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Assessment of Seasonal Changes on the Carbon Cycle in the Critical Zone of a Surface Water (SW)–Groundwater (GW) System

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Abstract: Groundwater is a valuable source of water for human consumption, and its quality is a current issue worldwide. Understanding carbon and water cycling presents the basis of biogeochemical reactions occurring in the aquifer; therefore, understanding their interaction is imperative for sustainable water management. In the paper, this interaction was investigated within the complex surface water (SW)–groundwater (GW) system in the Varaždin region (Croatia) by using a multi-parameter approach: $\delta^{13}\text{C}_{\text{DIC}}$ values, carbon species (DIC, DOC), $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, geochemical indicators (T, pH, DO, EC), and $\delta^{13}\text{C}$ measurements in solids. Both $\delta^{18}\text{O}/\delta^2\text{H}$ and $\delta^{13}\text{C}_{\text{DIC}}$ were recognized as good indicators to differentiate shallow and deep GW. Transit time of water (TT) was evaluated as an important parameter in controlling carbon cycling within the SW–GW system. Shallow GW is characterized by shorter TT, seasonal changes in carbon species and $\delta^{13}\text{C}_{\text{DIC}}$, and lower possibility of carbon capture in the system. Deep GW has longer TT without pronounced seasonal changes in carbon species and $\delta^{13}\text{C}_{\text{DIC}}$. The conceptual model of the carbon cycle revealed major sources and sinks of CO_2 in the study area. Our results suggest that GW acts as both source and sink for CO_2 , depending on the prevailing geochemical process. Surface waters are primarily a source of CO_2 , excluding the gravel pit, which acts primarily as a sink for CO_2 . Our study shows that the current SW–GW dynamics regulate carbon balance without having negative impacts on groundwater quality but also demonstrates that implementing carbon cycle in water management studies is of vital importance for sustainable use of groundwater.

Keywords: water cycle; carbon cycle; isotopic composition; dissolved inorganic carbon (DIC) flux; transit time (TT); Varaždin alluvial aquifer



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1. Introduction

Understanding carbon cycling in the critical zone is of high interest in Earth system sciences, with broad implications regarding water quality and quantity [1], especially nowadays, when climate changes are pronounced and efforts are being made to reduce CO_2 emissions into the atmosphere. The concept of the critical zone was introduced by the National Research Council [2] and denotes the zone extending from the top of the vegetation canopy through the soil and down to fresh bedrock, i.e., bottom of the groundwater [3]. The movement of CO_2 through the critical zone includes major processes that are sinking CO_2 in the global and local scale: conversion from the atmosphere into the ground via photosynthesis, root respiration, dissolving in precipitation towards groundwater where dissolution of carbonates occurs, leading to its storage in groundwater and soil. Conversely, CaCO_3 precipitation in soil and groundwater and decomposing of plants (organic matter) are processes that emit CO_2 in the atmosphere, alongside other natural (e.g., volcanic eruption) and anthropogenic sources (e.g., emission of fossil fuels, deforestation). Dissolved inorganic carbon (DIC) and its stable isotopic composition ($\delta^{13}\text{C}_{\text{DIC}}$) are governed by biogeochemical reactions and, therefore, experience seasonal variations [4–12]. During the transformation

of carbon (leaching from the surface, infiltration, precipitation of carbonate, dissolution of carbonate from different sources), changes in $\delta^{13}\text{C}_{\text{DIC}}$ occur [13,14]. Plants also play a substantial role in transforming carbon via photosynthesis. Three groups of plants are distinguished: C3 (e.g., grass, wheat, potato, pumpkin, and trees), C4 (e.g., maize and cabbage), and CAM (Crassulacean acid metabolism) (e.g., cacti), which have characteristically different carbon isotopic compositions.

Carbon and water cycles are linked in many ways, e.g., ocean–atmosphere exchange, volcanic outgassing, permafrost melting, ocean warming, photosynthesis, respiration, and weathering [15,16]. Because of their link, isotopic compositions of oxygen (O) and hydrogen (H), expressed as $\delta^{18}\text{O}$ and $\delta^2\text{H}$, are frequently used in surface water (SW)–groundwater (GW) investigations [17–20]. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data on atmospheric precipitation, SW, and GW are meaningful for hydrological, climatological, meteorological, and hydrogeological investigation because they give information on the recharge elevation, estimation of transit time, water–sediment interactions, and biogeochemical processes [21–30].

In this study, $\delta^{13}\text{C}_{\text{DIC}}$ values, carbon species (DIC, DOC), $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, and geochemical indicators were used to better understand the link between hydrological conditions and carbon behavior within complex SW–GW systems in the Varaždin region. It encompasses 200 km² of agricultural land, settlements, mining areas (gravel and sand excavations), a lot of small enterprises and Natura 2000 area (the Drava River). In recent years, knowledge about hydrogeological conditions within the alluvial aquifer and its hydraulic connection with surface waters (the Drava River and accumulation lake) has improved [19,20,31,32]. However, knowledge about carbon behavior in this system does not exist. Since the study area is very “anthropogenically active”, the question arises whether this complex SW–GW system can regulate the release of CO₂ into the atmosphere, and will it act as a sink or an additional source of CO₂. How would that effect the protected area and groundwater quality? Answers to these questions represent novelty in understanding carbon behavior in investigated SW–GW system and has implementation on a global scale, everywhere where such conditions exist. This knowledge is important for sustainable and effective SW–GW and land management for the future.

The main goals of this paper are: to identify the seasonal and spatial variation of dissolved carbon species and the isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) and investigate their relationship with groundwater hydrodynamics; to define and thermodynamically model carbon sources and sinks; to estimate annual DIC fluxes into deep and shallow GW and SW; and to create a conceptual model of the carbon cycle based on hydrological and isotopic data.

2. Materials and Methods

2.1. Study Area

The study area is positioned in the Drava River valley in the southwestern margin of the Danube basin, upstream of the Varaždin, a city in Northern Croatia (Figure 1). The alluvial aquifer is the only source for community water supply needs in the Varaždin region (approximately 170,000 inhabitants). Groundwater is also used for irrigation and industrial activities. According to the Corine land cover [33], the terrain’s surface is predominantly characterized by agricultural land (68%). Alongside irrigation, inorganic (synthetic), and organic fertilizers (manure) are added to the soil to enhance crop growth. Overfertilization, however, has led to high nitrate content in the groundwater and the shutting down of the Varaždin wellfield. The only active wellfield within the study area is Vinokovščak, situated between the Drava River and the derivation channel of the hydroelectric power plant Varaždin (Figure 1).

