127,604	162.13		
34	E3	Exit Novakovec, BWF	494,978	5,127,382	162.13		
35	E4	Exit Doljan, BWF	494,832	5,127,378	162.13		
36	ZV4	Well ZV4, Vinokovščak well field	485,842	5,133,689	174.80	45	10–40
37	Bela	Bela spring	480,891	5,117,696	218.54		

The Bartolovec wellfield site, situated approximately 7 km east of Varaždin town in the village of Bartolovec, serves as the primary water source for the majority of consumers in Varaždin County, meeting around 70% of the water needs for human consumption in the regional WSS. The annual average rate of pumped water is 264 L/s (data for 2022) from 9 wells (B1-B9), of which 5 capture water from the upper aquifer (depth up to 45 m) and 4 from the lower aquifer (depth up to 120 m). The Quaternary-age alluvial aquifer in this area is divided by a 5 m thick silty-clay aquitard between the shallow aquifer (SA) and the deeper aquifer (DA) [27]. This aquitard protects the DA from pollution from the surface due to its poor permeability. Pumped groundwater from wells is disinfected and mixed in a ring-shaped pipeline system with five exits designated for distribution: Varaždin, Ludbreg, Novakovec, Doljan, and Tonimir (Figure 1). Because water mixes in a ring-shaped pipeline, it is hard to know the specific source and quantity of water distributed in each direction. This information is especially important in case of incidents when potential deterioration of water quality in the water supply network could occur.

The Vinokovščak wellfield site is located approximately 3 km NW of Varaždin, where groundwater is pumped from 4 wells (ZV1-ZV4), with an average annual rate of 82 L/s (data for 2022, Figure 1). Due to the thinner alluvial aquifer in this area, the wells draw water from a maximum depth of 45 m. Screens in wells are installed along the depth of wells, facilitating the mixing of water from SA and DA during pumping. After disinfection, the pumped groundwater from wells is distributed to one pipeline towards the north part of Varaždin town and the NW part of Varaždin County.

Spring water from Bela is captured at an average rate of 30 L/s (Figure 1). It is located in the village of Bela at the foot of the Ivanščica Mountain, 20 km SW from the town of Varaždin. This water source gravitationally flows through the pipeline to the pumping station Filipići, where it is disinfected and distributed into the water supply network. The Bela spring represents the smallest groundwater source within the WSS, covering 8% of the region's water needs. Unlike the previously described groundwater sources, the catchment area of the spring Bela consists of carbonate-fissured rocks, mainly dolomite of the Triassic age [28].

## 2.2. Water Sampling

Raw water samples (prior disinfection) were collected on a monthly basis between December 2021 and December 2022 from groundwater sources at Bartolovec, Vinokovščak, and Bela for chemical and isotopic analyses (Figure 1, Table 1). At the Vinokovščak wellfield, one well (ZV-4) was sampled, while at the Bartolovec wellfield, samples were taken from three wells: two from SA (B-1 and Zp-7) and one from DA (Zd-4). Additionally, at the Bartolovec wellfield, samples were collected from all five (Figure 1, Table 1). Sampling from the distribution network was carried out twice, in July and November 2022. During the July 2022 campaign, reservoirs and public taps were sampled, while in the November 2022 campaign, reservoirs and hydrants were sampled (Figure 1, Table 1). Since the second campaign occurred during winter, public taps were closed to prevent pipe bursting due to low air temperatures.

Samples were poured into a 50 mL plastic bottle with a tight-fitting cap for stable isotope analyses and in 350 mL for chemical analyses. All samples were measured in the laboratory immediately upon returning from the field.

## 2.3. Water Analyses

Field measurements of electrical conductivity (EC), water temperature (T), pH, and dissolved oxygen content (DO) were conducted using a calibrated portable WTW instrument. Measured DO values for wells were excluded from consideration because they were affected by pumping. Total alkalinity was determined in the field by titration with 1.6 N H<sub>2</sub>SO<sub>4</sub> using phenolphthalein and bromocresol green-methyl red as indicators. Major cations and anions were analyzed using the ion chromatography technique on a Dionex ICS-6000 DC at the Hydrochemical Laboratory of the Croatian Geological Survey. The

analytical precision of cation and anion measurements, indicated by the ionic balance error (IBE), was computed on the basis of ions expressed in meq/l. The IBE value was observed to be within a limit of  $\pm 5\%$  [29,30].

The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  were determined using the Picarro L2130i (Santa, Clara, USA) in the Hydrochemical Laboratory of the Croatian Geological Survey. The instrument uses CRDS (Cavity Ring-Down Spectroscopy) technology [31]. All measurements were checked against USGS standards (USGS48  $-2.224 \pm 0.012\%$   $\delta^{18}\text{O}$ ;  $-2.0 \pm 0.4\%$   $\delta^2\text{H}$ ; USGS46a  $-30.09 \pm 0.05\%$   $\delta^{18}\text{O}$ ;  $-235.6 \pm 0.7\%$   $\delta^2\text{H}$ ), which were checked periodically against the International Atomic Energy Agency (IAEA) standards: Vienna Standard Mean Ocean Water 2 (VSMOW2) and Standard Light Antarctic Precipitation 2 (SLAP2). Measurement precision was  $\pm 0.2\%$  for  $\delta^{18}\text{O}$  and  $\pm 1\%$  for  $\delta^2\text{H}$ . It is generally known that all isotopic results are expressed as per the international measurement standard, VSMOW2 [32,33].

#### 2.4. Modeling

This study employed three approaches to calculate water mixing ratios: the mixing models. The first approach involves the application of mass balance calculations (MB), a commonly used method [34–36] where proportions of two-end members in the observed sample can be calculated using simple formulas based on conservative tracers  $\text{Cl}^-$  and  $\delta^{18}\text{O}$ .

Specifically, the calculations were performed using the following two equations:

$$f_{S1} = \frac{\text{Cl}_{\text{sample}}^- - \text{Cl}_{S2}^-}{\text{Cl}_{S1}^- - \text{Cl}_{S2}^-} \quad (1)$$

$$f_{S1} = \frac{\delta^{18}\text{O}_{\text{sample}} - \delta^{18}\text{O}_{S2}}{\delta^{18}\text{O}_{S1} - \delta^{18}\text{O}_{S2}} \quad (2)$$

where  $f_{S1}$  represents the fraction (between 0 and 1) of source water 1 estimated in a sample of mixed origin. The  $\text{Cl}_{\text{sample}}^-$  and  $\delta^{18}\text{O}_{\text{sample}}$  represent concentrations in waters from reservoirs, public taps, exits, and hydrants;  $\text{Cl}_{S1}^-$ ,  $\delta^{18}\text{O}_{S1}$ ,  $\text{Cl}_{S2}^-$ , and  $\delta^{18}\text{O}_{S2}$  represent concentrations in different groundwater sources.

The other two models were conducted using geochemical modeling software, which uses geochemical parameters to infer the physical and chemical processes that control water chemistry along flow paths, specifically within the water supply network (pipeline, reservoirs), and to quantify reactions occurring within this network. The inverse geochemical modeling (IM) was performed using the PHREEQC software, version 3-A [37]. It is based on a geochemical mole-balance program that calculates the phase mole transfers (the moles of minerals and gases that enter or leave a solution) to account for the differences observed between initial and final water composition along the flow path, in our case, within the network. The third approach involved using the NETPATH-WIN software for forward geochemical modeling (FM) [38,39]. In all three models, EC,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\delta^{18}\text{O}$  were used as constraints. Each of them has its advantages and disadvantages, which will be explained in more detail in the Results and Discussion chapter. The accuracy of the results was controlled according to the saturation index data for calcite and dolomite, which were compared with the actual values.

At the Bartolovec source, mixing models were performed in two steps because the mixing of SA and DA occurs at the source prior to water reaching the water supply network. The first step was to calculate the mixing proportions of groundwater from SA (represented by B-1 and Zp-7) and DA (represented by Zd-4) in the final waters of the wellfield, which are the exits (E1-E5). For the groundwater sources Vinokovščak and Bela, this step was unnecessary due to the presence of only one exit into the network. In the second step, mixing models in the network (reservoirs, hydrants, and public taps) were calculated, where exits from all water sources (E1-E5, ZV-4, and Bela) represented initial waters, and samples from the network (H1-7, PT1-7, and R1-13) represented final waters. The modeling

results are presented as percentage ratios of the initial waters in the final ones (ranging from 0 to 100%).

The validation of all three mixing models was performed by calculating sulfate concentrations in end members and comparing them with measured values. The sulfate concentration was chosen due to its conservative nature, inability to precipitate or to be added during disinfection, and it was not used as a tracer in calculations. Considering a 5% measurement error on IC, all values below 0.5 mg/L were taken as reliable results, while values exceeding this threshold were considered as poor results.

### 3. Results and Discussion

All measured parameters in raw water (groundwater sources) and water supply network, including mean (average), minimum, maximum, and standard deviation, are presented in Tables S1 and S2 in the Supplementary Material.

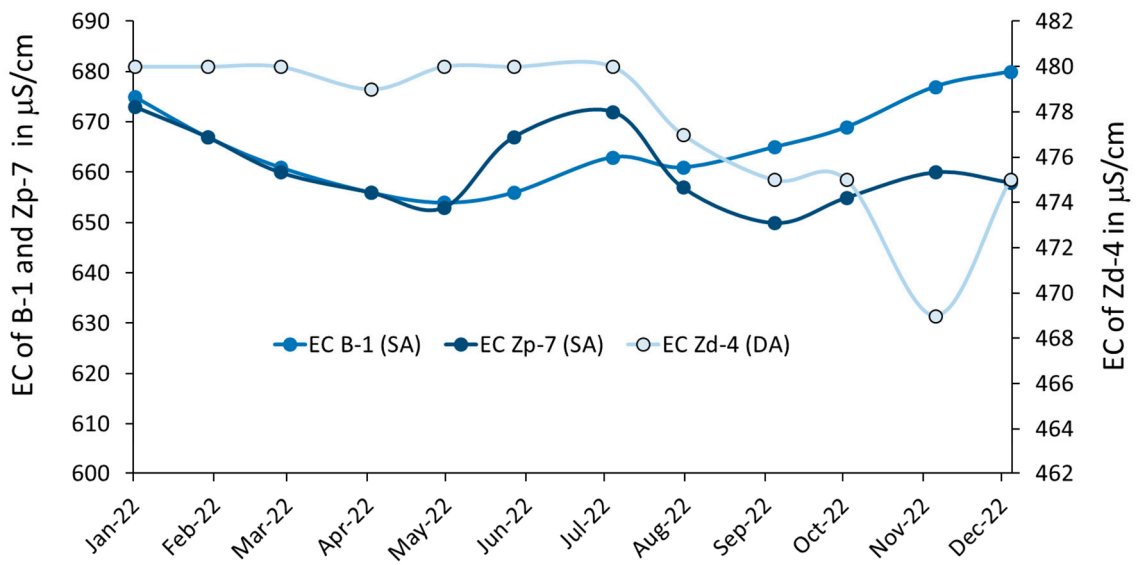
#### 3.1. Geochemical and Isotopic Characteristics of Groundwater Sources

##### 3.1.1. Bartolovec Wellfield

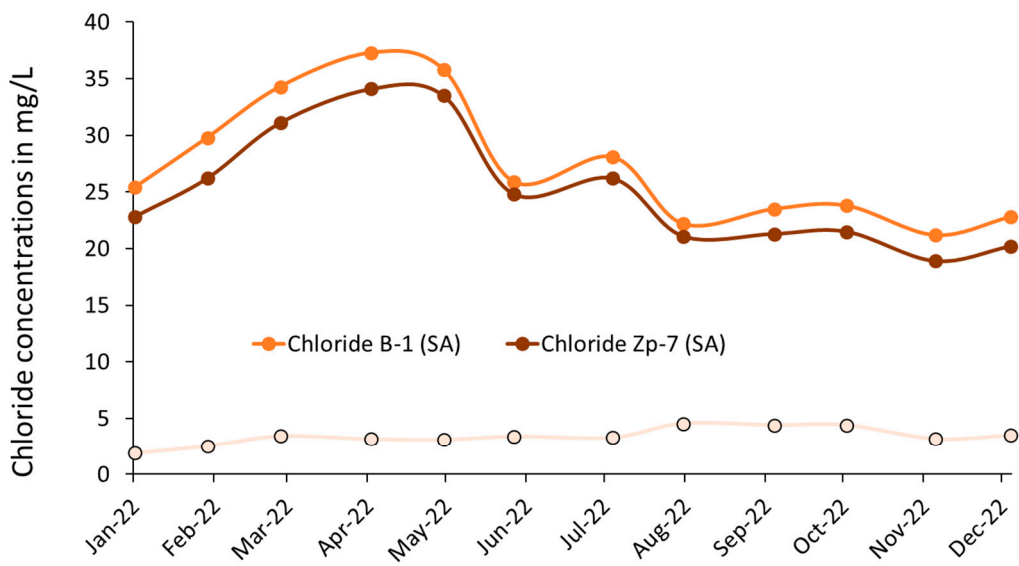
Measured temperature values in SA varied from 12.5–14.9 °C for well B-1 and 12.2–13.3 °C for well Zp-7 (Table S1). Although both wells capture the same aquifer, the observed difference in temperatures is attributable to the shallower depth of well B-1 (32 m) compared to well Zp-7 (45 m). Consequently, well B-1 is susceptible to water percolation from the surface during different seasons, while deeper Zp-7 remains unaffected by such phenomena. The average measured temperature in well Zd-4 during 12 months was 13.2 °C, indicating homogenization and longer transit time of water within the DA. Measured pH values showed differences between SA and DA. The pH values in SA varied from 7.2 to 7.7, showing higher oscillations throughout the year, while pH values in DA are slightly higher, ranging from 7.4 to 7.7 without significant oscillations during the year (Table S1).

Measured EC and nitrate concentrations in SA showed higher oscillations throughout the year compared to DA (Figure 2). Nitrate concentrations in well B-1 varied from 13.7 to 22.4 mg/L and in well Zp-7 from 19.0 to 26.0 mg/L, demonstrating significant oscillations during the year (Figure 2). The intensive agricultural production in the catchment area of these wells, coupled with a very thin surface-covering layer, contributes to leaching nitrates from the surface into the groundwater. However, this phenomenon is not observed in the well Zd-4, where nitrate concentrations range from 4.7 to 9.2 mg/L, additionally indicating a longer transit time of water in DA compared to SA. This observation confirms that the clay-silty layer that divides the aquifers has a protective function [25,40]. The measured EC values were higher in SA compared to DA. In SA (wells B-1 and Zp-7), EC values varied from 650 to 680  $\mu\text{S}/\text{cm}$ , while in DA, EC varied from 469 to 480  $\mu\text{S}/\text{cm}$  (Figure 2). This discrepancy is a consequence of higher concentration of dissolved solids in waters of SA relative to DA. In addition, the measured chloride concentrations in SA are significantly higher compared to DA. The average chloride concentration in well B-1 is 27.1 mg/L, and in well Zp-7, 24.7 mg/L, whereas in well Zd-4, the average is only 3.42 mg/L. High chloride and nitrate concentrations in the SA indicate washing out from the unsaturated zone, as previously observed in the study by Karlović et al. [41].

