

## 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].

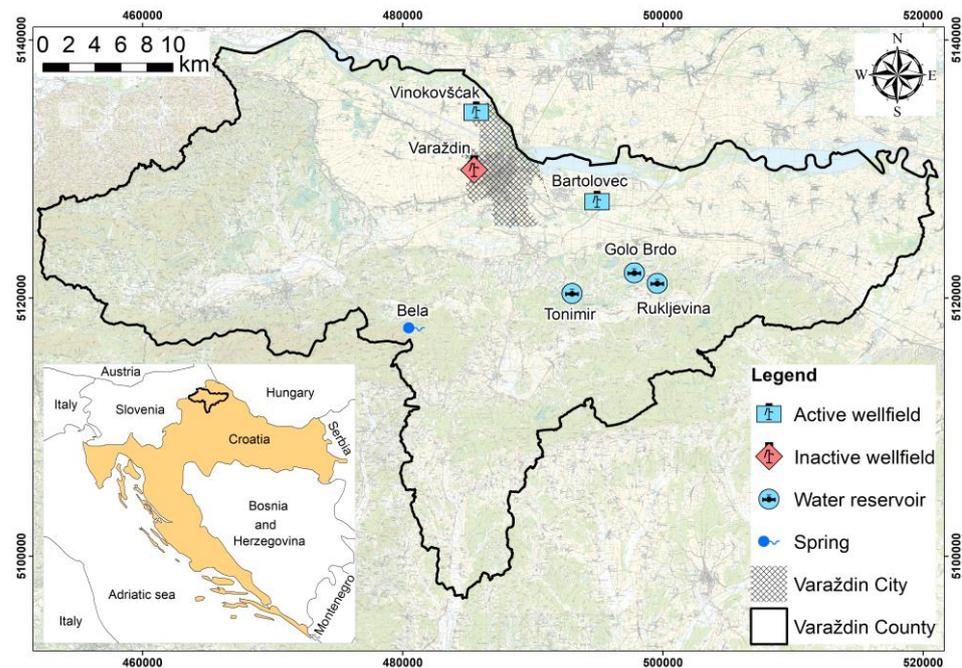
This paper explores the application of  $\delta^{18}\text{O}$  and statistical data processing on selected chemical parameters within a small part of the water supply network managed by Varkom Inc., Croatia. The objectives of the study were the following: (i) to characterize the water from the source 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

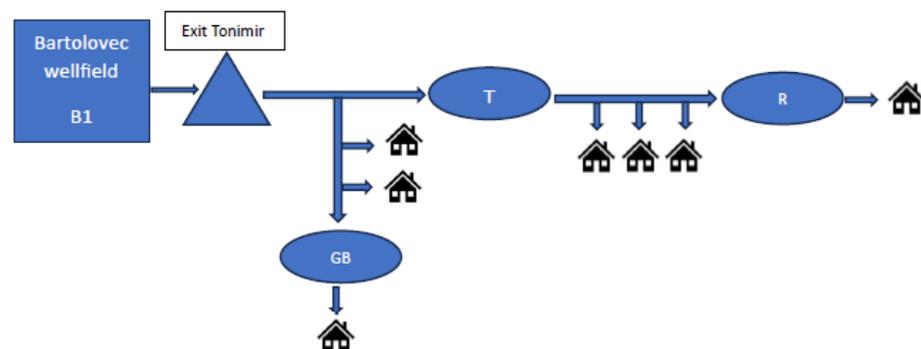
### 2.1. Research Area

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  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  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  $\delta^{18}\text{O}$ , the measurement precision was  $\pm 0.2\text{‰}$ , while for  $\delta^2\text{H}$ , it was  $\pm 0.9\text{‰}$ .