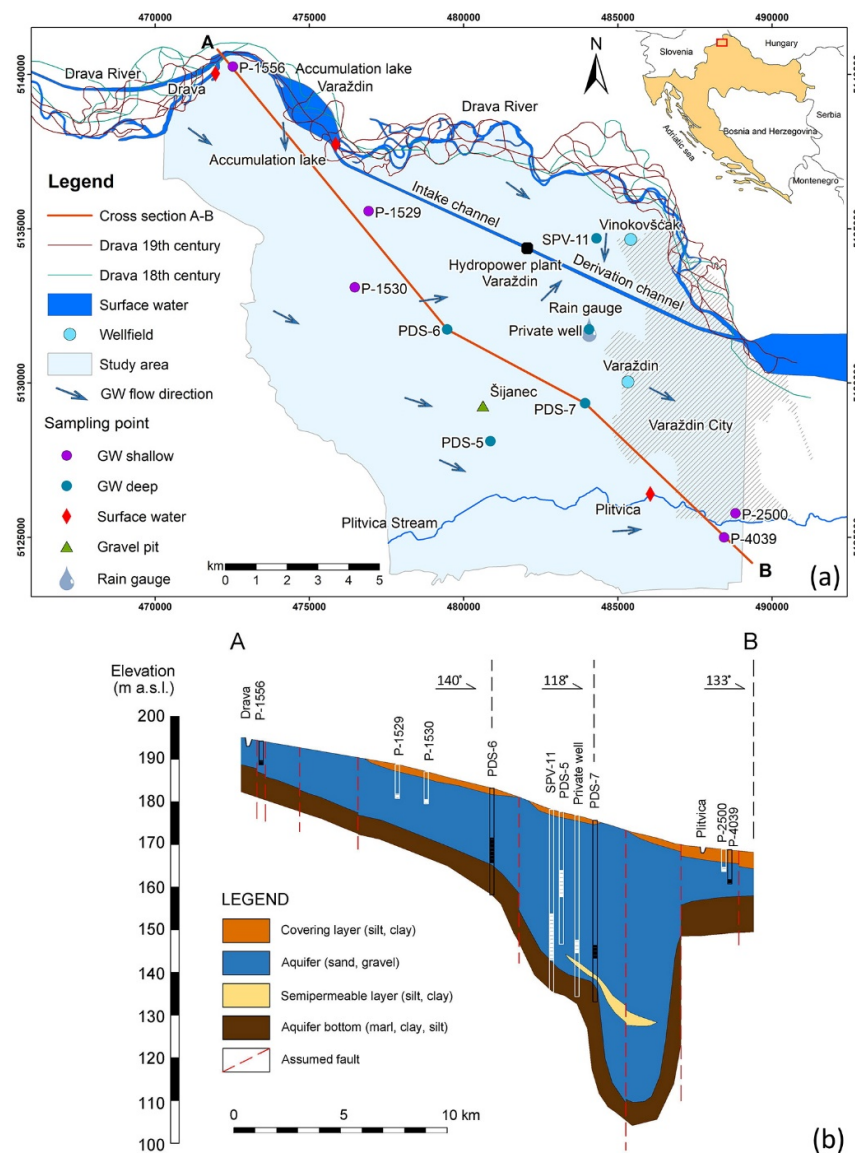


Figure 1. Map showing the geographical location of the study area with sampling sites (a), and the representative hydrogeological cross-section A–B (b). Observation wells (black) are located precisely on the cross-section, while the positions of the observation wells (white) are only approximated. The general groundwater flow direction is presented for average groundwater levels [32].

The aquifer is built of Quaternary alluvial deposits [34] dominated by gravel and sand, with silty and clayey lenses and interlayers [35,36]. Minerals that most often occur in deposits are gneiss, quartz, basic and neutral eruptive rocks, feldspars and other silicate minerals (e.g., epidote, amphibole, garnet, rutile, kyanite), limestone, and dolomite [37,38].

The Drava River changed its course many times during the Pleistocene and Holocene, forming numerous channels and meanders, which are still visible (Figure 1). In the old bed of the Drava River, the sedimentation process in still water prevailed for a long time, which resulted in deposition of fine sediments (e.g., clay, silt, and organic matter) and formation of distinctive oxbow facies [38]. The aquifer thickens towards the east, from less than 5 m in the marginal parts of the aquifer to about 65 m below the Varaždin City area (Figure 1, cross-section A–B).

The aquifer is unconfined and characterized by intergranular porosity. According to the conceptual model, it is divided into three layers: upper aquifer, semipermeable interlayer, and lower aquifer [32]. Groundwater generally flows in a SE direction (Figure 1). The bottom of the aquifer consists of impermeable marl, clay, and silt. The covering layer of

the aquifer is discontinuous, which allows rapid leaching of contaminants from the surface. The Šijanec gravel pit was formed by excavating gravel-sandy material, and its water level indicates the level of the groundwater in the aquifer. The Varaždin hydroelectric power plant was built in the 1970s and significantly influences the net flow of groundwater. It consists of an accumulation lake, an intake channel, the power plant, and a derivation channel (Figure 1). The aquifer is recharged through percolation from the Drava River and accumulation lake and precipitation infiltration. Karlović et al. [32] modeled long-term precipitation in the study area and concluded that the average annual precipitation is distributed as groundwater recharge, surface runoff, and actual evapotranspiration with 34%, 21%, and 45%, respectively. Groundwater discharge occurs through the derivation channel and the Plitvica stream [32,39].

The climate of the study area is Cfb type based on the Köppen–Geiger classification system [40]. The origin of precipitation is generally from the Atlantic air masses, with Mediterranean influence during cooler periods of the year [19]. Groundwater levels remain relatively stable between normal seasonal fluctuations, controlled mainly by the water level of the accumulation lake and the Drava River. Similarly, the flow rates of the Plitvica stream are also within the expected range, with variations depending on seasonal precipitation and water level. The Drava River flow regime is stable according to the measured flow rates because the flows are controlled by discharging water from the accumulation lake.

2.2. Sampling Procedure

Groundwater and surface water sampling was divided into five sampling campaigns during different hydrological and vegetation seasons between September 2018 and September 2019. Surface water sampling was conducted at four different sites, while groundwater samples were collected by pumping from 10 observation wells (Figure 1, Table 1). Among the sampling sites, four groups were singled out according to hydrological characteristics: (1) SW–Drava River, accumulation lake Varaždin and Plitvica stream; (2) gravel pit; (3) shallow groundwater observation wells (well depth ≤ 8 m); and (4) deep groundwater observation wells (well depth > 8 m) (Table 1). The water level was measured in the wells prior to pumping. The thickness of the unsaturated zone varies both spatially and temporally due to changes in hydrological conditions. Generally, the thickness is greater in the central part of the study area, especially for deeper wells (e.g., up to 8.02 m in PDS-6). In contrast, shallow wells near the study area's edge have lower unsaturated zone thicknesses (e.g., 2.26 m in P-1556) and fluctuations in groundwater levels within single wells range from 0.41 m in P-2500 to 1.15 m in PDS-6.

Table 1. Observation Wells Information.

Observation Well	Latitude (° N)	Longitude (° E)	Elevation (m a.s.l.)	Well Depth (m)	Type of Well	Depth Interval of the Screen (m)	Min Water Level (m a.s.l.)	Max Water Level (m a.s.l.)
Private well	46.325158	16.293106	176.00	15.0	Deep	5–15	169.28	169.90
PDS-5	46.292462	16.25173	178.36	31.0	Deep	13.7–19.7	174.25	174.86
PDS-6	46.324993	16.233373	184.07	25.0	Deep	11.7–17.7	176.05	177.20
PDS-7	46.303596	16.291492	175.71	42.5	Deep	29.3–32.3	170.26	170.84
P-1529	46.359419	16.200068	187.32	8.0	Shallow	n.a. ¹	181.98	182.40
P-1530	46.337192	16.194381	183.72	7.5	Shallow	n.a. ¹	177.46	178.31
P-1556	46.401421	16.142607	193.03	5.6	Shallow	n.a. ¹	190.11	190.77
P-2500	46.271647	16.354878	167.81	5.2	Shallow	n.a. ¹	164.61	165.02
P-4039	46.264594	16.350134	167.76	8.0	Shallow	n.a. ¹	164.62	165.29
SPV-11	46.351711	16.296098	177.69	40.0	Deep	24.5–35.8	170.96	171.51

Note(s): ¹ information about screen interval was unavailable.