Geochemical differences between SA and DA were also visible in their  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ , and  $\text{F}^-$  concentrations. In SA, these parameters are higher, with average values of 94.3 mg/L, 17.3 mg/L, 31.7 mg/L, 14.1 mg/L, 4.24 mg/L, 336.7 mg/L, and 0.39 mg/L, respectively, compared to DA, where the corresponding averages are 73.9 mg/L, 13.8 mg/L, 6.94 mg/L, 5.21 mg/L, 1.31 mg/L, 304.8 mg/L, and 0.30 mg/L (Table S1). According to the Piper diagram (Figure 3), both waters belong to the CaMg- $\text{HCO}_3^-$  hydrochemical type, which is a consequence of the dissolution of carbonate and silicate minerals that form the aquifer [27,42,43]. However, even on this diagram, differences between waters are visible.

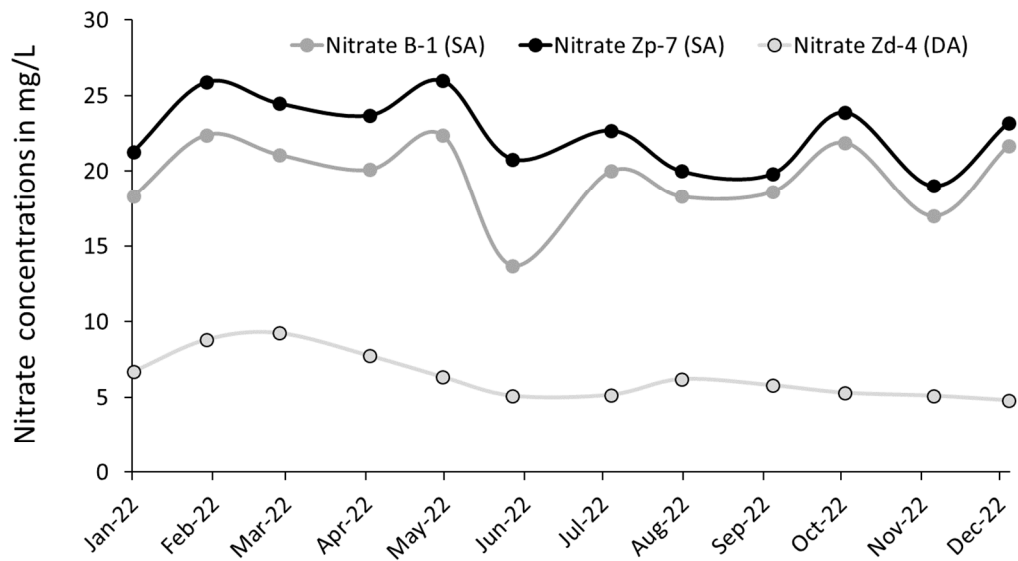


(a)



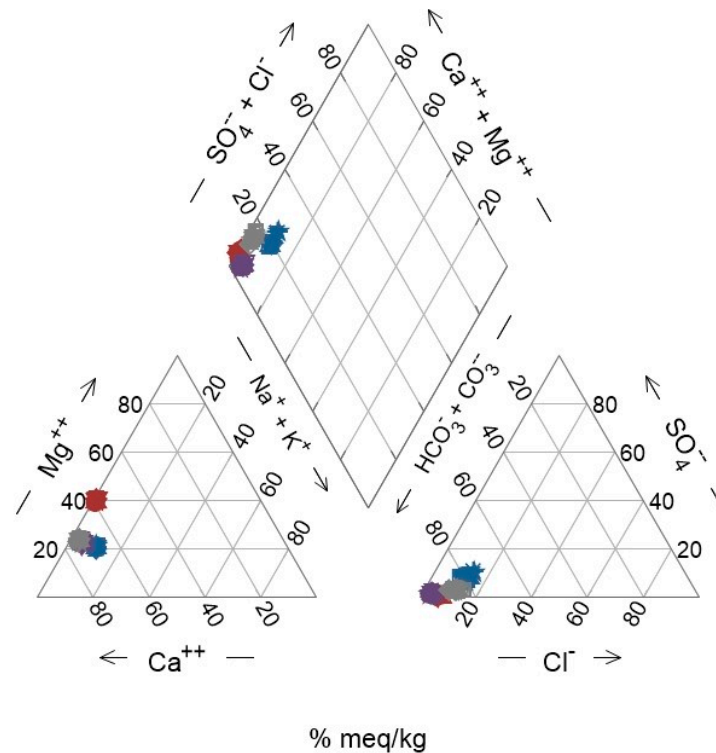
(b)

Figure 2. Cont.



(c)

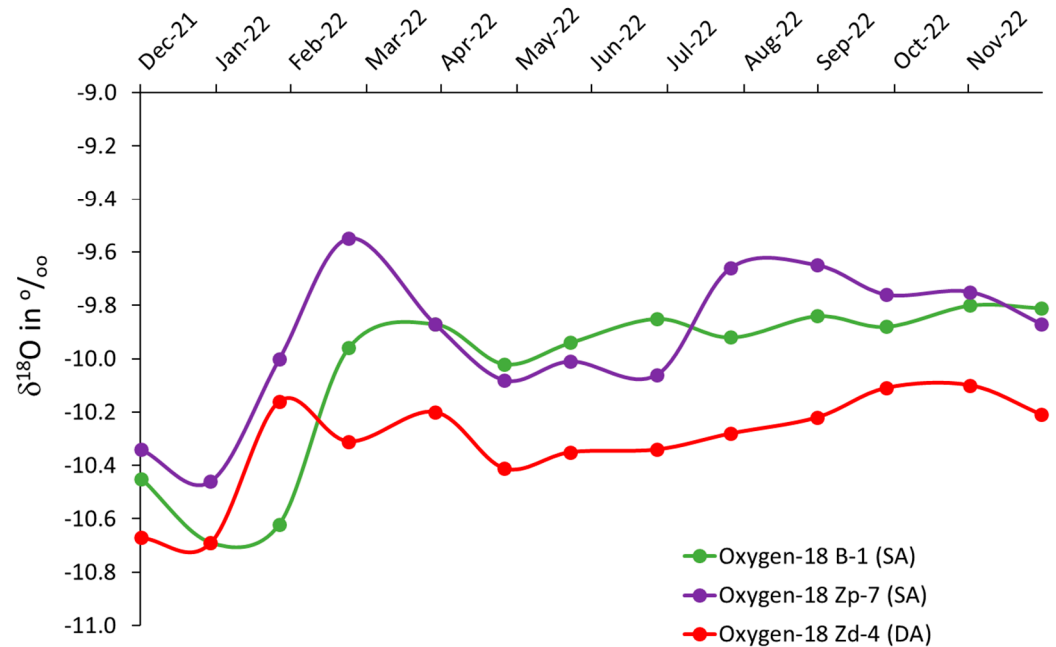
**Figure 2.** Measured monthly values of (a) EC, (b)  $\text{Cl}^-$ , and (c)  $\text{NO}_3^-$  in groundwater of Bartolovec wellfield.



**Figure 3.** Piper diagram of sampled wells and spring (red: Bela, blue: Zp-7 (SA), purple: Zd-4 (DA), and grey: ZV-4).

In addition to the aforementioned parameters, monthly measurements of stable oxygen and hydrogen isotopes in water also revealed differences between SA and DA, especially in the warmer part of the year (Figure 4). In SA,  $\delta^{18}\text{O}$  values range from  $-10.69$  to  $-9.55$  ‰ and  $\delta^2\text{H}$  from  $-74.5$  to  $-67.8$  ‰, while in DA, they range from  $\delta^{18}\text{O}$   $-10.69$  to  $-10.1$  ‰

for  $\delta^{18}\text{O}$  and from  $-73.6$  to  $-70.6$  ‰ for  $\delta^2\text{H}$  (Figure 4, Table S1). Variations between wells B-1 and Zp-7, although they capture the same aquifer, mirror the patterns observed with temperature, chloride, and nitrate concentrations. This phenomenon underscores the heterogeneous nature of SA. All these differences provide valuable insights for developing mixing models.



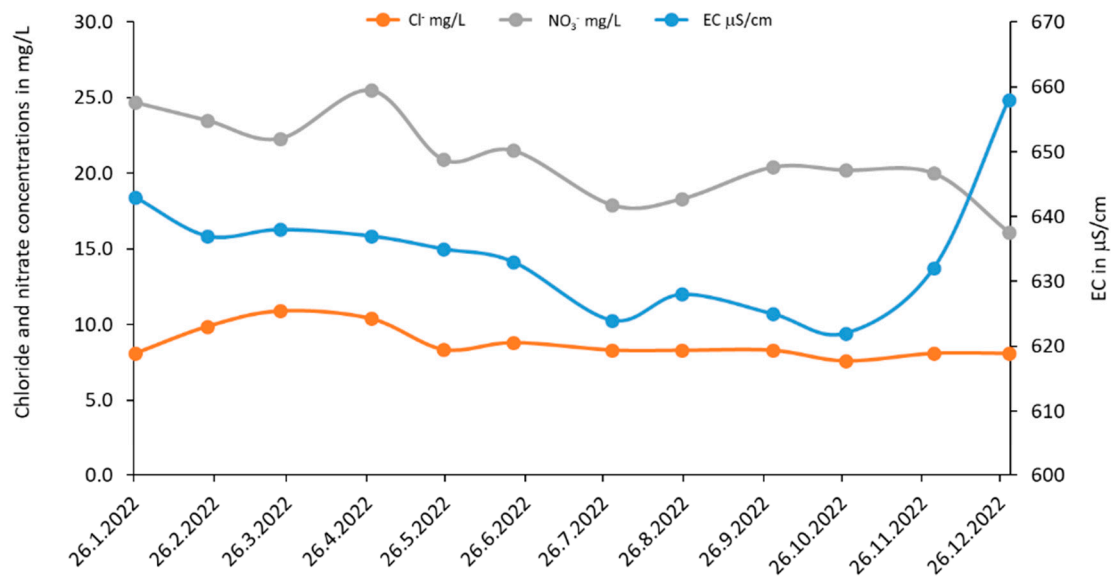
**Figure 4.** Monthly oscillation of  $\delta^{18}\text{O}$  (‰) values in groundwater of the Bartolovec wellfield.

### 3.1.2. Vinokovščak

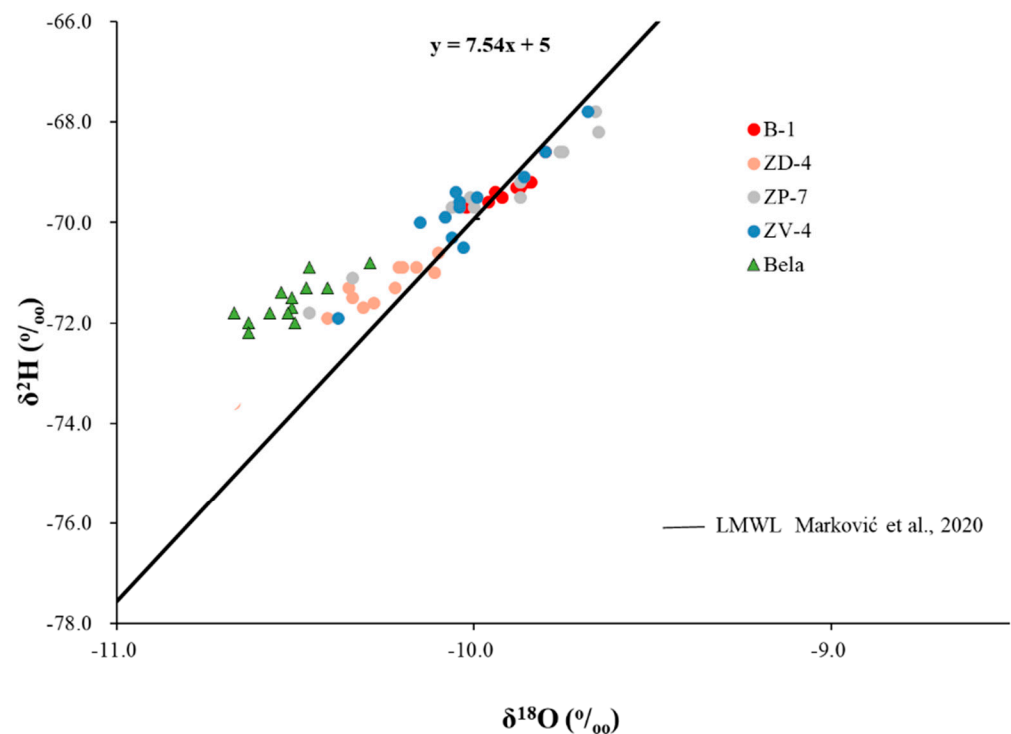
The measured EC values of groundwater at the Vinokovščak wellfield ranged from 622 to 658  $\mu\text{S}/\text{cm}$  (Figure 5). The temperature values ranged from 11.9 to 13.1  $^{\circ}\text{C}$ , while pH values ranged from 7.24 to 7.48 (Table S1). Chloride and nitrate concentrations ranged from 7.6 to 10.9 mg/L and 16.1 to 25.5 mg/L, respectively, without significant oscillations, although a decreasing trend was observed during the monitored period (Figure 5). The monitored year experienced very dry conditions, and this part of the study area is very well connected with the Drava River, especially during periods of low groundwater levels [41]. The Drava River has low concentrations of chloride and nitrate [41], which could contribute to the observed decreasing trend due to the higher river influence towards hydrological minimums.

The concentrations of major ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{HCO}_3^-$ ) also did not show significant oscillation, with measured average values of 98.5 mg/L, 19.3 mg/L, 29.2 mg/L, 4.14 mg/L, 1.52 mg/L, and 357 mg/L, respectively. According to the Piper diagram (Figure 3), monitored waters belong to the  $\text{CaMg-HCO}_3^-$  hydrochemical type, attributed to the dissolution of carbonate and silicate minerals that build the aquifer [27,42,43]. Interestingly, these waters have a similar  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio as waters from deep well Zd-4 of the Bartolovec wellfield, but chloride and sulfate concentrations are higher, reflecting different geochemical conditions within the aquifer (Figure 3).