### 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

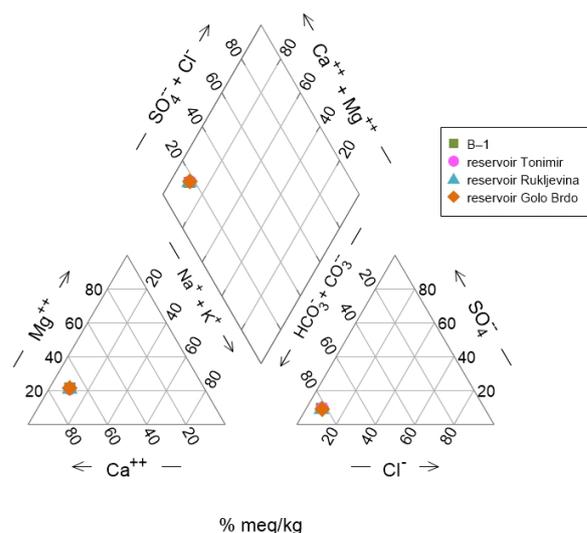
#### 3.1. Hydrochemical Characteristics of Sampled Water

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.

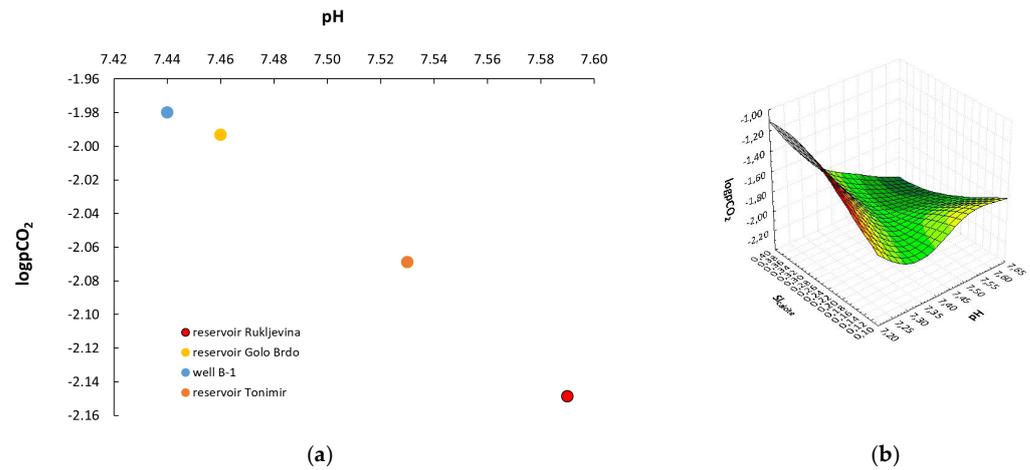
However, when observing the relationship between the pH, logpCO<sub>2</sub> pressure, and calcium saturation index (SI<sub>calcite</sub>), differences are noticed (Figure 4a,b). The well water exhibits a lower pH value and SI<sub>calcite</sub>, but higher logpCO<sub>2</sub>. On the other hand, reservoir 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.

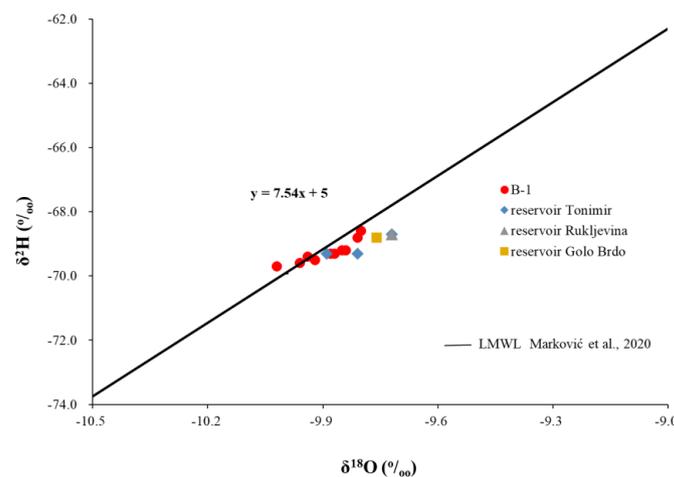
Location	Date	EC ( $\mu\text{S/cm}$ )	T ( $^{\circ}\text{C}$ )	pH	DO (mg/L)	ORP (mV)	$\text{HCO}_3^-$ (mg/L)	$\text{Cl}^-$ (mg/L)	$\text{SO}_4^{2-}$ (mg/L)	$\text{NO}_3^-$ (mg/L)	$\text{Ca}^{2+}$ (mg/L)	$\text{Mg}^{2+}$ (mg/L)	$\text{Na}^+$ (mg/L)	$\text{K}^+$ (mg/L)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
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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