More than three volumes of water were pumped out from each observation well (constant electrical conductivity was reached) before sampling to obtain a representative groundwater sample. In situ measurements of electrical conductivity (EC), water tempera-

ture (T), pH, and dissolved oxygen (DO) were made using a WTW multi-probe. Samples for major ion analysis were collected in 500 mL HPDE bottles with tight-fitting caps. Samples for dissolved organic and inorganic carbon (DOC, DIC) analyses were filtered through a 0.45 μm PVDF (polyvinylidene fluoride) filter and stored in 100 mL amber glass bottles. Samples for $\delta^{13}\text{C}_{\text{DIC}}$ analyses were filtered through a 0.45 μm PVDF filter and kept in 12 mL Labco glass serum ampoules filled to the top. Monthly composite precipitation samples (producer Palmex Ltd., Zagreb, Croatia) were collected using a rain gauge, transferred into HDPE (1 L) plastic bottles, and refrigerated until analyses. The major ions, DOC, DIC, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were measured in the Hydrochemical Laboratory of the Croatian Geological Survey, while $\delta^{13}\text{C}_{\text{DIC}}$ measurements were performed in the Department of Environmental Science laboratory, Jožef Stefan Institute.

Solid samples, e.g., aquifer sediment, soil, plants, and manure ($n = 17$), were collected across the study area in two field sampling campaigns (July 2018 and September 2019). Homogenized aquifer sediment samples were collected from the Drava riverbed and gravel pit to represent the aquifer carbonate deposits. Homogenized plant samples were taken directly from arable land to represent typical crops grown in the study area: cabbage, corn (grain, leaf), potato, wheat (grain, straw), pumpkin, and grass. Homogenized manure samples were collected from cow and chicken farms. Homogenized soil samples were collected at the surface of the terrain under an orchard and fields of corn, cabbage, and wheat. All samples were immediately stored in sealed polyethylene bags for transport to the Geochemical Laboratory of the Croatian Geological Survey. The preparation of solid samples consisted of freezing, freeze-drying, and grinding of plants, manure, and soil, and grinding carbonates in aquifer sediment into a fine fraction suitable for $\delta^{13}\text{C}$ analyses. The analyses of $\delta^{13}\text{C}$ in solid samples were performed in the Department of Environmental Science laboratory, Jožef Stefan Institute.

2.3. Analytical Methods

Determination of the major ions and dissolved carbon (DOC, DIC) in surface water and groundwater samples were analyzed following protocols reported in [31] and for analyses of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ following protocols in [19].

2.3.1. Determination of $\delta^{13}\text{C}_{\text{DIC}}$

The Isoprime 100 coupled to a MultiflowBio preparation module was used to determine $\delta^{13}\text{C}_{\text{DIC}}$ values. The method is described in detail in [41,42]. Briefly, 100–200 μL of phosphoric acid (100%) was added to a septum-sealed vial, which was then purged with pure He. Each analysis took approximately 5 min. A 1 mL water sample was then injected, and the headspace CO_2 was measured. To determine the optimal extraction procedure, a standard Na_2CO_3 solution (Carlo Erba reagents, Val de Reuil, France) with a known $\delta^{13}\text{C}_{\text{DIC}}$ value of $-10.8 \pm 0.2\text{‰}$ was used. The average sample repeatability was 0.2‰. One-point normalization was performed, and all samples were measured in two repetitions. Stable isotopes are reported in the δ notation [43,44].

2.3.2. Determination of $\delta^{13}\text{C}$ in Plant and Manure Samples

Ground plant and manure samples (approx. 1 mg) were transferred to tin capsules, and their carbon isotopic composition ($\delta^{13}\text{C}$) was measured using an IsoPrime 100 mass spectrometer coupled to a PyroCube preparation module (Elementar Analysensysteme GmbH, Langenselbold, Germany). Measurement repeatability and quality were controlled with the IAEA CH-3 = $-24.724 \pm 0.041\text{‰}$, IAEA CH-6 = $-10.449 \pm 0.033\text{‰}$ reference materials and, additionally, sugar with a $\delta^{13}\text{C}$ value of $-25.2\text{‰} \pm 0.2\text{‰}$. The results were normalized against the IAEA CH-3 and IAEA CH-6 reference materials. All samples were measured in triplicate.

2.3.3. Determination of $\delta^{13}\text{C}_{\text{carb}}$

About 1 mg of the carbonate sample was weighed in the ampoule and purged with helium. Each sample analysis took about 5 min. Then, 0.2 mL of H_3PO_4 was added [45]. The resulting CO_2 was measured from gas caps with an IsoPrime 100 isotope mass spectrometer coupled to a MultiflowBio preparation module. Repeatability and measurement quality were controlled using two reference materials: IAEA CO-1 ($2.492\text{‰} \pm 0.030$) and NBS19 ($1.95\text{‰} \pm 0.035$). Each sample was measured three times. Unprocessed data were normalized against IAEA CO-1 and NBS19 reference materials.

2.3.4. Determination of $\delta^{13}\text{C}_{\text{bulk}}$ and $\delta^{13}\text{C}_{\text{org}}$ in Soil

Approximately 3–5 mg of the soil sample was added and transferred into tin capsules to determine $\delta^{13}\text{C}_{\text{bulk}}$. Each sample analysis took about 10 min. To determine $\delta^{13}\text{C}_{\text{org}}$, carbonate was first removed with 3M HCl. The samples were analyzed as for plants and manure. All samples were measured in duplicate.

2.4. Data Processing

Saturation indices and CO_2 partial pressure (pCO_2) were calculated to evaluate chemical speciation and estimate the carbon sequestration pool within the SW–GW system using PHREEQC software [46]. Carbonate fraction in soil was calculated according to the following equation [47]:

$$\delta^{13}\text{C}_{\text{bulk}} = x \delta^{13}\text{C}_{\text{org}} + (1 - x) \delta^{13}\text{C}_{\text{carb}}, \quad (1)$$

where x is (%) of carbonate fraction in soil, $\delta^{13}\text{C}_{\text{carb}} = -0.1\text{‰}$ (averaged measured value for carbonate), and $\delta^{13}\text{C}_{\text{bulk}}$ is measured bulk value of sample.

The flux of inorganic carbon into groundwater [g/m^2] was calculated by multiplying DIC [mol/L] with groundwater recharge R [mm/y] and converting units into GtCy^{-1} . The groundwater recharge was calculated using the effective infiltration rate multiplied by average precipitation amount for the monitored period. The flux of inorganic carbon into surface waters [g/m^3] was calculated by multiplying the DIC [mol/L] with the discharge Q [m^3/s] and converting units into GtCy^{-1} . The inorganic carbon flux was not calculated since there was no information about discharge from the accumulation lake and gravel pit.