On the contrary, measured stable oxygen and hydrogen values closely resemble those of the Bartolovec wellfield (Figure 6). It was observed that  $\delta^{18}\text{O}$  oscillated within the range of  $\pm 0.2$  ‰, consistent with the measurement error. Similarly,  $\delta^2\text{H}$  varied around measurement error of  $\pm 1$  ‰. This initial observation was the first hint that  $\delta^{18}\text{O}$  would not be the most suitable parameter for mixing modeling. Furthermore, some values are plotted above the LMWL in the  $\delta^{18}\text{O}$ – $\delta^2\text{H}$  diagram, especially wells DA and ZV-4, which is explained in detail in [11].



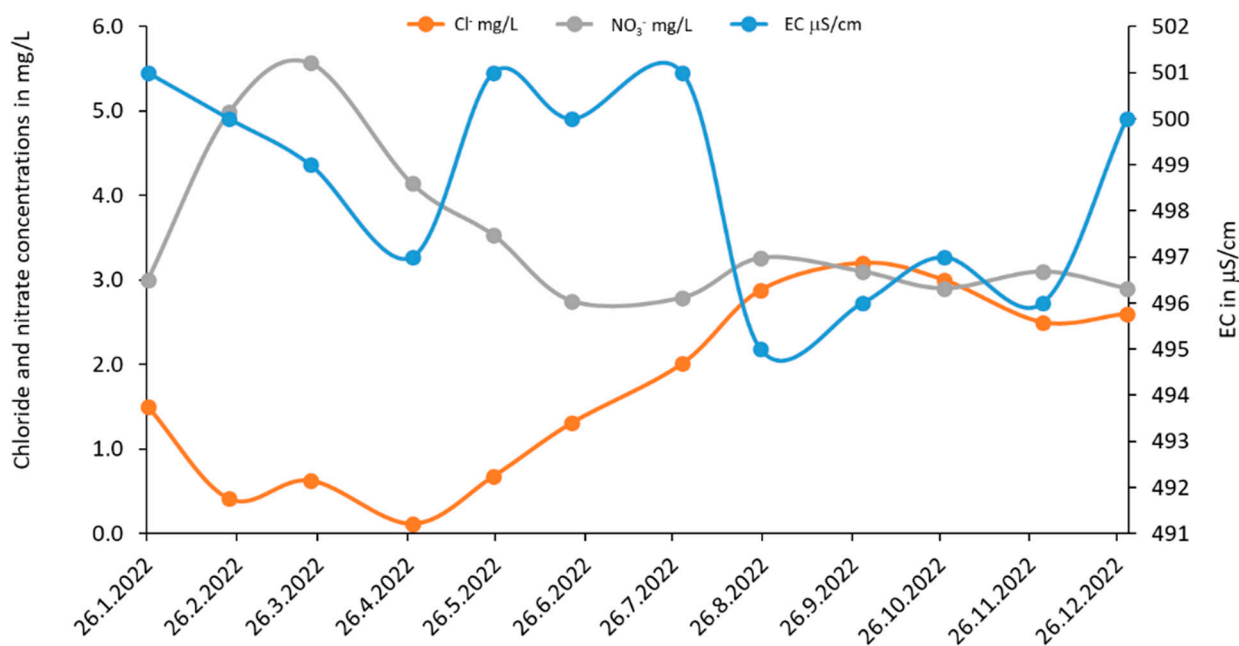
**Figure 5.** Measured monthly values of EC,  $\text{Cl}^-$  and  $\text{NO}_3^-$  in groundwater of Vinokovščak wellfield.



**Figure 6.** Distribution of groundwater  $\delta^{18}\text{O}$  (‰) and  $\delta^2\text{H}$  (‰) values around the local meteoric water line (LMWL) (according to [11]).

### 3.1.3. Bela

All measured hydrochemical parameters at this groundwater source are a consequence of the long transient time of the groundwater [44]. The measured water temperature ranged from 11.1 to 11.3 °C, while the pH values ranged from 7.4 to 7.6 (Table S1). The same behavior is observed in EC values, ranging from 495 to 501  $\mu\text{S}/\text{cm}$  (Figure 7). Higher oscillations were observed in chloride, nitrate, and sulfate concentrations (Figure 7, Table S1), which is attributable to the influence of surface water. The spring is situated along the Varaždin–Podrute road, and it is divided by road by stream. During the high-water periods, surface runoff into the spring occurs.



**Figure 7.** Measured monthly values of EC, Cl<sup>−</sup> and NO<sub>3</sub><sup>−</sup> in groundwater of Bela spring.

Compared to the other two groundwater sources, the spring water contains high concentrations of Mg<sup>2+</sup> (22.9–25.6 mg/L) due to the dolomite dissolution in the catchment area of the spring. Measured average values of other major ions Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and HCO<sub>3</sub><sup>−</sup> are 62.5 mg/L, 1.16 mg/L, 0.49 mg/L, and 314.4 mg/L, respectively. According to the Piper diagram, spring water belongs to the CaMg-HCO<sub>3</sub><sup>−</sup> hydrochemical type (Figure 3), noticeably different compared to the other two sources.

The measured δ<sup>18</sup>O values range from −10.67 to −10.29 ‰, and the δ<sup>2</sup>H ranged from −72.20 to −70.80 ‰ (Table S1). These values are the most negative of all investigated groundwater sources and are shifted from the LMWL for Varaždin (Figure 6). This discrepancy can be attributed to several factors. Firstly, the catchment area of the spring is situated at a higher elevation (averaging about 700 m a.s.l.) with the highest peak exceeding 1000 m a.s.l., resulting in higher, more negative δ<sup>18</sup>O values in spring water. Secondly, the transit time in such aquifer types is long, over 50 years [44]. During this period, the winters were colder, with high amounts of snow [45] serving as the major source of recharge.

### 3.2. Geochemical and Isotopic Characteristics of Water from Water Supply Network—Reservoirs, Public Taps and Hydrants

#### 3.2.1. Reservoirs

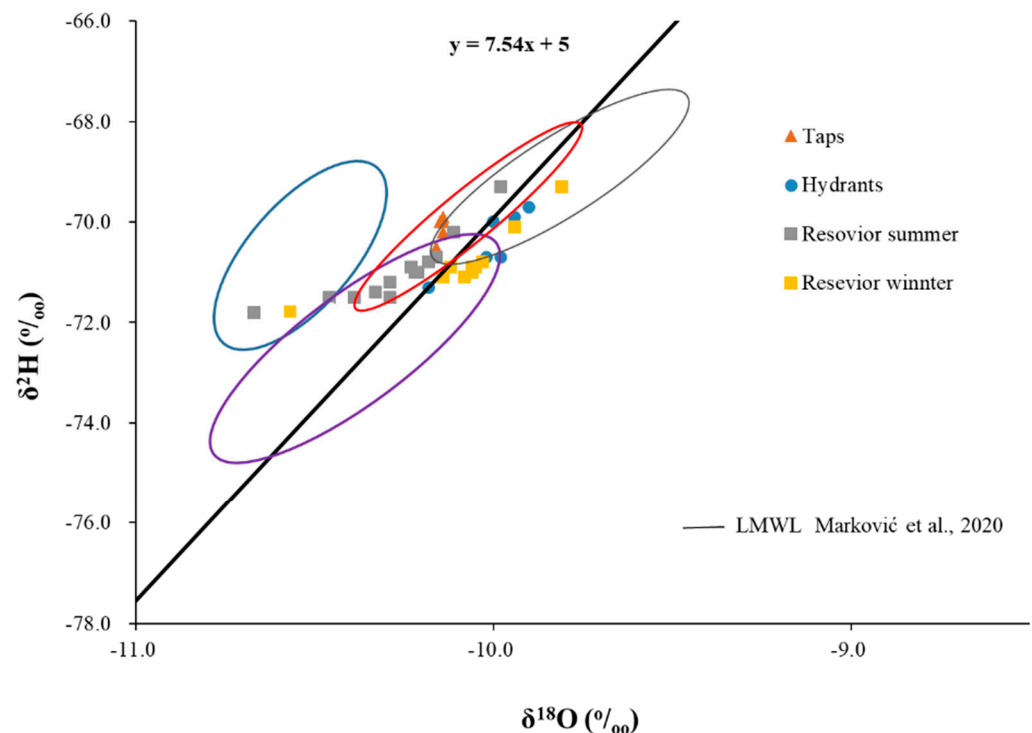
According to the measured data for reservoirs, pH values ranged from 7.3 to 8.2, temperatures from 11 to 21 °C, DO from 0.8 to 10.4 mg/L, EC from 486 to 683 µS/cm, and HCO<sub>3</sub><sup>−</sup> from 295 to 360 mg/L. In reservoir water, high oscillation of basic cations and anions was observed due to the mixing of different groundwater sources. An important finding was that none of the measured concentrations exceeded those measured in the groundwater source, indicating no significant impact (contamination) within the network. Measured values ranged as follows: Ca<sup>2+</sup> from 61.3 to 96.8 mg/L; Mg<sup>2+</sup> from 13.7 to 26.8 mg/L; Na<sup>+</sup> from 1.3 to 14.9 mg/L; K<sup>+</sup> from 0.4 to 4.47 mg/L; Cl<sup>−</sup> from 2.94 to 22.4 mg/L; SO<sub>4</sub><sup>2−</sup> from 8.86 to 32.4 mg/L; and NO<sub>3</sub><sup>−</sup> from 2.5 to 22.4 mg/L. The measured stable isotope values for δ<sup>18</sup>O varied from −10.67 to −9.81 ‰, and for δ<sup>2</sup>H from −71.9 to −69.3 ‰.

#### 3.2.2. Public Taps and Hydrants

Similar to the reservoirs, the geochemical parameters of sampled waters from public taps and hydrants showed variability, but concentrations did not exceed the maximum

values of groundwater sources. The measured pH values ranged from 7.28 to 7.69, EC from 483 to 676  $\mu\text{S}/\text{cm}$ , temperature from 8.3 to 23.1  $^{\circ}\text{C}$ , DO from 0.8 to 8.9 mg/L, and  $\text{HCO}_3^-$  from 302 to 366 mg/L. The concentrations of major ions were as follows:  $\text{Ca}^{2+}$  from 71.8 to 98.2 mg/L;  $\text{Mg}^{2+}$  from 13.8 to 19.0 mg/L;  $\text{Na}^+$  from 4.0 to 15.0 mg/L,  $\text{K}^+$  from 1.4 to 4.5 mg/L;  $\text{Cl}^-$  from 4.5 to 22.8 mg/L;  $\text{SO}_4^{2-}$  from 7.9 to 16.6 mg/L; and  $\text{NO}_3^-$  from 5.20 to 22.0 mg/L.

The measured stable isotope values for  $\delta^{18}\text{O}$  ranged from  $-10.22$  to  $-9.81$  ‰, and for  $\delta^2\text{H}$  from  $-71.3$  to  $-69.3$  ‰. Preliminary stable isotope results for reservoirs, public taps, and hydrants were plotted against LMWL (Figure 8). It was observed that the summer sampling campaign for reservoirs and public taps differs from the winter sampling (reservoirs and hydrants). This discrepancy can be attributed to different factors such as water temperature variations, fractionations within pipes, different pumping regimes, etc. Regardless of all these influences, it was observed that values are distributed within the elliptical shapes, which represent their origin. Moreover, one reservoir in both sampling campaigns showed the same origin (reservoir R1 and the Bela source). Consistent with the geochemical parameters, there were no outliers observed, confirming no contamination within the water supply network.



**Figure 8.** The relationship between  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in drinking water supply network, plotted alongside the LMWL (according to Marković et al., 2020 [11]). The range of measured stable isotopes for groundwater sources is illustrated in the form of elliptical shapes, with each color representing a different source: blue—Bela; red—Vinokovščak; purple—DA Bartolovec; grey—SA Bartolovec.

### 3.3. Origin of Water in the Water Supply Network

#### 3.3.1. Origin of Water at Exits at the Bartolovec Wellfield

In the Bartolovec wellfield, mixing modeling was conducted on four of the five exits, as exit Tonimir exclusively receives water from well B-1 (SA). Also, it was observed that modeling with  $\delta^{18}\text{O}$  as constraints did not show satisfactory matches in most calculations, so these results were not considered. Chloride emerged as the most effective constraint in the majority of MB model calculations, with a generally better fit observed in the IM and FM models compared to MB models (Table 2).

**Table 2.** Results of MB, FM, and IM modeling evaluated against measured values at all exits. Red color—not good matching; yellow color—poor matching; green color—excellent matching.

exit Doljan	MB model 1		MB model 2		MB model 3		FM model		IM model		Measured	Calculated MB1	Calculated MB2	Calculated MB3	Calculated FM	Calculated IM	Calculated MB 1	Calculated MB 2	Calculated MB 3	Calculated FM	Calculated IM	
	DA	SA	DA	SA	DA	SA	DA	SA	DA	SA	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	deviation	deviation	deviation	deviation	deviation	
Dec-21	78%	22%	71%	29%	73%	27%	71%	29%	72%	28%	12.4	11.6	13.3	12.8	13.3	13.0	0.17	1.04	0.52	1.05	0.70	
Jan-22	80%	20%	76%	24%	69%	31%	76%	24%	77%	23%	15.2	14.4	15.5	17.3	15.5	15.2	0.16	0.35	2.55	0.38	0.06	
Feb-22	77%	23%	73%	27%	70%	30%	73%	27%	74%	26%	16.2	15.6	16.7	17.4	16.7	16.4	0.13	0.61	1.45	0.63	0.28	
Mar-22	77%	23%	75%	25%	74%	26%	75%	25%	75%	25%	13.1	13.1	13.6	14.0	13.6	13.7	0.00	0.63	1.04	0.61	0.73	
Apr-22	78%	22%	76%	24%	79%	21%	76%	24%	76%	24%	13.5	13.1	13.7	12.9	13.7	13.7	0.08	0.30	0.13	0.30	0.20	
May-22	67%	33%	58%	42%	85%	15%	58%	42%	59%	41%	15.7	12.8	14.6	9.1	14.6	14.4	0.61	0.23	1.36	0.24	0.28	
Jun-22	70%	30%	59%	41%	85%	15%	59%	41%	61%	39%	16.0	12.7	14.8	9.7	14.8	14.5	0.69	0.25	1.31	0.25	0.32	
Jul-22	69%	31%	60%	40%	79%	21%	60%	40%	60%	40%	16.9	13.9	16.1	11.7	16.2	16.2	0.61	0.16	1.07	0.15	0.14	
Aug-22	80%	20%	67%	33%	79%	21%	69%	31%	71%	29%	14.1	11.2	14.4	11.5	13.9	13.5	0.60	0.36	0.55	0.04	0.13	
Sep-22	79%	21%	67%	33%	78%	22%	70%	30%	71%	29%	14.0	11.7	14.7	12.0	13.9	13.7	0.47	0.84	0.41	0.03	0.07	
Oct-22	64%	36%	61%	39%	74%	26%	55%	45%	58%	42%	17.5	15.0	15.7	12.6	17.2	16.5	0.51	0.37	1.02	0.07	0.20	
Nov-22	65%	35%	59%	41%	75%	25%	56%	44%	59%	41%	16.5	14.5	15.8	12.1	16.6	15.9	0.42	0.14	0.92	0.13	0.11	
Dec-22	75%	25%	62%	38%	62%	38%	64%	36%	65%	35%	14.7	12.2	15.5	15.3	15.0	14.7	0.51	0.93	0.77	0.37	0.01	
																	std	0.74	0.30	0.61	0.29	0.23

exit Ludbreg	MB model 1		MB model 2		MB model 3		FM model		IM model		Measured	Calculated MB1	Calculated MB2	Calculated MB3	Calculated FM	Calculated IM	Calculated MB 1	Calculated MB 2	Calculated MB 3	Calculated FM	Calculated IM	
	DA	SA	DA	SA	DA	SA	DA	SA	DA	SA	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	deviation	deviation	deviation	deviation	deviation	
Dec-21	99%	1%	93%	7%	99%	1%	93%	7%	99%	1%	7.2	6.3	7.8	6.4	7.8	6.4	0.18	0.75	0.17	0.75	0.16	
Jan-22	100%	0%	99%	1%	98%	2%	99%	1%	98%	2%	9.1	9.2	9.5	9.8	9.4	9.8	0.11	0.38	0.76	0.36	0.74	
Feb-22	100%	0%	97%	3%	99%	1%	97%	3%	99%	1%	9.6	9.6	10.4	9.9	10.4	9.9	0.02	0.93	0.29	0.94	0.34	
Mar-22	99%	1%	98%	2%	105%	−5%	98%	2%	100%	0%	7.1	7.5	7.6	6.0	7.6	7.2	0.46	0.62	0.23	0.61	0.11	
Apr-22	100%	0%	98%	2%	100%	0%	98%	2%	100%	0%	7.2	7.3	7.7	7.2	7.7	7.3	0.10	0.58	0.01	0.61	0.10	
May-22	100%	0%	99%	1%	100%	0%	100%	1%	100%	0%	5.4	6.0	6.1	5.9	6.1	6.0	0.71	0.86	0.60	0.84	0.71	
Jun-22	71%	29%	98%	2%	100%	0%	98%	2%	100%	0%	5.3	12.4	6.9	6.5	7.0	6.5	8.52	1.98	1.40	2.01	1.47	
Jul-22	71%	29%	100%	0%	100%	0%	100%	0%	100%	0%	6.7	13.7	6.5	6.4	6.5	6.5	8.45	0.03	0.06	0.03	0.04	
Aug-22	100%	0%	100%	0%	99%	1%	100%	0%	99%	1%	6.7	6.5	6.5	6.6	6.5	6.7	0.04	0.04	0.01	0.04	0.05	
Sep-22	100%	0%	99%	1%	99%	1%	99%	1%	99%	1%	6.3	6.8	7.1	7.0	7.1	7.0	0.60	0.98	0.79	0.94	0.89	
Oct-22	100%	0%	95%	5%	99%	1%	94%	6%	97%	3%	6.5	6.2	7.4	6.5	7.6	6.9	0.06	1.11	0.04	1.34	0.53	
Nov-22	100%	0%	97%	3%	100%	0%	97%	3%	100%	0%	5.0	5.9	6.6	5.9	6.6	5.9	1.09	1.91	1.09	1.97	1.09	
Dec-22	100%	0%	99%	1%	92%	8%	99%	1%	94%	6%	6.3	6.2	6.5	8.2	6.5	7.7	0.02	0.26	2.33	0.24	1.63	
																	std	3.09	0.46	0.69	0.44	0.50

Table 2. Cont.

exit Varaždin	MB model 1		MB model 2		MB model 3		FM model		IM model		Measured	Calculated MB1	Calculated MB2	Calculated MB3	Calculated FM	Calculated IM	Calculated MB 1	Calculated MB 2	Calculated MB 3	Calculated FM	Calculated IM	
	DA	SA	DA	SA	DA	SA	DA	SA	DA	SA	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	deviation	deviation	deviation	deviation	deviation	
Dec-21	100%	0%	100%	0%	71%	29%	99%	1%	99%	1%	8.2	6.2	6.1	13.3	6.4	6.4	0.41	0.44	6.19	0.36	0.36	
Jan-22	100%	0%	94%	6%	70%	30%	94%	6%	95%	5%	10.7	9.2	10.8	17.2	10.8	10.5	0.30	0.11	7.79	0.09	0.03	
Feb-22	100%	0%	93%	7%	62%	38%	93%	7%	93%	7%	10.7	9.6	11.5	19.6	11.5	11.5	0.22	0.99	10.79	0.99	0.92	
Mar-22	99%	1%	94%	6%	62%	38%	94%	6%	94%	6%	8.5	7.4	8.9	17.1	8.9	8.8	0.23	0.48	10.34	0.48	0.34	
Apr-22	100%	0%	93%	7%	49%	51%	93%	7%	93%	7%	8.7	7.3	9.0	20.7	9.1	9.2	0.29	0.37	14.47	0.39	0.52	
May-22	73%	27%	31%	69%	92%	8%	31%	69%	31%	69%	21.9	11.6	20.1	7.7	20.1	20.1	2.14	0.37	2.94	0.37	0.38	
Jun-22	100%	0%	31%	69%	90%	10%	31%	69%	32%	68%	22.8	6.5	20.7	8.6	20.7	20.4	3.37	0.44	2.95	0.44	0.50	
Jul-22	100%	0%	31%	69%	87%	13%	31%	69%	33%	67%	24.8	6.5	23.4	9.7	23.4	22.8	3.80	0.30	3.12	0.30	0.41	
Aug-22	87%	13%	63%	37%	78%	22%	66%	34%	63%	37%	15.6	9.6	15.3	11.9	14.7	15.4	1.23	0.06	0.77	0.18	0.05	
Sep-22	85%	15%	62%	38%	75%	25%	66%	34%	62%	38%	15.6	10.3	15.8	12.8	14.8	15.8	1.11	0.22	0.58	0.16	0.25	
Oct-22	65%	35%	27%	73%	82%	18%	16%	84%	28%	72%	25.5	14.8	24.1	10.6	26.9	23.9	2.22	0.28	3.10	1.68	0.33	
Nov-22	84%	16%	67%	33%	81%	19%	64%	36%	67%	33%	15.0	9.8	14.1	10.6	14.7	14.0	1.07	0.19	0.90	0.06	0.21	
Dec-22	84%	16%	61%	39%	63%	37%	63%	37%	65%	35%	14.6	10.1	15.6	15.2	15.2	14.7	0.93	1.24	0.69	0.67	0.08	
																	std	1.20	0.34	4.56	0.44	0.24
exit No- vakovec	MB model 1		MB model 2		MB model 3		FM model		IM model		Measured	Calculated MB1	Calculated MB2	Calculated MB3	Calculated FM	Calculated IM	Calculated MB 1	Calculated MB 2	Calculated MB 3	Calculated FM	Calculated IM	
	DA	SA	DA	SA	DA	SA	DA	SA	DA	SA	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	deviation	deviation	deviation	deviation	deviation	
Dec-21	1%	99%	7%	93%	0%	100%	65%	35%	31%	69%	29.8	30.2	28.6	30.4	34.5	22.9	0.42	0.24	0.72	5.62	1.43	
Jan-22	1%	99%	5%	95%	0%	100%	39%	61%	16%	84%	35.2	35.1	34.1	35.4	39.0	31.2	0.02	0.24	0.24	4.58	0.83	
Feb-22	0%	100%	6%	94%	0%	100%	53%	47%	11%	89%	35.0	35.8	34.4	35.8	40.9	32.9	0.97	0.13	0.97	7.14	0.43	
Mar-22	0%	100%	9%	91%	0%	100%	100%	0%	6%	94%	33.1	33.2	30.8	33.2	40.4	31.6	0.12	0.48	0.12	8.82	0.30	
Apr-22	0%	100%	4%	96%	20%	80%	57%	44%	4%	96%	33.6	33.8	32.7	28.5	37.9	32.7	0.24	0.18	1.06	5.23	0.18	
May-22	0%	100%	3%	97%	0%	100%	64%	36%	33%	67%	28.1	26.4	25.8	26.4	30.2	19.7	0.35	0.48	0.35	2.55	1.75	
Jun-22	0%	100%	6%	94%	0%	100%	74%	26%	21%	79%	29.5	26.9	25.7	26.9	31.7	22.6	0.54	0.78	0.54	2.67	1.42	
Jul-22	2%	98%	6%	94%	0%	100%	6%	94%	9%	91%	30.9	30.5	29.4	30.9	31.3	28.7	0.08	0.32	0.00	0.48	0.46	
Aug-22	8%	92%	12%	88%	0%	100%	12%	88%	10%	90%	30.6	28.5	27.6	30.5	31.3	28.1	0.44	0.62	0.02	0.82	0.52	
Sep-22	7%	93%	10%	90%	0%	100%	83%	17%	8%	92%	30.5	28.8	28.2	30.5	36.1	28.6	0.35	0.48	0.00	6.78	0.39	
Oct-22	13%	87%	11%	89%	0%	100%	0%	100%	10%	90%	30.4	27.6	28.1	30.8	30.8	28.3	0.58	0.48	0.48	0.48	0.43	
Dec-22	12%	88%	9%	91%	0%	100%	2%	98%	9%	91%	30.2	27.4	28.3	30.4	30.5	28.2	0.58	0.40	0.24	0.39	0.41	
																	std	0.26	0.19	0.37	2.96	0.50

Nevertheless, all three models showed that at exit Doljan, depending on the pumping regime, more than 50% and up to 77% of water is pumped from the DA and distributed towards the southern part of the network. On the other hand, exit Ludbreg primarily supplies the eastern part of the network with DA water, ranging from 92 to 100% (Table 2). At the exit Varaždin, up until April 2022, water was mainly pumped from the DA, between 93 to 99% of the supply. After that, the regime of pumping changed, favoring SA water from 62 to 72%, before reverting back to dominantly DA water (Table 2). At the exit, Novakovec primarily supplies the eastern part of the network with the SA water, ranging from 92 to 100% (Table 2).

### 3.3.2. Reservoirs, Public Taps and Hydrants

Similar to the exits, the best fitting obtained by MB models is achieved using chloride as constraints, and generally, the IM and FM models display a better fit than MB. After validation, it was observed that IM models yielded the best results, which are discussed further in the text. Despite slightly more difficulties appearing here, given that most of the results showed a good match, it is evident that this modeling approach needs to be further elaborated. The differences exist due to the varied chemical and isotopic composition of many wells, which are alternately integrated into the water supply. It is likely that more accurate results would be obtained by sampling all wells at the water pumping stations rather than just their representatives. In addition, the chemical composition of water changes while standing in reservoirs. During the warm months with higher temperatures, evaporation occurs, which affects the composition of  $\delta^{18}\text{O}$ , while stagnant water leads to precipitation of carbonates, which changes the EC. Moreover, the amount of free chlorine decreases, and the number of bacteria that can affect nitrification processes increases. Chlorination, albeit to a minor extent, affects chloride concentration, thereby potentially influencing the results. It is possible that each of these processes can affect the modeling result. In addition, by introducing additional indicators of water quality (anions, cations), the accuracy of the models can be increased, as well as by expanding the sampling locations.

A simple Piper diagram showed at a glance that only one reservoir (R1) during both sampling campaigns was filled from only one groundwater source, Bela (Figure 9). However, all other network sampling points demonstrated a mixing of different sources.

It was observed that in the western part of the water supply network, reservoirs predominantly contain a mixture of waters from Bartolovec (exits E1 and E4) and Bela water sources (Figure 10c). Unfortunately, due to the absence of taps in this area, sampling was not conducted. In the northern part of the network, a mixture of waters between Vinokovščak and Bartolovec sources was observed (Figure 10c). Hydrants and taps in closer proximity to the Vinokovščak source had higher ratios, although certain instances of these higher ratios were unexpected. Moreover, differences between summer and winter periods were apparent. The southern and eastern part of the network is mainly filled with water from the Bartolovec source (exits E2 and E3) and B1 (Figure 10a–c). Mixing ratios showed that the main groundwater source is Bartolovec, which has an essential DA role. Examination of pumping amounts during the sampling dates corroborated the modeled values.

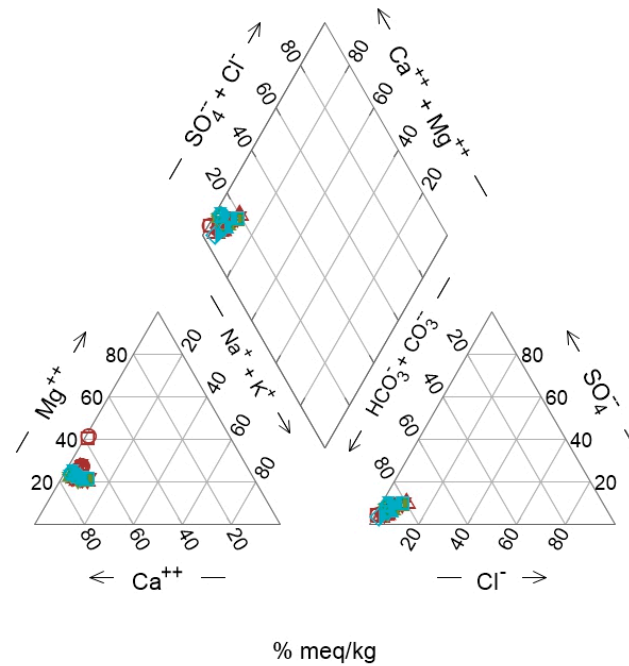


Figure 9. Piper diagram of sampled waters from the network (brown color—reservoirs; green color—public taps; blue color—hydrants).