All graphical representations were made using a combination of MS Excel 2016, Surfer 7.6, ArcMap 10.2.1, and AutoCAD 2021. The maps are presented in the official reference coordinate system for map projection in Croatia (HTRS96/TM).

3. Results and Discussion

3.1. Hydrochemical and Isotopic Composition of GW and SW

The minimum, maximum, and average physical, physicochemical, chemical, and isotopic $\delta^{13}\text{C}_{\text{DIC}}$ parameters in surface water and groundwater samples from five sampling campaigns (September and December 2018, April, June, and September 2019) are given in Table 2. More details on the isotopic composition of hydrogen and oxygen in precipitation, groundwater, and surface waters are available in [19]. All $\delta^{13}\text{C}$ data associated with this article are available in Supplementary Material. Additional two-year physical and chemical data for groundwater were presented in [31]. However, physical and chemical data for surface waters were not published in the previous work.

Table 2. The minimum, maximum, and average physical, physicochemical, chemical, and isotopic parameters for surface water (SW) and groundwater (GW) for five sampling campaigns.

Sampling Point	SW			Gravel Pit			GW Shallow			GW Deep		
Values	Min	Max	Average	Min	Max	Average	Min	Max	Average	Min	Max	Average
EC ($\mu\text{S}/\text{cm}$)	232	584	403	229	332	283	660	1091	807	434	769	669
T ($^{\circ}\text{C}$)	3.3	22.7	13.9	3.0	32.1	18.3	8.8	15.6	13.3	12.1	13.6	12.8
pH	6.93	8.09	7.87	7.04	10.09	8.61	6.93	7.6	7.22	6.91	7.56	7.22
DO (mg/L)	6.4	12.7	9.4	10.5	19.5	14.6	0.2	11.8	5.6	1.5	11	7.3
Ca ²⁺ (mg/L)	38.9	85.6	55.0	13.3	35.4	25.3	87.5	136.2	111.3	74.0	120.8	104.5
Mg ²⁺ (mg/L)	6.6	17.1	11.7	14.5	17.0	16.3	16.5	25.3	20.5	16.3	21.5	19.5
Na ⁺ (mg/L)	3.5	11.4	7.6	6.0	8.9	7.3	5.3	80.0	24.2	2.4	10.4	6.1
K ⁺ (mg/L)	0.7	3.3	1.9	0.6	1.1	0.9	1.1	6.7	3.4	0.4	12.6	4.1
DIC (mg/L)	23.4	65.0	39.3	12.4	28.7	22.2	46.2	99.9	77.0	49.3	79.1	70.0
DOC (mg/L)	0.9	12.6	3.4	4.2	24.3	13.3	0.2	5.4	1.0	0.1	1.0	0.4
HCO ₃ [−] (mg/L)	122	334	203	66	149	116	238	512	395	254	406	360
$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	−13.6	−9.7	−11.5	−9.9	−0.5	−4.1	−14.5	−10.7	−12.9	−12.9	−10.9	−11.7
$\delta^{18}\text{O}$ (‰)	−10.93	−8.44	−9.73	−7.52	−5.85	−6.71	−10.40	−8.94	−9.80	−10.87	−9.38	−10.09
$\delta^2\text{H}$ (‰)	−76.2	−56.6	−66.9	−52.7	−47.4	−49.6	−71.5	−61.2	−67.1	−75.6	−65.3	−70.7
Cl [−] (mg/L)	5.5	13.8	9.5	12.4	15.9	13.8	7.1	212.7	46.8	6.7	19.5	12.7
SO ₄ ^{2−} (mg/L)	18.4	27.2	22.3	22.2	27.4	24.4	20.1	35.4	26.0	22.0	33.6	26.9
PO ₄ ^{3−} -P (mg/L)	<0.01	0.07	0.03	0.01	0.06	0.03	<0.01	0.16	0.04	<0.01	0.04	0.02
NH ₄ ⁺ (mg/L)	<0.01	0.18	0.03	<0.01	0.35	0.12	<0.01	0.06	0.03	<0.01	0.02	0.02
NO ₂ [−] (mg/L)	0.006	0.101	0.03	0.014	0.199	0.07	<0.001	0.026	0.007	<0.001	0.033	0.006
NO ₃ [−] (mg/L)	5.3	23.2	11.3	5.1	13.7	11.2	<0.1	58.9	35.5	<0.1	95.6	49.0
SiO ₂ (mg/L)	1.0	18.9	10.3	3.2	25.0	12.2	10.1	24.7	14.5	11.5	18.9	14.6

The lowest EC values were measured in the gravel pit and the highest in the shallow GW samples. The high EC values in shallow GW indicate a higher dissolved solid content than in deep GW and SW. The highest temperature variations ($\Delta T = 28.8^{\circ}\text{C}$) were observed in SW, while the lowest $\Delta T = 1.5^{\circ}\text{C}$ was detected in deep GW samples. High temperature variations in SW are related to seasonal changes. Depending on the observation well's position in the aquifer, the DO in the groundwater samples varied from extremely low (0.2 mg/L) to high (11.8 mg/L). Surface waters were saturated with DO. pH-values varied from slightly acid to slightly alkaline for all sampled waters. Micronutrient ($\text{PO}_4^{3-}\text{-P}$, NO_2^- , NH_4^+) concentrations in SW varied from under the detection limit to slightly elevated. The high nitrate concentrations in the groundwater were likely connected with anthropogenic influences, such as agricultural production and waste waters (Karlović et al., 2021a). The highest concentration of Cl^- and SO_4^{2-} was measured in the shallow GW samples, followed by deep GW samples, and the lowest in SW. The silica content (as SiO_2) varied in SW, while only a slight variation was observed in GW.

According to the hydrochemical classification based on the major ionic composition, five different water types can be distinguished (Figure 2). GW belongs to the $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ hydrochemical type, except for GW from P-4039, which belongs to the $\text{Na}^+\text{-Ca}^{2+}\text{-HCO}_3^-$ and the $\text{Na}^+\text{-Ca}^{2+}\text{-HCO}_3^-\text{-Cl}^-$ hydrochemical type. Observed hydrochemical types are due to weathering and dissolution of silicate (e.g., micas and feldspar) and carbonate (limestone, dolomite) minerals that compose aquifer sediments [31], which influences the carbon cycle in GW. SW belongs to the $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ hydrochemical type, while gravel pit water belongs to the $\text{Mg}^{2+}\text{-Ca}^{2+}\text{-HCO}_3^-$ hydrochemical type (mainly dolomite) as the consequence of biota activities that are related to the seasonal changes.

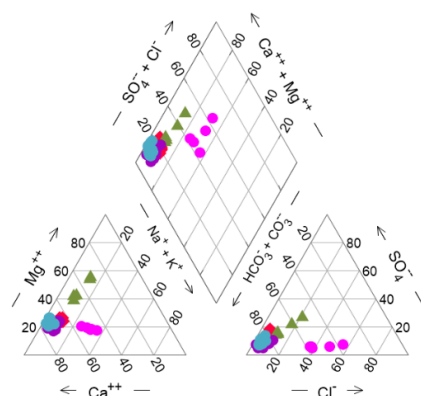


Figure 2. Piper diagram of sampled waters. Blue circles—GW deep; Violet circles—GW shallow; Pink circles—GW shallow water from P-4039; Red diamonds—SW; Green triangles—gravel pit.