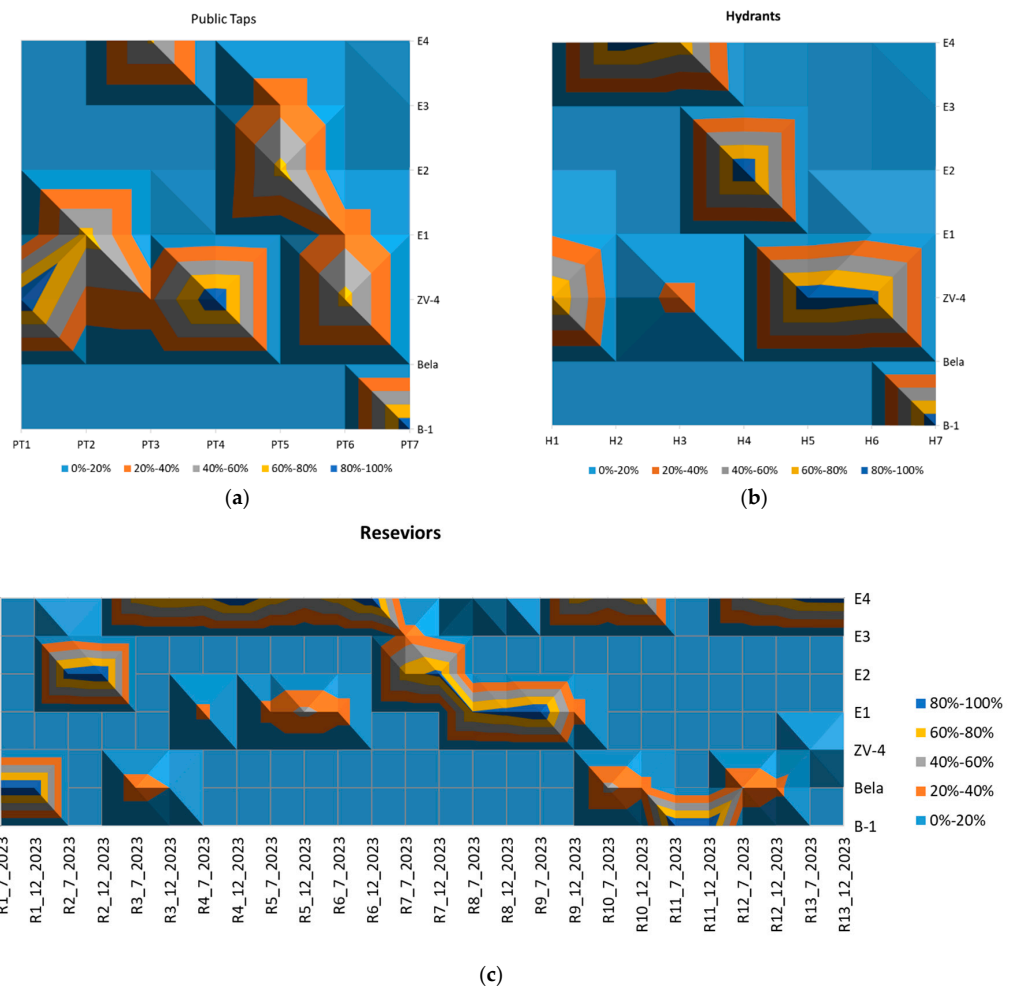


Figure 10. Mixing ratios in (a) public taps, (b) hydrants, and (c) reservoirs.

#### 4. Conclusions

In a time when water scarcity is an issue not just in developing countries but also in all countries over the globe due to climate change's impact on groundwater recharge, understanding the water supply network is the key to good water supply management. By using hydrochemical parameters, such as basic anions and physical-chemical properties of water, which are measured in everyday routine in water supplier laboratories, combined with water stable isotopes, extended anion and cation analysis, and geochemical modeling (MB, IM, FM), the water within the water supply network could be comprehensively characterized as shown in this paper. In the Varaždin WSS, all measured parameters are below Maximum Contaminant Level (MCL) values, ensuring the safety of water for human consumption. The differences between water sources were observed based on basic chemical composition. Furthermore, the Piper diagram provided a simplified overview of mixing patterns within the water supply network. Although all three modeling approaches showed satisfactory results, IM results were more reliable than FM and BM. Mixing modeling demonstrated the mixing of all three sources at the western, southwestern, and northern parts of the water supply network. Conversely, the eastern and southeastern parts of the network depend primarily on the DA water from the Bartolovec groundwater source, suggesting that these parts of the network are very vulnerable in the event of an emergency at that source. That should be additionally taken into account during the risk assessment of the water supply system and the establishment of control measures that will further increase the safety of the water supply (enabling the supply of water from other existing sources and increasing the water storage capacity in the threatened area; short-term measure: supplying water by mobile water tanks). Although  $\delta^{18}\text{O}$  did not provide good mixing results due to fractionation in pipelines, it revealed that water in reservoirs is in equilibrium with air (no evaporation effects), indicating well-sealed and impermeable reservoirs. The results showed that geochemical modeling could be effectively applied in water security management plans. The proposed methodology can be applied globally in a variety of water supply system settings, especially where tremendous water losses are present, e.g., due to leaking pipes, etc.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/su16219558/s1>, Table S1: Results of hydrochemical analysis of sampled groundwater sources; Table S2: Results of hydrochemical analysis of public taps, hydrant, and reservoirs.

**Author Contributions:** Conceptualization, N.N.-H., I.K. (Igor Karlović) and T.M.; methodology T.M.; software, N.N.-H., T.M. and I.K. (Igor Karlović); validation, T.M.; formal analysis, N.N.-H. and T.M.; investigation N.N.-H., I.K. (Igor Karlović) and T.M.; resources N.N.-H. and T.M.; writing—original draft preparation, N.N.-H.; writing—review and editing, T.M., I.K. (Igor Karlović) and I.K. (Ivan Kovač); visualization T.M. and I.K. (Igor Karlović). All authors have read and agreed to the published version of the manuscript.

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### **Paper 3**

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Article

# Assessment of Groundwater Vulnerability from Source to Tap Using TIN Approach

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## Abstract

Groundwater and water supply systems are increasingly vulnerable to contamination, yet most assessments consider either hydrogeological or infrastructure risks. This study introduces the Total Integrated Network (TIN) approach, a framework designed to evaluate vulnerability comprehensively from source to tap. Field investigations were conducted in Varaždin County, Croatia, focusing on the Belski Dol spring, Briška reservoir, and PS Filipići. Hydrochemical analyses, stable isotope of water ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ), tritium, noble gases, and radon concentrations were monitored and combined with system-level assessments. Results show that the Belski Dol spring exhibits high stability and low vulnerability, with a TIN index of approximately 25%, supported by long groundwater residence times and consistent water quality. PS Filipići displayed moderate vulnerability (35%), while the Briška reservoir showed the highest index (53%), linked to elevated radon and nitrate concentrations and infrastructure-related risks. These findings indicate that natural hydrogeological protection alone cannot ensure safe drinking water. The TIN approach highlights the importance of integrating aquifer conditions with distribution system performance to identify critical control points and prioritize interventions. This integrated methodology offers a more realistic basis for water safety management, supporting proactive measures to safeguard supply resilience and public health.



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**Keywords:** isotopes; chemistry; vulnerability of groundwater and water supply system; TIN approach

## 1. Introduction

Groundwater vulnerability refers to the intrinsic characteristics of the subsurface that determine the susceptibility of groundwater to contamination from human activities [1,2]. This concept evaluates how easily pollutants can reach groundwater, considering factors such as soil and subsoil permeability, depth to the water table, type of aquifer, recharge rate, and the presence of protective layers [3]. Groundwater vulnerability is commonly classified as intrinsic, based solely on natural factors or specific, which incorporates both natural features and particular contaminants [2,4].

Several methods have been developed to assess groundwater vulnerability, assisting in the protection of aquifers from contamination [5–8]. Among the most recognized index-based methods are DRASTIC, GOD, SI, and SINTACS, each varying in complexity, applicability, and type of data required [5–8].

The DRASTIC method, developed by Aller et al. in 1987 [5] for the US Environmental Protection Agency (EPA), assesses vulnerability using seven parameters: depth to groundwater, net recharge, aquifer media, soil media, topography (slope), impact of the unsaturated zone, and hydraulic conductivity. Each parameter in DRASTIC is assigned a weighted value reflecting its relative influence on groundwater vulnerability, making it adaptable to specific hydrogeological contexts [5]. Despite its wide acceptance and ease of use, DRASTIC has limitations, such as subjectivity in assigning ratings, parameter redundancy, and limited suitability for karst aquifers where lateral contaminant flow is significant [9]. Foster introduced the GOD method in 1987, designed explicitly for rapid vulnerability assessment in regions with limited hydrogeological data [6]. GOD simplifies vulnerability estimation using only three parameters: Groundwater occurrence (aquifer confinement), Overlying lithology, and Depth to groundwater. GOD's strength is simplicity and suitability for large-scale assessments, yet it struggles to capture the variability in aquifer conditions adequately, especially where vulnerability differences are subtle [10]. The Susceptibility Index (SI) developed in Portugal by Ribeiro in 2000 modifies the DRASTIC framework, excluding certain parameters such as soil media and the unsaturated zone, while adding a land-use factor. The inclusion of land-use enhances SI's ability to identify anthropogenic influences, such as agricultural pollution, notably improving its predictive accuracy for specific contaminants like nitrates [11]. Nevertheless, SI may overestimate vulnerability by neglecting dilution effects or the recycling processes of groundwater contamination [12]. The SINTACS method, proposed by Civita and De Maio in 2004, emerged from Italy as an enhancement of the DRASTIC approach specifically tailored for Mediterranean hydrogeological conditions [7]. Like DRASTIC, SINTACS uses seven parameters—depth to groundwater, effective infiltration, unsaturated zone characteristics, soil texture, aquifer media, hydraulic conductivity, and topographic slope. However, it offers more precise weightings to reflect specific hydrogeological scenarios. SINTACS's flexibility allows it to better account for localized hydrogeological differences, thus providing reliable vulnerability mapping, especially in porous aquifer systems.

Comparative studies have shown that the GOD method frequently produces oversimplified results compared to DRASTIC or SI, particularly when examining areas with moderate vulnerability variations [10,11]. Meanwhile, the SI method generally demonstrates stronger correlations with actual groundwater contamination data such as nitrate concentrations, making it particularly suitable for agricultural contexts [11,12]. Similarly, SINTACS has been successfully validated in various Mediterranean regions, effectively reflecting observed contamination patterns due to its locally adaptive weighting scheme [7]. Validation of vulnerability mapping typically involves comparing mapped vulnerability classes with observed groundwater quality parameters, emphasizing the practical importance of accurate parameter weighting and selection [13,14]. Nonetheless, the effectiveness of all these methods largely depends on data availability, appropriate parameter selection, and the extent to which local hydrogeological variability is accurately represented [15]. Overall, integrating or comparing multiple methods such as DRASTIC, GOD, SI, and SINTACS is recommended to enhance the reliability of groundwater vulnerability assessments and thus better inform policy decisions for aquifer protection [7,10,12,14].

Water supply system (WSS) vulnerability encompasses the susceptibility of the water infrastructure and its operation to various hazards that could compromise water quality and the continuity of supply [16,17]. These hazards may include physical infrastructure failures, contamination events, cyber-attacks, natural disasters, and operational shortcomings [18]. Assessing the vulnerability of WSS involves identifying weaknesses in their infrastructure, operations, or management that may lead to contamination, interruption, or degradation

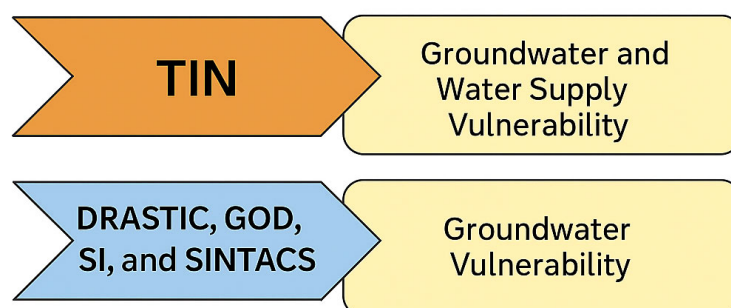
of water quality [19]. Several methodologies are employed for this purpose, each suited to specific contexts and data availability.

The All-Hazards Approach, promoted notably in the Technical Guide TG-374 of the United States Army Center for Health Promotion and Preventive Medicine, evaluates risks from various potential threats (natural disasters, sabotage, accidents) by systematically assessing different WSS components such as sources, treatment plants, storage facilities, and distribution networks [20]. Another common method involves the use of Index-Based or Multi-Indicator Approaches, which combine various indicators, hydraulic, environmental, structural, and socio-economic to quantify vulnerability levels through weighted scoring [9]. These indicators are typically visualized spatially with GIS tools, providing practical and accessible results for decision-makers [10]. The Process-Based Simulation Approach employs hydraulic modeling software like EPANET to simulate contamination scenarios, system pressure changes, or pipe failures, providing detailed insights into WSS behavior under stress conditions [21]. This approach offers detailed predictive capability but requires extensive and accurate system data. Additionally, Complex Network Theory evaluates water systems as spatial networks. It identifies critical components, such as bottlenecks or essential connections, through network metrics like node connectivity and redundancy [22]. This method effectively highlights structural vulnerabilities but often overlooks aspects like water quality or contamination propagation. The Fuzzy Fault-Tree Analysis method addresses uncertainties inherent in data-limited systems. It uses a hierarchical structure to model failure probabilities and system vulnerabilities, allowing planners to prioritize mitigation measures effectively despite uncertainty [23]. The Risk-Based Asset Assessment framework is a traditional risk management approach widely adopted by utilities. It evaluates assets based on identified threats, vulnerability levels, and potential consequences of failure, providing clear prioritization for mitigation and resource allocation [19]. Governance and policy-oriented frameworks, such as the Driver-Pressure-State-Impact-Response (DPSIR) model and Water Safety Plans (WSP), integrate technical assessment with institutional and governance considerations, addressing socio-economic factors that influence overall system vulnerability [24]. Finally, specialized Climate Change Vulnerability Assessments explicitly evaluate WSS vulnerability related to climate risks, such as droughts, floods, and extreme events. Scenario-based modeling assesses system resilience under different climate conditions, informing adaptive strategies for future planning [25].

Despite significant progress in groundwater and water supply system vulnerability assessments, no existing study has yet succeeded in jointly evaluating the sensitivity of both the aquifer (hydrogeological system) and the water supply system (WSS) using a unified set of parameters. Traditionally, vulnerability assessments have been conducted separately for these two components. Some focus on the aquifer itself, particularly its intrinsic vulnerability to surface contamination [5,6], while others target the water supply infrastructure, such as source works, pipelines, reservoirs, and treatment plants, often using risk or failure analysis frameworks [19,23]. In groundwater vulnerability studies, methods like DRASTIC, GOD, and SI typically emphasize aquifer scale conditions, evaluating sensitivity on a catchment level or source protection area, rather than at the level of individual abstraction points [5,8]. This presents a critical gap: such approaches implicitly assume homogeneity of risk within the same aquifer, disregarding the local-scale heterogeneity that strongly influences the actual vulnerability of a specific spring or well [10,13]. In reality, hydrogeological heterogeneity, such as variations in permeability, porosity, structural features, and unsaturated zone thickness means that two wells located in the same aquifer can exhibit vastly different vulnerability levels. A recharge zone may protect one well due to thick low-permeability overburden, while another well nearby may be highly exposed due to thin or fractured cover layers [7,9]. Moreover, water supply system vulnerability

assessments often begin downstream of the abstraction point, assuming the water source is adequately protected or uniformly vulnerable. This neglects source specific risk, which can critically impact overall WSS resilience. There is thus a pressing need for integrated methodologies that evaluate the combined vulnerability of the source aquifer unit and the water abstraction infrastructure using harmonized parameters such as recharge, land-use, geological media, well construction details, and system redundancy [12,25].

An integrated approach would bridge hydrogeological and WSS assessments and could support more precise risk-based zoning, resource allocation, and emergency planning, especially in complex or fractured aquifers where uniform vulnerability assumptions are misleading. The literature increasingly emphasizes this need for convergence, yet a comprehensive framework is still lacking [15,22]. This study introduces the Total Integrated Network (TIN) vulnerability approach, a comprehensive methodology for evaluating water quality risks along the entire source-to-tap pathway. In contrast to established methods such as DRASTIC, GOD, SI, and SINTACS, which focus solely on groundwater vulnerability, the TIN integrates both aquifer and water supply system vulnerabilities into a unified assessment (Figure 1). The TIN approach is designed to address both natural and anthropogenic factors that influence water vulnerability along the source-to-tap pathway. By integrating aquifer sensitivity with infrastructure and operational vulnerabilities, the TIN provides a more realistic and location specific understanding of risk. This enables utilities and decision-makers to prioritize interventions, allocate resources more efficiently, and implement targeted protection and monitoring strategies. Ultimately, the TIN supports proactive and adaptive water supply management, enhancing system resilience and safeguarding public health.

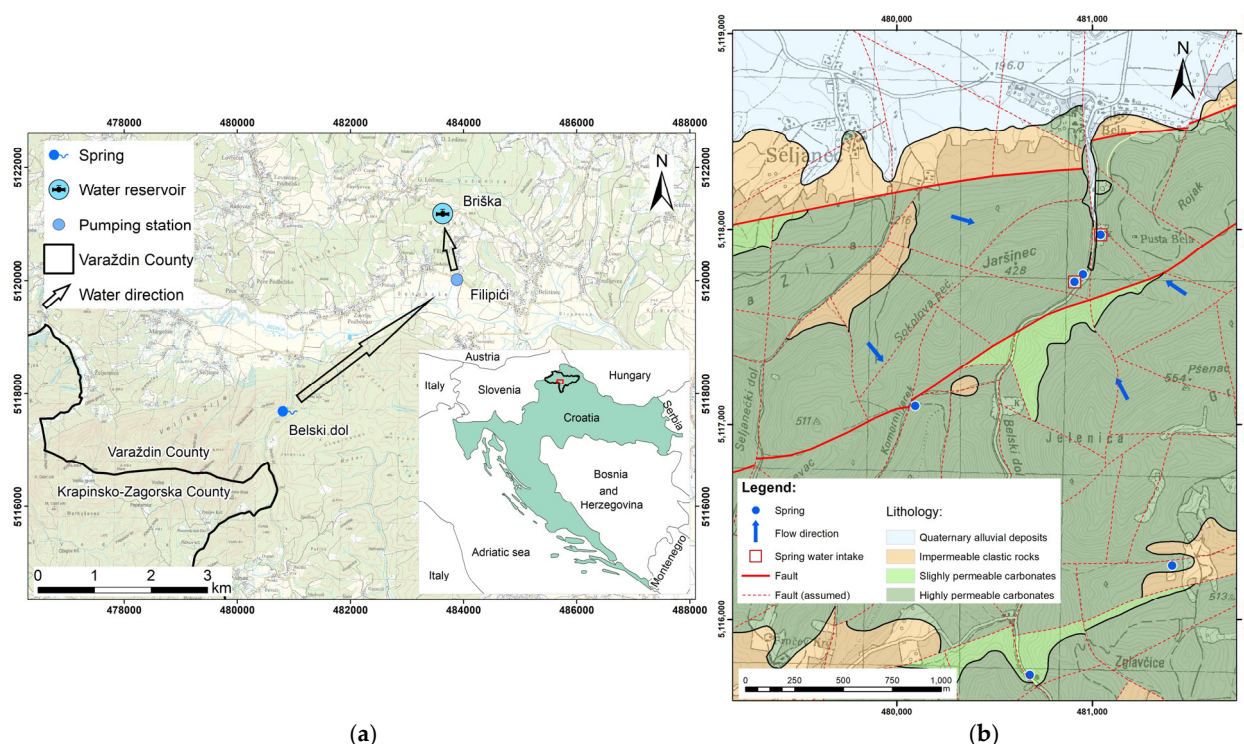


**Figure 1.** Conceptual comparison between traditional groundwater vulnerability methods and the Total Integrated Network (TIN) approach.

## 2. Materials and Methods

### 2.1. Study Area

The study area is situated in the Varaždin County in northwestern Croatia, where potable water is distributed by public water supplier Varkom Inc. (Figure 2). The Belski Dol spring is located within Varaždin County, between the settlements of Podrute and Bela. It lies on the southeastern slopes of Mount Ivanščica, approximately 750 m from Bela and about 3 km from Podrute. The spring area sits at an elevation of approximately 230 m above sea level and is adjacent to the Belski stream and county road ŽC 2107. The spring comprises two main sources, the Upper and Lower springs which are about 350 m apart. The Upper spring is situated on the left side of the road (looking toward Bela), separated by the Belski stream, while the Lower spring lies to the right of the road, bordered by a stormwater drainage channel. The surrounding landscape is marked by a combination of forested hills and karst valleys, which are representative of the Ivanščica massif's dynamic topography.



**Figure 2.** Position map of the study area: (a) studied system with marked sampling points; (b) hydrogeological map of the Belski Dol spring catchment.

The geological composition of the Belski Dol catchment is diverse, reflecting the broader stratigraphic characteristics of the Ivanščica region. The terrain consists predominantly of Mesozoic and Cenozoic sedimentary rocks. Notably, four main lithological groups are present: (i) highly permeable carbonate rocks: dolomites, dolomitic limestones, and limestones. (ii) slightly permeable carbonate rocks: siliceous dolomites, cherty limestones, thin-bedded limestones, and flysch with chert and sandstone intercalations. (iii) impermeable clastic rocks: including sandstones, shales, marls, conglomerates, and clays. (iv) Quaternary alluvial deposits: composed of sands, gravels, silts, and clays of variable grain size and permeability (Figure 2) [26].

These formations reflect the region's tectonic complexity, with numerous faults and fractures that contribute to groundwater movement. Breccia formations in the area, consisting of shallow-water carbonate clasts in deeper pelagic matrices, further indicate a complex depositional history.

The Belski Dol spring system is part of the Ivanščica fractured/fissured karst aquifer. The Upper spring was originally captured in 1972 for the village of Završje, with a measured discharge of approximately 5 L/s and an overflow of around 36 L/s. Since 1992, the Upper spring supplies about 28 L/s to the water network. It is enclosed by a 10 × 8 m fenced area. The Lower spring was integrated into the supply system in 1992 and features a non-concentrated capture system. It collects water from an alluvial fan using perforated Ø400 mm pipes laid in a 20 m stretch. Its yield is around 38 L/s. Together, the two springs provide approximately 63 L/s. Subsurface water travels from the Lower spring to a collection chamber through a gravity-fed closed pipeline, which also receives water from the Upper spring. From there, it is routed by gravity to the Filipiči pumping station (PS) after which is pumped up to the Briška reservoir (R). From the reservoir, water is distributed by gravity through a pipeline to consumers.

## 2.2. Water Analyses

### 2.2.1. Physico-Chemical Analysis

Field measurements of electrical conductivity (EC), water temperature (T) and pH, were performed using a calibrated portable WTW instrument from December 2021 till December 2023 monthly at the Belski Dol spring. At reservoir Briška and PS Filipići, sampling campaigns were carried out twice in 2022 and twice in 2023. Total alkalinity was determined on-site by titration with 1.6 N H<sub>2</sub>SO<sub>4</sub>, using phenolphthalein and bromocresol green–methyl red as indicators. Major cations and anions were analyzed using ion chromatography on a Dionex ICS-6000 DC system (Thermo Fisher Scientific Inc., Waltham, MA, USA) at the Hydrochemical Laboratory of the Croatian Geological Survey, with analytical precision assessed via the ionic balance error (IBE), calculated from ion concentrations expressed in meq/L and found to be within the acceptable limit of ±5%. The long-term dataset is part of water sampling campaigns conducted at spring, PS Filipići and reservoir Briška, as part of the operational monitoring by Varkom Inc.

### 2.2.2. Stable Water Isotope Analysis

The δ<sup>18</sup>O and δ<sup>2</sup>H values were determined using a Picarro L2130i analyzer (Santa Clara, CA, USA) at the Hydrochemical Laboratory of the Croatian Geological Survey. All measurements were calibrated against USGS standards (USGS48:  $-2.224 \pm 0.012\text{‰}$  for δ<sup>18</sup>O,  $-2.0 \pm 0.4\text{‰}$  for δ<sup>2</sup>H; USGS46a:  $-30.09 \pm 0.05\text{‰}$  for δ<sup>18</sup>O,  $-235.6 \pm 0.7\text{‰}$  for δ<sup>2</sup>H), which were periodically verified against International Atomic Energy Agency (IAEA) reference materials: Vienna Standard Mean Ocean Water 2 (VSMOW2) and Standard Light Antarctic Precipitation 2 (SLAP2). Measurement precision was ±0.2‰ for δ<sup>18</sup>O and ±1‰ for δ<sup>2</sup>H. Instrument drift control, use of internal laboratory standards, and QA/QC procedures followed the protocol described in [27].

### 2.2.3. Noble Gas and Tritium Measurement

Water samples were taken into copper tubes equipped with stainless steel pinch-off clamps. During sampling, the pressure of the water was kept as high as dissolved gases could not release from the water. Samples were analyzed in the Isotoptech Zrt. Debrecen, Hungary, according to the method described in Papp et al., 2012 [28]. Measured data were interpreted by inverse modeling of noble gas concentrations [29–31].

### 2.2.4. Radon Analysis

Radon concentration in water was measured using the RAD8 radon detector, produced by DURRIDGE Company Inc. (Billerica, MA, USA). A 250 mL water sample was collected in a clean glass vial, taking care to avoid the presence of air bubbles in order to prevent radon loss. The vial was then securely sealed and connected to the RAD8 system using a closed-loop aeration setup. The radon concentration in the original water sample is then calculated using the measured air concentration and the established partition coefficient for radon between water and air. Results were corrected by using Capture 8 software [32].

## 2.3. Total Integrated Network Vulnerability Approach (TIN)

By tracing water and its quality changes from recharge zones, through abstraction and conveyance, storage, and distribution, the TIN approach identifies and quantifies cumulative and segment specific risks. This holistic methodology enables: spatial mapping of vulnerability hot spots across both the aquifer and WSS infrastructure; temporal assessment of changes in vulnerability due to natural processes (e.g., recharge variability) and operational factors (e.g., system maintenance, leakage); identification of critical control points (CCPs) where interventions can most effectively reduce overall risk.

The proposed approach utilizes 10 parameters, half of which are routinely monitored by all water supply companies in accordance with the obligations of the Drinking Water Directive (EU) 2020/2184 [33]. Tables 1 and 2 provide an overview of the relevance of each parameter and what changes in their values can indicate within both the groundwater system and the water supply system (WSS).

**Table 1.** Parameter indication in the groundwater system.

Parameter	Vulnerability Focus	Interpretation of Increase/Change
Electrical Conductivity (EC)	Change over time	Possible pollution, saltwater intrusion, recharge decline
Temperature (T)	Change over baseline	Influence of surface water or climate change
pH	Shift from neutral	Acidification or possible contamination
Nitrates (NO <sub>3</sub> <sup>-</sup> )	Change and absolute vs. MAC	Anthropogenic input (agriculture, sewage)
Chlorides (Cl <sup>-</sup> )	Change over time	Salinization, urban runoff, agricultural return flow
δ <sup>18</sup> O	Isotopic shift	Change in recharge source, evaporation signal
δ <sup>2</sup> H	Isotopic shift	Change in recharge source, evaporation signal
Tritium ( <sup>3</sup> H)	Change over time	Modern recharge or fast flow path, estimation of mean residence time (MRT)
Radon ( <sup>222</sup> Rn)	Absolute vs. threshold	High natural radioactivity, fractured rock zones, fault zones, deep groundwater circulation
Noble Gases	Change or deviation from norms	Recharge temperature, origin depth, useful as a tracer of MRT

**Table 2.** Parameter indication in the WSS.

Parameter	Vulnerability Focus	Interpretation of Increase/Change
Electrical Conductivity (EC)	Change vs. supply baseline	Deterioration of water quality
Temperature (T)	Sudden increase	Contamination or surface exposure, leakage, stagnant water
pH	Sudden fluctuation	Corrosion risk, stagnant water in the system
Nitrates (NO <sub>3</sub> <sup>-</sup> )	Change and absolute vs. MAC	Health risk, microbiological activities within system
Chlorides (Cl <sup>-</sup> )	Sudden increase	Pipe corrosion, contamination
δ <sup>18</sup> O	Deviation from known source	Source change, uncontrolled mixing, leakage
δ <sup>2</sup> H	Deviation from known source	Source change, uncontrolled mixing, leakage
Radon ( <sup>222</sup> Rn)	Absolute value vs. MAC and higher values than source	Radiation concern, leakage

Each parameter is assigned a set of quantitative criteria used to define a vulnerability score ranging from 1 (Very Low) to 5 (Very High) (Table 3). These scores contribute to the overall weighted vulnerability calculation. In practice, threshold values should be tailored to the specific system and dataset, but the following table provides a general scoring framework. For each parameter, the vulnerability score is based on the observed variability, expressed either as a percentage change from a baseline or Maximum Allowable Concentration (MAC) value, or as an absolute concentration difference, as shown in Table 3. However, these parameter fluctuations needed to be quantified, which was performed using the Z-score. The Z-score expresses how much each measured value deviates from the mean in units of standard deviation. This approach allows for a clear comparison of variability among different sampling sites.