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of GW and SW were distributed along the two LMWLs Varaždin indicating meteoric origin (Figure 3). However, it was observed that values from shallow GW were around the LMWL based on 2017 to 2020 measurements [19], while values from deep GW were close to the LMWL based on 2007 to 2010 measurements [48]. This result indicates that the transit time (TT) of groundwater is different based on the position within the aquifer, i.e., shorter TT (a couple years) in shallow and longer TT (ten or more years) in deep GW. These results are consistent with previous research: Karlović et al. [20] observed the time delay in SW—GW temperature oscillations, indicating longer transit time towards the east where the aquifer deepens; Karlović et al. [49] modeled groundwater flow and nitrate transport and identified inertia regarding nitrate attenuation in deeper part of the aquifer during the 20-year period, which also suggests longer transit time in deep GW. Values from SW, except values from gravel pit where evaporation is expressed, show very good overlapping with GW, especially with the shallow value, indicating recharge in this part of the aquifer.

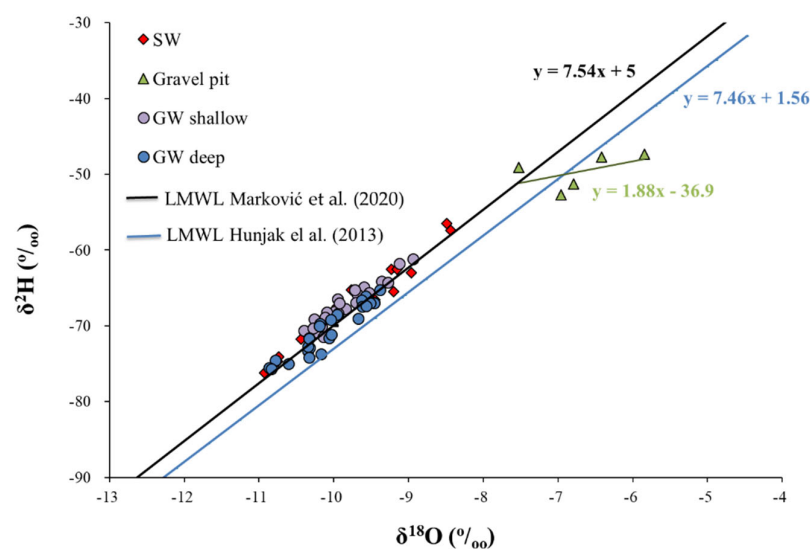


Figure 3. Distribution of GW and SW $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values around the LMWLs Varaždin (modified after [19]).

3.2. Spatial and Seasonal Variation of Carbon Species and Evaluation of Biogeochemical Processes

The highest DIC values in GW are observed in the central part of the study area (Figure 4a). The highest DOC values are measured in SW, especially in the gravel pit (Figure 4b). However, DIC values in these waters are low compared to GW (Figure 4a,b).

The calculated log pCO₂ values are undersaturated with CO₂ in gravel pit water, while SW and GW samples are oversaturated with respect to the atmosphere (Figure 4c).

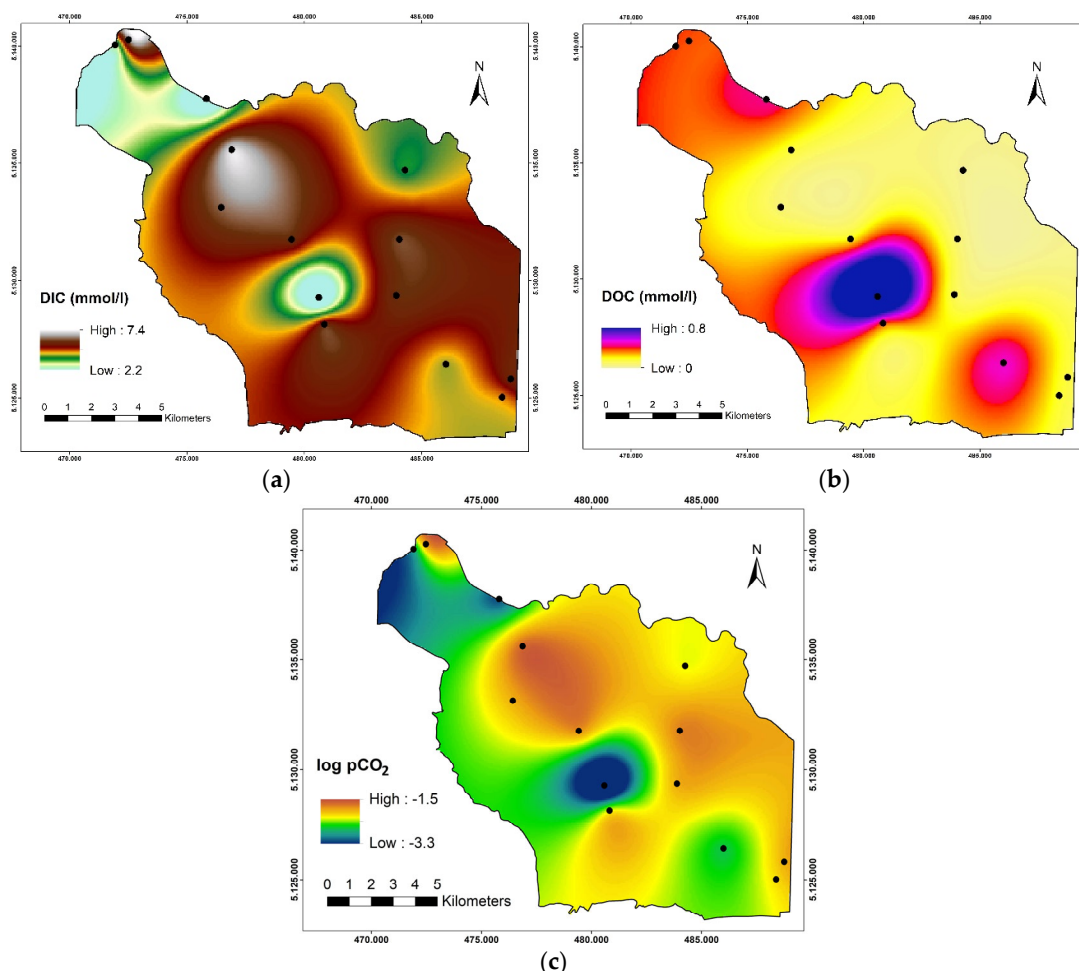


Figure 4. Spatial distribution of average values within Varaždin SW–GW system: (a) DIC; (b) DOC; (c) log pCO₂.

The results show that the spatial distribution of the average values of log pCO₂, DIC, and DOC (Figure 4) in the studied SW–GW system depends on the proximity to the river and accumulation lake, GW level, extraction depth (Table 1), presence of oxbow sediments, and land use. Generally, DIC and log pCO₂ in GW increased, while DOC concentrations decreased with the distance from the river and lake to the center of the study area (Figure 4). However, these concentrations changed according to land use and the influence of irrigation. The spatial distribution trend of DIC, DOC, and log pCO₂ was not entirely in line with the direction of groundwater flow, which indicates that local geochemical processes within the aquifer system have a greater influence on all three parameters than regional groundwater flow.