**Table 3.** Vulnerability scoring scale.

Score	Vulnerability Focus	Description
1	Very Low	Background fluctuation or minimal impact; variation less than 10% of the baseline value.
2	Low	Weak signal of fluctuation; may not be conclusive on its own. Variation between 10% and 20% of the baseline value.
3	Moderate	Noticeable signal of fluctuation; variation between 20% and 30% of the baseline value.
4	High	Significant signal of fluctuation; variation between 30% and 50% of the baseline value.
5	Very High	Strong signal of fluctuation; variation greater than 50% of the baseline value.

Once individual vulnerability scores are assigned to each parameter based on the criteria described above, the following calculation steps are applied to integrate them into the overall *TIN* method index:

Each parameter is assigned a weighting factor reflecting its relative importance or diagnostic value in assessing system vulnerability. These weights can be uniform or adapted based on expert judgment, sensitivity analysis, or system-specific relevance.

Since parameters are measured on different scales or units, normalization must be applied to ensure comparability.

$$\text{Weighted Score}_i = \text{Vulnerability Score}_i \times \text{Weight}_i \quad (1)$$

Then the *TIN* vulnerability index is computed as a weighted average of all individual scores:

$$\text{TIN}_{index} = \left( \sum_{i=1}^n \text{Weighted Score}_i / \sum_{i=1}^n \text{Max possible score} \times \text{Weight}_i \right) \times 100\% \quad (2)$$

where  $n$  = total number of parameters included.

The final *TIN* Index value is expressed as a percentage, representing the proportion of the maximum possible vulnerability score. Based on this percentage, the system's vulnerability is classified into three categories: values ranging from 0% to 30% indicate low vulnerability, values between 31% and 60% correspond to moderate vulnerability, while values from 61% to 100% reflect high vulnerability. This classification enables clear interpretation of results and supports risk-informed decision-making in groundwater and water supply system management.

### 3. Results and Discussion

In this chapter, the *TIN* method is applied to the Belski Dol spring and the part of the water supply system fed by this source to assess their vulnerability.

#### 3.1. Hydrochemical Properties of Spring and WSS Waters

The Piper diagram shows that water samples from Belski Dol spring, the Briška reservoir, and the PS Filipiči belong to the CaMg–HCO<sub>3</sub> hydrochemical type (Figure 3). Calcium and bicarbonate are the dominant ions, indicating water rock interaction primarily with carbonate formations (dolomite and limestone). The similarity between all three samples suggests that there are no significant geochemical changes observed within the water supply network, indicating consistency in water quality from source to distribution points.

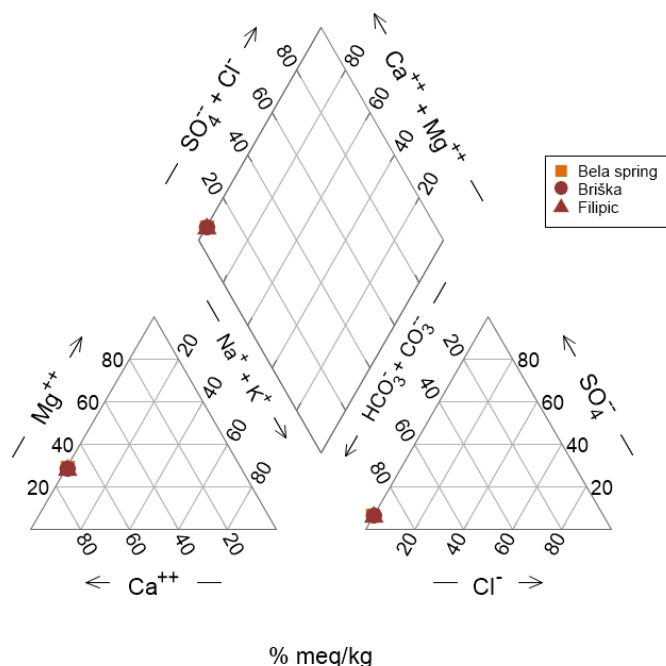


Figure 3. Piper diagram of sampled waters.

The EC of the spring water ranges from 480 to 501  $\mu\text{S}/\text{cm}$ , with an average of 494  $\mu\text{S}/\text{cm}$  and with a standard deviation of 6.9  $\mu\text{S}/\text{cm}$  (Table 4a). This low variation indicates that the mineralization of the water is stable over time. The water temperature is very constant as EC, between 11.0 and 11.3  $^{\circ}\text{C}$ , with an average of 11.2  $^{\circ}\text{C}$  and with a standard deviation of only 0.1  $^{\circ}\text{C}$ , which is within the measurement error. The pH values range from 7.05 to 7.61, with an average of 7.47 and a standard deviation of 0.13, showing that the water is consistently slightly alkaline without extreme changes that could occur due contamination breakthrough. All three parameters indicate that groundwater has long residence time.

Table 4. (a) Statistical data of measured parameters (Croatian Geological Survey). (b) Statistical data of measured parameters (Varkom Inc.).

(a)															
Belski Dol	EC ( $\mu\text{S}/\text{cm}$ )	T ( $^{\circ}\text{C}$ )	pH	$\text{HCO}_3^-$ (mg/L)	$\text{Cl}^-$ (mg/L)	$\text{SO}_4^{2-}$ (mg/L)	$\text{NO}_3^-$ (mg/L)	$\text{Ca}^{2+}$ (mg/L)	$\text{Mg}^{2+}$ (mg/L)	$\text{Na}^+$ (mg/L)	$\text{K}^+$ (mg/L)	$\delta^{18}\text{O}$ (‰)	$\delta$ (‰)	$\text{NH}_4^+$ (mg/L)	$\text{NO}_2^-$ (mg/L)
min	480	11	7.05	295	0.117	9	1.1	58.6	22.9	0.972	0.3	-10.82	-73.9	<0.01	<0.01
max	501	11.3	7.61	380	3.2	14.4	5.57	72.3	36.6	1.5	0.8	-10.21	-70.8	<0.01	<0.01
average	494	11.2	7.47	327	1.8	11.1	3	63.4	27.5	1.3	0.5	-10.5	-71.7	<0.01	<0.01
std	7	0.1	0.13	18	0.7	1.2	1	3	2.5	0.1	0.1	0.16	0.76	0	0

(b)								
PS Filipići					Briška Reservoir			
	T ( $^{\circ}\text{C}$ )	pH	$\text{NO}_3^-$ (mg/L)	EC ( $\mu\text{S}/\text{cm}$ )	T ( $^{\circ}\text{C}$ )	pH	$\text{NO}_3^-$ (mg/L)	EC ( $\mu\text{S}/\text{cm}$ )
min	10.0	6.64	2	430	9.6	6.64	2.1	421
max	19.9	8.14	4.71	754	19.1	8.06	5.4	615
average	13.5	7.51	3.41	457	12.7	7.52	3.6	456
std	1.7	0.2	0.32	19.2	1.7	0.21	0.5	16.1

Bicarbonate concentrations vary between 295 and 380 mg/L, averaging 327 mg/L, with a standard deviation of 18 mg/L, again pointing out the stability of the groundwater system. In addition, chloride, nitrate and sulphate are showing the same (Table 4a). Chloride concentrations are very low, ranging from 0.117 to 3.2 mg/L, with an average of 1.8 mg/L and a standard deviation of 0.7 mg/L. Sulfate concentrations range from 9 to 14.4 mg/L, with an average of 11.1 mg/L and a standard deviation of 1.2 mg/L. The

nitrate content ranges from 1.1 to 5.57 mg/L, with an average of 3.0 mg/L and a standard deviation of 1.0 mg/L. These values reflect low to moderate nitrate levels, always well below the MAC for the drinking water. Finally, ammonium and nitrite are consistently below detection limits (<0.01 mg/L), which confirms no reductive condition in the aquifer and the absence of recent contamination. Sodium concentrations are low, between 0.97 and 1.5 mg/L, with an average of 1.3 mg/L and with a standard deviation of 0.1 mg/L, while potassium values range from 0.3 to 0.8 mg/L, averaging 0.5 mg/L, with a standard deviation of 0.1 mg/L. Both cations show very limited variability, typical for natural groundwater without influence of waste water contamination, road salting, etc. Calcium concentrations vary between 58.6 and 72.3 mg/L, with an average of 63.4 mg/L and with a standard deviation of 3.0 mg/L, while magnesium concentrations vary from 22.9 to 36.6 mg/L, with an average of 27.5 mg/L and with a standard deviation of 2.5 mg/L. These two parameters together indicate a moderately hard water type with relatively stable composition. Moderate water hardness over time in the supply network may lead to chemical corrosion of pipes, clogging due to carbonate scaling, and ultimately a potential negative impact on the integrity of the distribution system [34,35].

The stable isotopes  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  also display narrow ranges:  $\delta^{18}\text{O}$  varies between  $-10.82$  and  $-10.21\text{‰}$ , with an average of  $-10.5\text{‰}$  and a standard deviation of  $0.16\text{‰}$ , while  $\delta^2\text{H}$  ranges from  $-73.9$  to  $-70.8\text{‰}$ , averaging  $-71.7\text{‰}$  with a standard deviation of  $0.76\text{‰}$ . In addition, values are lying close the local meteoric water line (LMWL) from Marković et al. [27], indicating precipitation origin. The standard deviations of both isotopes fall within the measurement error, which indicates a long residence time of the groundwater, consistent with the stability of EC, temperature, and pH values.

To support this theory, the recharge temperature was calculated based on noble gas measurements. These measurements provide an independent proxy for past recharge conditions, as dissolved noble gases in groundwater are sensitive to temperature at the time of infiltration. Thus, the noble gas derived recharge temperature serves as additional evidence for validating the interpretation of groundwater origin and residence time. The temperature derived from noble gas measurements is approximately  $8\text{ °C}$ . This clearly indicates a higher recharge altitude, since in the lowlands the average temperature is  $10.5\text{ °C}$  [27]. In addition, calculated MRT based upon  $^3\text{H}/^3\text{He}$  is 25 years.

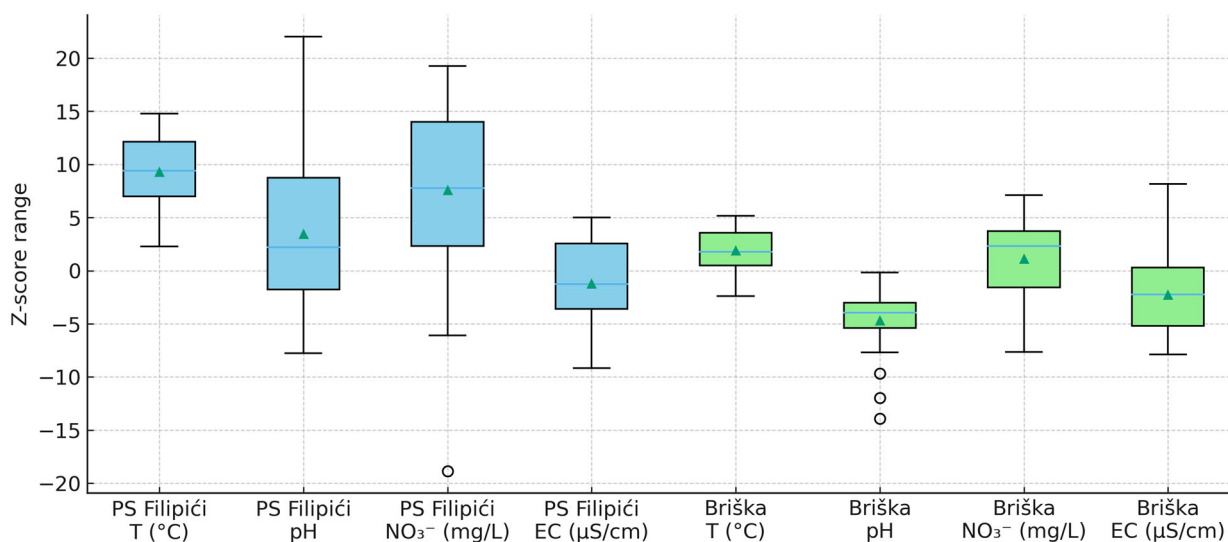
Considering that the Briška reservoir was sampled twice and the Filipići pumping station was sampled only once and analyzed in detail for the same parameters as for the spring (except for  $^3\text{H}/^3\text{He}$  and noble gases), it was not possible to establish a trend from the available data. However, the results could be compared with the spring water. Statistical analysis was carried out using Varkom data, but only for the chemical parameters EC, temperature, pH, and  $\text{NO}_3^-$  (Table 4b).

As water moves away from the spring source at Bela toward the downstream sites of the PS Filipići and the Briška reservoir, a decrease in calcium and magnesium concentrations was observed (Table 5). This progressive reduction is not merely a dilution effect, but is closely linked to carbonate precipitation processes. As pH increases along the flow path, the water becomes supersaturated with respect to carbonate minerals, favoring the deposition of calcite and dolomite. The removal of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  through mineral precipitation explains the observed decrease in concentrations downstream and over time.