$\delta^{13}\text{C}_{\text{DIC}}$ values varied seasonally from -13.6 to -0.5‰ in SW samples and from -14.5 to -10.7‰ in GW samples (Table 2 and Table S1). The shallow GW samples had more negative $\delta^{13}\text{C}_{\text{DIC}}$ values than samples from GW deep. The $\delta^{13}\text{C}_{\text{plant}}$ of plant samples ranged from -29.9‰ to 12.8‰ (Figure 5, Table S2). The plants in the studied system were mainly C3 plants, except corn and cabbage, which were C4 plants. The average $\delta^{13}\text{C}_{\text{carb}}$ value was -0.1‰ , ranging from -2.9‰ to 0.5‰ . The average $\delta^{13}\text{C}$ value in soil samples was -24.8‰ , ranging between -27.1 and -23.2‰ , while bulk samples had more positive $\delta^{13}\text{C}$ values and varied from -27.3 to -22.5‰ , indicating some carbonate contribution. Considering the average $\delta^{13}\text{C}_{\text{carb}}$ value of -0.1‰ (aquifer sediments in Figure 5), the

soil carbonate fraction is estimated to be $\leq 4.3\%$ (Equation (1)). The highest carbonate contribution was observed in soil samples from the Šijanec area, which is attributed to the degradation of cabbage cultivated in this area.

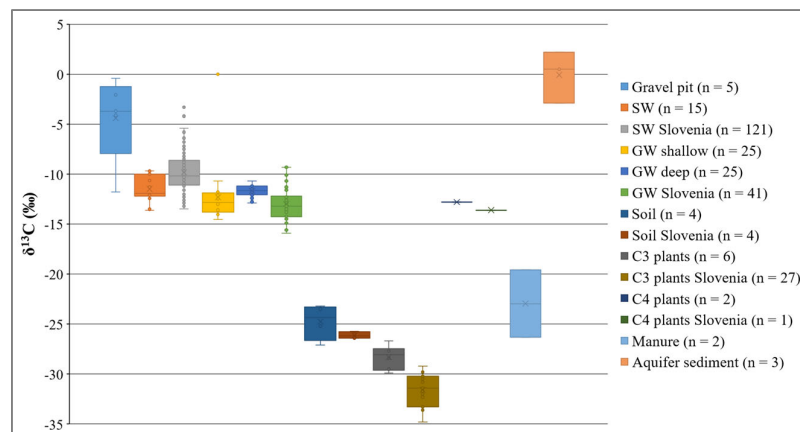


Figure 5. The $\delta^{13}\text{C}$ of plants, soil, manure, aquifer sediment, $\delta^{13}\text{C}_{\text{DIC}}$ of SW and GW in the Varaždin aquifer area compared to the $\delta^{13}\text{C}$ and $\delta^{13}\text{C}_{\text{DIC}}$ values (river water, groundwater) from the nearby Slovenian Sava study area [5,6,50,51].

The highest seasonal oscillations of $\delta^{13}\text{C}_{\text{DIC}}$ values, carbon species (DOC, DIC), carbonate cations (Ca^{2+} , Mg^{2+}), and $\log \text{pCO}_2$ were observed in the gravel pit (Figure S1). Here, the surface water was undersaturated with atmospheric CO_2 (Figure 6a). The gravel pit is small, approximately 12,000 m² with a water depth of 1.5 m to 2.5 m, and it is hydraulically connected with deep GW [52]. The surrounding GW contains high nitrate (60.9 mg/L) and total nitrogen (16.1 mg/L) concentrations [31]. Since this nitrogen-rich groundwater recharges the gravel pit, the pit is full of living microorganisms from April to September (especially in June), containing a large amount of biota, such as eukaryotic algae and Cyanobacteria [52]. The increased input of nutrients into the gravel pit can induce eutrophication (Figure 6b). This biota controls carbon cycling in the gravel pit water by assimilating CO_2 from water to the point of CO_2 depletion, followed by dissolving atmospheric CO_2 in water that is again assimilated. The result is undersaturation in the water regarding $\log \text{pCO}_2$ in the warmer part of the year (Figure S1). In addition, they produce organic carbon, causing high DOC concentrations (Figure 4b), and can incorporate carbonate on their skeletons, facilitating the precipitation process as nuclei, which are needed for starting the calcite precipitation [53]. These processes cause a decrease in Ca^{2+} (Figure S1) and DIC levels in the water.

In the Drava River and the accumulation lake, seasonal oscillations of $\delta^{13}\text{C}_{\text{DIC}}$ values, carbon species (DOC, DIC), carbonate cations (Ca^{2+} , Mg^{2+}), and $\log \text{pCO}_2$ were also observed, but not in such amplitude as in the gravel pit (Figure S1). More negative $\delta^{13}\text{C}_{\text{DIC}}$ values and higher DOC concentrations were also observed during the warmest parts of the year (April to September), which can be attributed to the higher degradation of organic matter leached from terrestrial material into the SW system. Nevertheless, more positive $\delta^{13}\text{C}_{\text{DIC}}$ values were observed during winter and spring due to higher discharge–dilution effect (Table S1). Negligible seasonal oscillations in DOC, DIC, and $\delta^{13}\text{C}_{\text{DIC}}$ were observed in samples from the Plitvica stream, which is attributed to its drainage role in the deeper part of the aquifer [39].