**Table 5.** Measured hydrochemical and isotopic parameters from source throughout WSS.

Location	Date	EC (μS/cm)	T (°C)	pH	HCO <sub>3</sub> <sup>-</sup> (mg/L)	Cl <sup>-</sup> (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	NO <sub>3</sub> <sup>-</sup> (mg/L)	Ca <sup>2+</sup> (mg/L)	Mg <sup>2+</sup> (mg/L)	Na <sup>+</sup> (mg/L)	K <sup>+</sup> (mg/L)	δ <sup>18</sup> O (‰)	δ (‰)	NH <sub>4</sub> <sup>+</sup> (mg/L)	NO <sub>2</sub> <sup>-</sup> (mg/L)	<sup>222</sup> Rn (Bq/L)	σ
Belski Dol	28 June 2024	499	11.2	7.32	380	1.7	11	3.4	72.3	36.6	1.3	0.6	-10.82	-72.6	<0.01	<0.01	12.6	±0.6
Reservoir Briška	28 June 2024	510	14.7	7.38	324	2.4	10.8	3.3	66.7	32.4	1.4	0.6	-10.8	-73	<0.01	<0.01	22.4	±0.5
PS Filipiči	28 June 2024	505	13.3	7.56	322	2.1	10.8	3.3	69.7	35.1	1.6	0.6	-10.8	-73	<0.01	<0.01	8.7	±0.7
Belski Dol	29 May 2025	500	11.3	7.42	380	1.3	9.8	1.3	64.2	28.4	1.5	0.5	-10.68	-73.9	<0.01	<0.01	13.3	±0.5
Reservoir Briška	29 May 2025	515	13.5	7.64	320	3	10.7	2.8	61.3	26.8	1.3	0.4	-10.49	-71.9	<0.01	<0.01	26.3	±0.4
Location	Date	He (ccSTP/g)	Ne (ccSTP/g)	Ar (ccSTP/g)	Kr (ccSTP/g)	Xe (ccSTP/g)	<sup>3</sup> He (ccSTP/g)	R/Ra	<sup>3</sup> H	Error TU								
Belski Dol	28 June 2024	5.74 × 10 <sup>-8</sup>	2.21 × 10 <sup>-7</sup>	3.95 × 10 <sup>-4</sup>	9.54 × 10 <sup>-8</sup>	1.42 × 10 <sup>-8</sup>	1.20 × 10 <sup>-13</sup>	1.50	3.38	0.08								

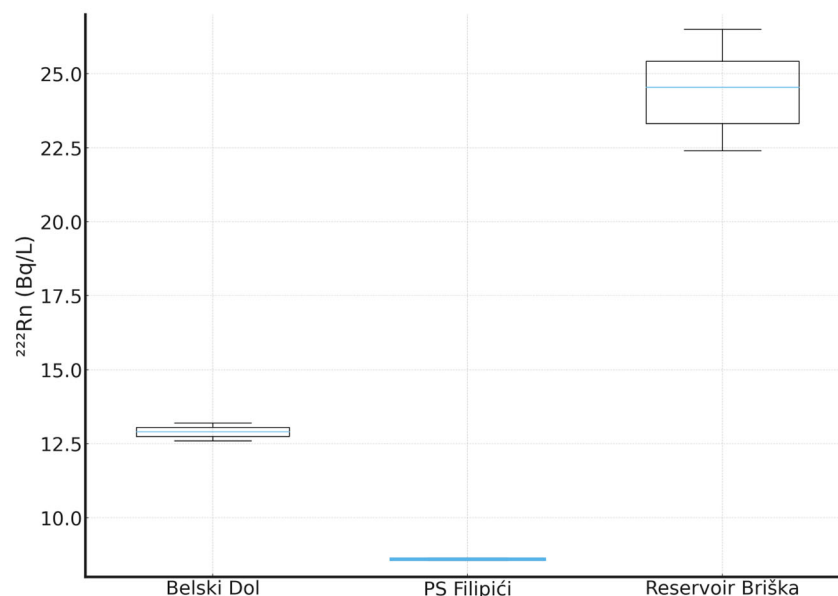
Looking at Figure 4, at PS Filipiči, the distribution is noticeably wider across most parameters, particularly for pH and nitrate, which display strong positive and negative deviations from the mean. This suggests substantial temporal or local variability in chemical conditions. Temperature also shows a moderate spread, while EC exhibits both upward and downward fluctuations, pointing to instability in physical water properties as well. In contrast, Briška reservoir demonstrates generally narrower distributions, reflecting more stable water quality conditions. pH still shows a notable spread, but is significantly less variable than at Filipiči. Nitrate and EC have moderate ranges, though their deviations remain confined within a tighter band. Temperature at Briška reservoir is the most stable parameter, with minimal variation in Z-scores.



**Figure 4.** Distribution of monitored elements in the WSS waters. Note: The edges of the box mark the first and third quartiles, the whiskers show the minimum and maximum, a triangle represents the mean, and the central line indicates the median.

On the other hand, at Belski Dol spring, radon concentrations are relatively stable and tightly clustered between 12.6 and 13.3 Bq/L, indicating only minor variability over time (Figure 5). The Briška reservoir displays the highest concentrations, ranging from 22.4 to 26.3 Bq/L, with a wider spread compared to Belski Dol, suggesting more dynamic conditions or stronger radon inputs at this location. In contrast, PS Filipiči shows the lowest

radon level, with only a single recorded value of 8.7 Bq/L, representing the minimum observed concentration across all sites.



**Figure 5.** Relationship between measured  $^{222}\text{Rn}$  concentration in the spring and throughout the WSS. Note: The edges of the box mark the first and third quartiles, the whiskers show the minimum and maximum, and the central line indicates the median.

The unusually high  $^{222}\text{Rn}$  concentration observed in the Briška reservoir compared to the source Belski Dol can be explained by the cumulative effects of soil-rock radon emanation coupled with aged distribution infrastructure. Belski Dol, being close to the source, exhibits relatively modest radon levels (12.6–13.3 Bq/L) and is less exposed to external contamination. However, at Briška reservoir, water travels through older pipelines and possibly through soils or fractured bedrock that allow radon to diffuse or emanate into the water column, which together with microleaks and pipe joint degradation may boost radon levels. Such phenomena were observed by Özden et al., demonstrating how soil properties such as porosity, moisture, and radium content strongly influence radon release from the ground [36]. In addition, Sukanya & Sabu outline how aquifer-rock contact and aged pathways (via fractures or disturbed soil) enhance radon concentration in downstream water [37]. Taken together, these findings provide a coherent explanation for the higher  $^{222}\text{Rn}$  levels observed in the Briška reservoir relative to the Belski Dol spring.

### 3.2. Vulnerability of the Spring Catchment and of WSS

In order to assess the TIN vulnerability of the study sites, a set of eight hydrochemical and isotopic parameters was selected for the WSS locations: Briška reservoir and PS Filipići. These parameters include EC, T, pH,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , the stable isotopes  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , and  $^{222}\text{Rn}$ . For the source spring Belski Dol, the same eight parameters were considered, but the analysis was extended to include tritium and noble gases, as these provide additional information on groundwater residence time and recharge conditions. The interpretation of our results reflects the scope of the available dataset, and the limited sampling frequency for certain parameters is a factor in the baseline uncertainty.

The methodology followed the approach described in the TIN framework, in which each parameter is assigned a vulnerability score ranging from 1 (low) to 5 (high) presented in Table 3. The scoring was based on the degree of deviation from reference conditions. For the WSS locations, the reference baseline was the values measured at Belski Dol spring on the same sampling date, thus representing the natural source water quality. In contrast,

for Belski Dol itself, the reference was defined as the mean of its own values over the monitoring period, so that the index reflects temporal variability of the spring rather than spatial differences. For most parameters, the score was assigned according to the percentage deviation from the baseline: values within  $\pm 10\%$  correspond to a score of 1, deviations of 10–20% to a score of 2, 20–30% to 3, 30–50% to 4, and  $>50\%$  to 5. In addition, regulatory thresholds were applied as overriding conditions: nitrate concentrations above 50 mg  $\text{NO}_3^-/\text{L}$ , pH values below 6.5 or above 9.5, and temperatures exceeding 25 °C automatically receive the highest score of 5. For stable isotopes, absolute differences relative to the baseline were used instead of percentages, with threshold bands defined in per mil (‰). The  $\delta^{18}\text{O}$  values received scores of 1 for differences  $<0.10\text{‰}$ , 2 for 0.10–0.20‰, 3 for 0.20–0.30‰, 4 for 0.30–0.50‰, and 5 for  $>0.50\text{‰}$ . For  $\delta^2\text{H}$ , the thresholds were set at 1, 2, 3, and 5‰ for scores 1 to 4, with values above 5‰ receiving a score of 5.

Once all parameters had been scored, the TIN vulnerability index for each site and date was calculated as the arithmetic mean of the scores, normalized to a percentage of the maximum possible value. For Belski Dol, an additional adjustment was applied to account for the evidence of long groundwater residence time provided by tritium and noble gas measurements, which indicate a mean residence time of about 25 years and recharge under cold climatic conditions. This information implies a higher degree of natural protection of the source.

The results show that Belski Dol spring consistently exhibits the lowest TIN vulnerability, with an overall index of 25.5%, placing it in the category of low vulnerability. PS Filipići has a somewhat higher index of 35%, reflecting moderate deviations from the source conditions. The Briška reservoir displays the highest values, with an average index of 52.5%, corresponding to moderate vulnerability (Figure 6). This higher vulnerability is primarily associated with greater deviations in radon, nitrate, and conductivity compared to the Belski Dol baseline. Taken together, the analysis demonstrates that the natural spring Belski Dol is well protected and chemically stable, while the WSS sites show increased vulnerability, with Briška reservoir being the most affected.

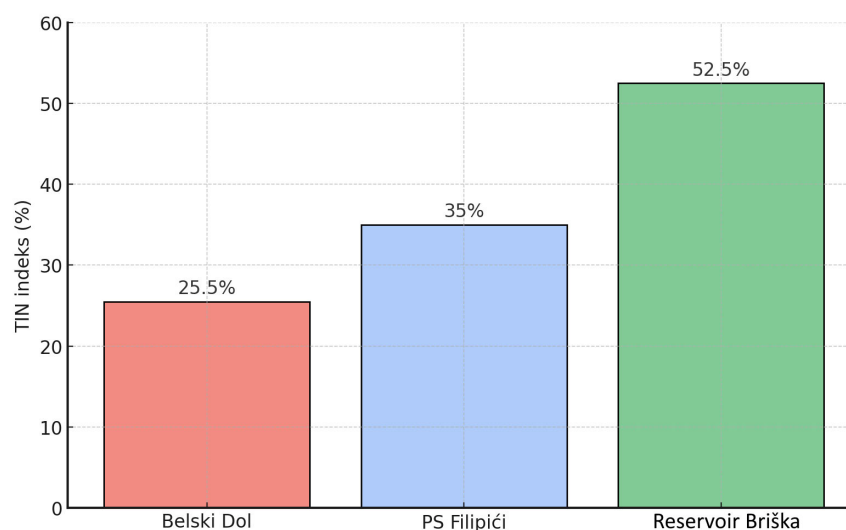


Figure 6. TIN vulnerability assessments results.

#### 4. Conclusions

Our TIN concept advances traditional groundwater vulnerability assessments by explicitly considering the entire water delivery network, thus supporting more robust risk management and safeguarding of drinking water resources. Moving beyond conventional

aquifer assessments to a holistic system perspective, this approach provides water managers with a practical framework for enhancing operational security.

The results showed that the Belski Dol spring is characterized by high hydrochemical stability, long residence times and overall low vulnerability, while also exhibiting a minimal diffuse nitrate risk, which further supports its role as a reliable and naturally well-protected drinking water source. On the other hand, the WSS part of the study area (Briška reservoir and PS Filipići) showed increased vulnerability due to deviations in parameters such as radon, nitrates, and electrical conductivity. The Briška reservoir exhibited the highest vulnerability index, indicating problems from PS Filipići in the form of aged pipelines and potential pathways for radon emanation, as well as for the future pollution.

The integrated evaluation confirmed that hydrogeological protection alone is not sufficient to ensure water safety. Instead, continuous monitoring across both natural and engineered components is essential. By incorporating hydrochemical, isotopic, and radiological parameters, the TIN method allowed identification of critical control points where interventions would be most effective, such as targeted monitoring at the Briška reservoir and maintenance of distribution infrastructure.

**Author Contributions:** Conceptualization, T.M.; methodology, T.M.; validation, T.M., formal analysis, T.M., N.N.-H. and L.P.; investigation, T.M. and I.K.; data curation, T.M. and N.N.-H.; writing—original draft preparation, T.M.; writing—review and editing, N.N.-H., L.P. and I.K.; visualization, I.K. All authors have read and agreed to the published version of the manuscript.

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## Abbreviations

The following abbreviations are used in this manuscript:

CCP	Critical Control Point
DPSIR	Drive-Pressure-State-Impact_Response Framework
DRASTIC	A Standardized System for Evaluating Ground Water Pollution Potential Using Hydrogeologic Settings
EC	Electrical Conductivity
EPA	The Environmental Protective Agency
EPANET	A modeling software of US EPA for modeling water distribution systems
GOD	A methodology for Evaluating Ground Water Vulnerability
IAEA	International Atomic Energy Agency
LMWL	Local Meteoric Water Line
MAC	Maximum Allowable Concentration
MRT	Mean Residence Time
PS	Pumping Station
R	Reservoir

SI	Susceptibility Index
SINTACS	A method developed in Italy for evaluating Ground Water Vulnerability
SLAP2	Standard Light Antarctic Precipitation 2
T	Temperature
TIN	Total Integrated Network Vulnerability Approach
USGS	The U.S. Geological Survey
VSMOW2	Viena Standard Mean Ocean Water 2
WSP	Water Safety Plan
WSS	Water Supply System

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## Curriculum Vitae

Nikolina Novotni-Horčička (born 1972, Varaždin, Croatia) completed her secondary education in Varaždin and graduated in Chemistry from the Faculty of Science, University of Zagreb, in 1996, earning a Master's degree.

She began her career the same year at Varkom d.o.o. Varaždin in the Sewerage Department as a supervisor at the biological wastewater treatment plant. Her responsibilities included wastewater analysis, laboratory organization, and activities related to obtaining authorized laboratory status.

In late 1999, she was appointed Head of the Drinking Water Laboratory within the Water Supply Department of Varkom d.o.o., a position she has held since. She is responsible for organizing and supervising drinking water quality control, ensuring compliance with national legislation and applicable standards, and continuously improving quality management systems in public water supply. Her professional and research interests include groundwater quality, nitrate contamination, drinking water safety, and sustainable water resource management.

In 2002, following one year of professional training at the Croatian Institute of Public Health, she obtained certification to perform chemical and microbiological water analyses. She has completed continuous professional training and holds certifications as an internal auditor for ISO 22000 (including HACCP), ISO 9001, ISO 14001, and Information Security Management Systems (ISMS).

Since 2011, she has been an active member of the Drinking Water Commission within the Croatian Water and Wastewater Utility Association, contributing to regulatory working groups and the organization of the international conference Current Issues in Water Supply and Sewerage.

In 2019, she enrolled in the doctoral programme at the Faculty of Geotechnical Engineering, University of Zagreb (Varaždin), focusing on interdisciplinary research in groundwater quality, water supply systems, and sustainable water management. She has published extensively in peer-reviewed journals and professional forums.

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