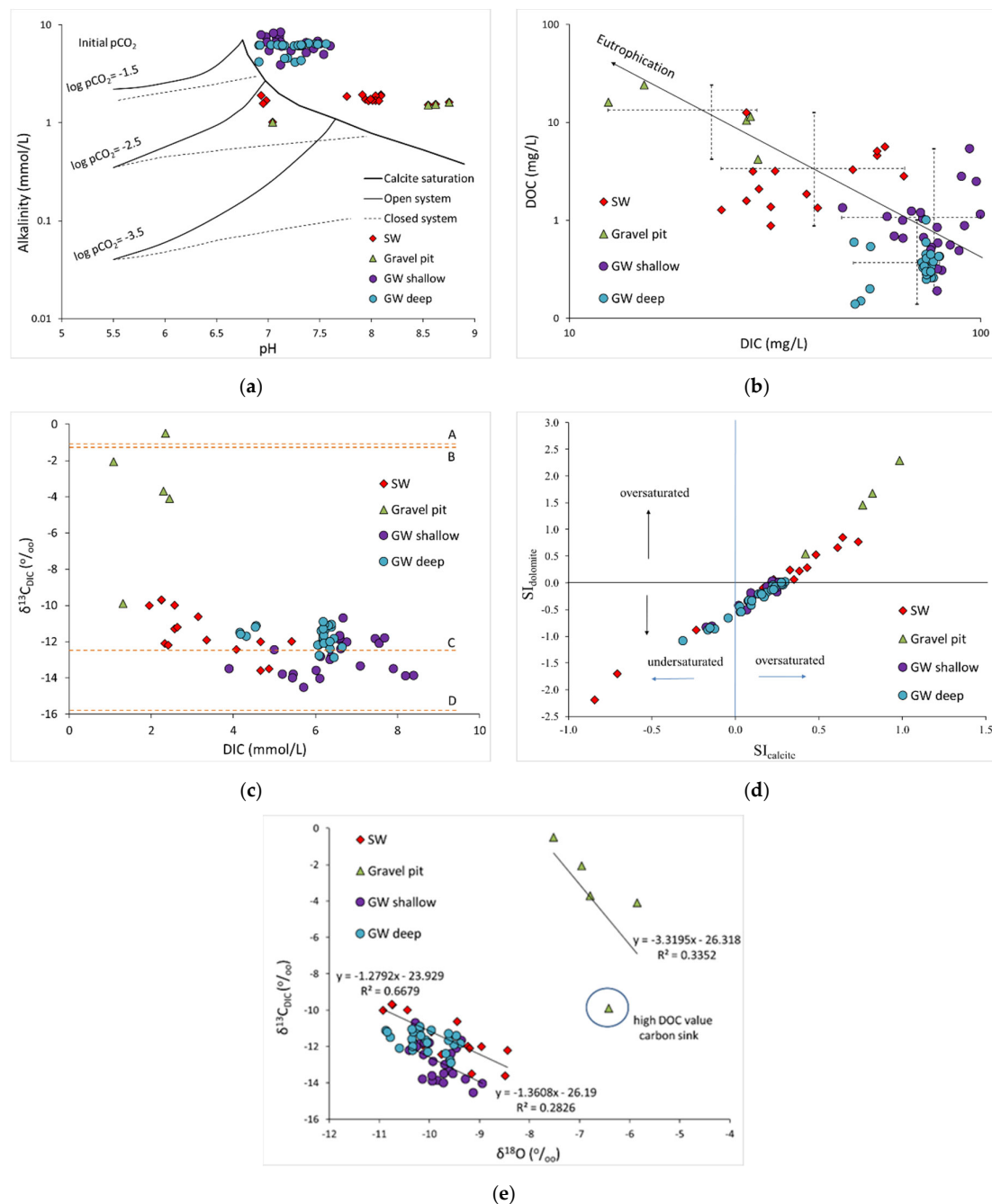


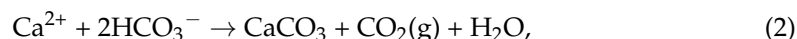
Figure 6. Plots of selected chemical and isotopic parameters: (a) Variation of alkalinity vs. pH; (b) DOC vs. DIC; (c) Variation in the $\delta^{13}\text{C}_{\text{DIC}}$ vs. DIC in the groundwater–surface water aquifer system. Orange dashed lines represent fractionation lines: (A) Open system DIC equilibration with the atmosphere with an average value of -1.2‰ ; (B) Dissolution of carbonate with $\delta^{13}\text{C}_{\text{carb}}$ of -0.1‰ , providing the $\delta^{13}\text{C}_{\text{DIC}}$ of -1.1‰ ; (C) Open system equilibration of DIC with soil CO_2 originating from degradation of organic matter with $\delta^{13}\text{C}_{\text{CO}_2}$ of -24.4‰ ; (D) Nonequilibrium carbonate dissolution with $\delta^{13}\text{C}_{\text{CO}_2}$ of -24.4‰ ; (d) relationship between saturation indices of calcite and dolomite; (e) relationship between $\delta^{18}\text{O}$ of groundwater and $\delta^{13}\text{C}_{\text{DIC}}$.

In the shallow GW, more negative $\delta^{13}\text{C}_{\text{DIC}}$ values were measured compared to deep GW, indicating shorter TT of water as it was observed in a case of stable water isotopes values. More negative $\delta^{13}\text{C}_{\text{DIC}}$ values were measured in P-1556 and P-4039 during winter-spring sampling campaigns, which is associated with an increase in groundwater level, interaction of GW with oxbow sediments, and/or rinsing the unsaturated zone. Oxbow

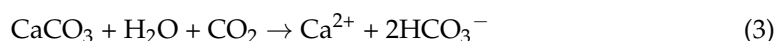
sediment contains degrading organic matter, while the unsaturated zone contains organic matter that has migrated from the surface and soil zone. The seasonal variations of log pCO₂ (Figure S2) are much more pronounced in shallow GW than in deep GW due to the influence of CO₂ from the soil, representing an open system (Figure 6a,c). However, oscillations in DOC, DIC, $\delta^{13}\text{C}_{\text{DIC}}$, and log pCO₂ are less evident in deep GW parts where SW and precipitation are mixed (Figure S2). The transit time of water is an important parameter in controlling carbon cycling within the groundwater system, i.e., shorter time results in rapid changes in carbon species, thus, lowering the possibility of carbon capture in the critical zone system, and vice versa, for longer TT.

3.3. Carbon Sources and Sinks in SW–GW System

Thermodynamic modeling was used to identify whether SW and GW present active sources and sinks for atmospheric CO₂ in the Varaždin area. The results indicate that water in the gravel pit acts as an active sink in summer and autumn because log pCO₂ is below or close to atmospheric log pCO₂ pressure (−3.5 bar), which ensures the dissolution of atmospheric CO₂ gas (Figure 6a,d,e). Only in spring and winter, it acts as a source of CO₂ to the atmosphere. The water is oversaturated with calcite and dolomite (Figure 6d). During the precipitation of calcite, CO₂ is released according to the following equation:



and CO₂ consumption during the calcite weathering (see also the Conceptual model):



However, existing biota in the water of the gravel pit does not allow the release of the CO₂ to the atmosphere via assimilation (photosynthesis), and the eutrophication process is dominant (Figure 6b). In addition, higher $\delta^{13}\text{C}_{\text{DIC}}$ values indicate an open system equilibration with the atmosphere as the most probable process governing $\delta^{13}\text{C}_{\text{DIC}}$ (Figure 6a).

River, lake, and stream waters are oversaturated regarding log pCO₂, slightly saturated in calcite, and unsaturated in the case of dolomite for most of the monitored period (Figure 6d). In the Plitvica stream, the eutrophication process is present during the warmer part of the year (red diamonds close to the eutrophication line, Figure 6b). In all three SWs, biota is present, but not in the same amount as in the gravel pit [54]. In the accumulation lake, higher $\delta^{13}\text{C}_{\text{DIC}}$ values indicate that equilibration with air CO₂ is the most probable process governing $\delta^{13}\text{C}_{\text{DIC}}$ (Figure 6a). River water samples are scattered around the line C, representing open system equilibration of DIC, with soil CO₂ coming from the degradation of organic matter with $\delta^{13}\text{C}_{\text{CO}_2}$ of −24.4‰ (Figure 6c). Consequently, the monitored river, lake, and stream waters act periodically as carbon sinks, but predominantly are carbon sources.

Both shallow and deep GW are oversaturated with respect to log pCO₂ and calcite (Figure 6a,d). However, both are undersaturated in dolomite (Figure 6d). The calculated carbonate contribution leached from soil to groundwater is low at about 4%. According to Figure 6c, the minority of shallow and deep GW are around the line C. Most deep GW samples plot above the line C, with $\delta^{13}\text{C}_{\text{carb}}$ of −0.1‰, indicative of carbonate dissolution. The shallow GW samples plot mainly above the line, representing nonequilibrium carbonate dissolution by H₂CO₃ originating in soil (line D). In addition to carbonate minerals, aquifer sediment contains silicate minerals. Weathering of silica minerals in the GW was identified by [31]. The weathering of silica minerals is a longer process than carbonate dissolution [55], and it is typical for aquifers with longer TT. Therefore, this process probably contributes to CO₂ formation in the deep GW, causing higher alkalinity of samples (Figure 6a).

3.4. Conceptual Model for Catchment Area Based on Hydrological and Carbon Isotopic Data

Based on the obtained results, the conceptual model for the critical zone of the Varaždin alluvial aquifer system is created. The sources of carbon in the study area can be divided into two groups: natural (organic matter in soil and sediments, atmosphere) and anthropogenic (fossil fuel consumption, agricultural production, animal and human waste). All aspects of biogeochemical processes (photosynthesis, evaporation/precipitation, leaching, decomposition of organic matter, carbonate precipitation and dissolution) are presented with $\delta^{13}\text{C}$ values of environmental matrixes in SW, GW, carbonate, soil, manure, plants, and relationships between sources and sinks of CO_2 in the Varaždin aquifer (Figure 7).

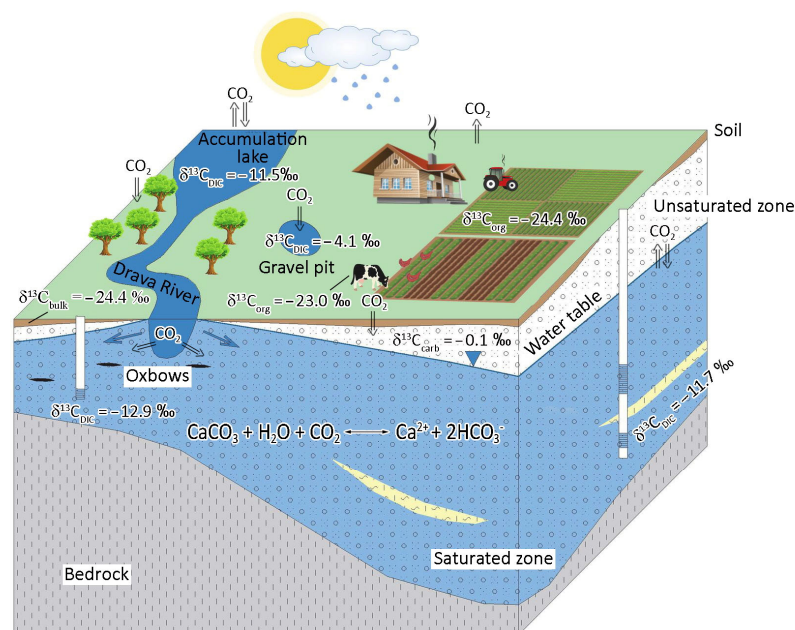


Figure 7. A conceptual 3D block diagram presenting a conceptual model of the critical zone in the Varaždin SW-GW system.

The studied surface waters (Drava River, Plitvica stream, and accumulation lake) represent the sources of CO_2 in the atmosphere and groundwater, while the gravel pit acts as a CO_2 sink with slow-moving (standing) water, meaning that CO_2 is close to equilibration with atmospheric CO_2 . Most of the time, groundwater represents a sink, but when precipitation of carbon minerals occurs, it acts as the source of CO_2 . Groundwater, especially the shallow part, as long as carbonate dissolution occurs, acts as a sink for CO_2 , not just from soil and the unsaturated zone but also from river and lake waters, because they recharge the groundwater. On the other hand, when carbonate precipitation occurs, GW acts as a source of CO_2 , which is most of the time.

The estimated DIC flux into groundwater varies from 0.32 GtCy^{-1} (deep groundwater) to 0.34 GtCy^{-1} (shallow groundwater). Estimated fluxes of dissolved inorganic carbon for surface water are lower, from 0.02 GtCy^{-1} in the Plitvica stream to 0.12 GtCy^{-1} in the Drava River. Estimated carbon fluxes for groundwater are slightly higher than the ones reported by [56]. Alternatively, estimated carbon fluxes for surface water are lower than those for global rivers of 0.4 GtCy^{-1} [57,58].

4. Conclusions

This paper provides first insights about SW–GW interaction in relation to the aqueous carbon cycle in the study area. Carbon behavior in the SW–GW system was investigated using a multi-parameter approach, within which an evaluation was made of seasonal fluctuations, major biogeochemical processes, the role of CO_2 sinks or sources, and carbon fluxes.

Both $\delta^{18}\text{O}/\delta^2\text{H}$ in water and $\delta^{13}\text{C}_{\text{DIC}}$ have proven to be valuable indicators to distinguish shallow and deep GW, i.e., to differentiate parts of the aquifer according to the transit time of water, which appears to be an important parameter in controlling carbon cycling within the system. Shorter transit time (a couple of years) is characteristic for shallow GW, resulting in rapid changes in carbon species and lower possibility of carbon capture in the system. The lowest $\delta^{13}\text{C}_{\text{DIC}}$ value in shallow GW is related to the influence of CO_2 from soil and is subject to seasonal change. Conversely, seasonal changes are not observed in deep GW, where more positive $\delta^{13}\text{C}_{\text{DIC}}$ values are attributed to carbonate dissolution and longer transit time (ten or more years). The spatial variation of dissolved carbon species in groundwater is conditioned by the geometry of the aquifer, which deepens towards the east.

As conceptually illustrated in Figure 7, our results suggest that groundwater acts as both source and sink for CO_2 , depending on the prevailing geochemical process. Chemical weathering is the main process that drives the carbonate geochemical cycle: in our study the predominant process of CO_2 consumption is during weathering (water/rock interactions) in deep GW, while during precipitation of carbonate minerals, the groundwater is a source of CO_2 to the atmosphere. The river, lake, and stream waters are primarily a source of CO_2 , while the gravel pit acts primarily as a sink for CO_2 . Most positive $\delta^{13}\text{C}_{\text{DIC}}$ value in the gravel pit is a result of eutrophication during the spring/summer season. In comparison to rivers on a global scale, lower estimated carbon fluxes for surface water indicate that the groundwater is not overloaded with carbon from surface water. Our study demonstrates that SW–GW dynamics regulate carbon balance without having negative impacts on groundwater quality by changing the conditions within the aquifer.

The importance of this study is emphasized in the study area, since groundwater is the only source of water for human consumption. Therefore, understanding the interaction between the carbon and water cycles is necessary in any system that relies on sustainable groundwater, since it represents the basis of biogeochemical processes occurring in the aquifer. The methodology used in this study can be implemented by water supply managers in a variety of risk assessments, climate studies, waste managing practice programs, and remediation strategies.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/w14213372/s1>. Table S1. $\delta^{13}\text{C}_{\text{DIC}}$ values (‰) in water samples; Table S2. $\delta^{13}\text{C}$ values (‰) in solid samples; Figure S1. Time series of (a) $\delta^{13}\text{C}_{\text{DIC}}$; (b) DIC; (c) DOC; (d) log p CO_2 ; (e) Ca^{2+} ; (f) Mg^{2+} in surface water; Figure S2. Time series of (a) $\delta^{13}\text{C}_{\text{DIC}}$; (b) DIC; (c) DOC; (d) log p CO_2 ; (e) Ca^{2+} ; (f) Mg^{2+} in groundwater

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