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Regional Isotopic Signatures of Groundwater in Croatia

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Abstract: Tracer methods are useful for investigating groundwater travel times and recharge rates and analysing impacts on groundwater quality. The most frequently used tracers are stable isotopes and tritium. Stable isotopes of oxygen (δ^{18}O) and hydrogen (δ^{2}H) are mainly used as indicators of the recharge condition. Tritium (^{3}H) is used to estimate an approximate mean groundwater age. This paper presents the results of an analysis of stable isotope data and tritium activity in Croatian groundwater samples that were collected between 1997 and 2014 at approximately 100 sites. The composition of the stable isotopes of groundwater in Croatia originates from recent precipitation and is described using two regional groundwater lines. One of them is applied to groundwater accumulated in the aquifers in the Pannonian part of Croatia and the other is for groundwater accumulated in the Dinaric karst of Croatia. The isotope content shows that the studied groundwater is mainly modern water. A mix of sub-modern and modern water is mostly accumulated in semi-confined porous aquifers in northern Croatia, deep carbonate aquifers, and (sub)thermal springs.

Keywords: stable isotopes; tritium activity; spatial distribution of an approximate groundwater age; karst aquifer system; porous aquifer system; Croatia

1. Introduction

Water molecules have isotopic "fingerprints" according to the differing ratios of their oxygen and hydrogen isotopes and their radioisotope activity. The most frequently used isotopes in groundwater hydrology are stable isotopes and tritium, which naturally occur in the environment. Consequently, they are called "environmental isotopes". All three isotopes enter the hydrological cycle via precipitation. Stable isotopes of oxygen (δ^{18}O) and hydrogen (δ^{2}H) are mainly used as indicators of the recharge condition. Tritium (^{3}H) is used to estimate the approximate groundwater age.

The global monitoring of the isotopic composition of monthly precipitation is carried out through the Global Network of Isotopes in Precipitation (GNIP), which was established in 1961 by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO). The objective of this network is the systematic collection of the isotopic data of precipitation and the determination of temporal and spatial variations in the isotopes within precipitation. Isotopic data include the tritium activity concentration and stable isotopes of hydrogen and oxygen isotopes (δ^{2}H and δ^{18}O values), as well as climatological data (mean monthly temperature, monthly precipitation amount, and atmospheric water vapour pressure) [1].

The stable isotopes of hydrogen (^{1}H, ^{2}H) and oxygen (^{16}O, ^{18}O) are natural environmental tracers with broad applications in groundwater hydrology [2–8]. They help to reveal the groundwater origin and recharge [9–11], as well as the mean groundwater age in some cases [12,13]. The content of stable isotopes in water is affected by the sources of precipitating air masses, which are linked to climate characteristics such as ambient temperature, precipitation amount, wind speed, and humidity. Fractionation processes are responsible for the spatial and temporal variations in water isotope composition [14–16], as well as orographic effects [17], distance from the coast, and latitude [18,19].

The isotopic composition of groundwater in both karst and alluvial aquifers in Croatia was previously studied for different purposes. The study of general functioning of the karst hydrogeological system [20] and the delineation of catchment areas of karst springs [21] were performed using an analysis of the distribution of stable isotopes in groundwater. Using stable isotope composition, the recharge areas of karst aquifers were considered [22–25]. A lumped parameter approach was used for the groundwater age estimation [12,26]. Several studies have been carried out where isotope composition of precipitation, surface water, and groundwater were employed for identification of groundwater recharge sources and for improvement of the conceptual model of the porous aquifer systems [27–31].

The isotopic composition of groundwater was studied in the neighbouring countries also. Mezga et al. [32] presented the isotopic composition of sampled groundwater that was monitored over three years and performed a comparison with previous studies regarding the isotopic composition of precipitation, surface water, and groundwater in Slovenia. Nikolov et al. [33] concluded that most of the analysed groundwater in Vojvodina (Serbia) can be characterized as modern waters, recharged mostly from precipitation.

Tritium (^{3}H) is the radioactive isotope of hydrogen with a half-life of 12.32 years [34]. It decays into helium−3 (^{3}He). Tritium is naturally produced in the atmosphere by the reaction of cosmic radiation with nitrogen atoms. In hydrology and oceanography, ^{3}H content is expressed in tritium units (TU). Other disciplines may use the ^{3}H activity concentration in Bq (Bequerel), where 1 TU = 0.118 Bq/L [35,36]. The natural ^{3}H activity concentration in precipitation varies within the range of 5 to 10 TU, depending on the location [9,37]. Prior to atmospheric nuclear bomb testing in the 1950s, the mean ^{3}H activity concentrations were approximately 2 to 8 TU [38]. Due to nuclear bomb testing, the maximum concentrations of ^{3}H in the precipitation in the northern hemisphere reached more than 5000 TU in 1963 [39]. The data over the last twenty years show an almost constant mean annual ^{3}H concentration [40,41]. However, seasonal variations are observable. The lowest ^{3}H concentrations are distributed in the winter months. Duliński et al. [40] suggest that these low ^{3}H activity concentrations likely reflect episodes of specific circulation patterns over Europe, where the fast transport of oceanic water vapour from the Atlantic Ocean to central Europe occurs without significant rainout and moisture exchange with the surface of the continent. The maximum monthly ^{3}H activity concentration is observed in the late spring and summer months [23,40,42–47]. The extremely high ^{3}H activity concentrations occasionally recorded are likely linked to episodic emissions of technogenic tritium on the European continent [48]. The possible sources are nuclear power reactors and the applications of artificial tritium in medicine and the watch industry [40].

Since it is relatively geochemically conservative, tritium is an excellent tracer for the investigation of groundwater flow dynamics as well as giving an approximate groundwater age at a time scale of less than 100 years [2,26,49,50]. Groundwater ^{3}H activity concentrations reflect the ^{3}H activity concentration when the water, which contributes to groundwater recharge, was in the contact with the atmosphere. Since ^{3}H decays to ^{3}He, the application of the ^{3}H/^{3}He method, which measures the relative abundance of ^{3}H and ^{3}He in a groundwater sample [49], allows for a more precise definition of the groundwater age.

This study aims to evaluate the regional isotopic signatures of groundwater in Croatia. The study is focused on comparisons between groundwater stable isotopes and precipitation isotope data. To achieve this, we analyse the existing data on stable isotopes (δ^2H and δ^{18}O) and tritium activity (^{3}H) stored in the database of the Croatian Geological Survey (HGI-CGS), as well as data from published papers. Isotopic data are taken from studies on drinking groundwater. An overview of the sampling sites from different aquifer systems in which water samples were collected between 1997 and 2014 is presented, and the descriptive statistics of isotopic data are shown. We also discuss data distribution and the various correlations among the data.

2. Materials and Methods

2.1. Study Area

Croatia is a small southern European country, comprising an area of only 56,538 km^2. From a hydrogeological and even water management standpoint, the country can be divided into two hydrogeological regions: the Northern or Pannonian region and the Southern or Dinaric karst region (Figure 1). Northern Croatia is situated in a southwestern part of the Pannonian Basin where large lowlands are dominant along the two Danube tributaries—the river Sava and Drava and their major tributaries—and along the river Danube in the east-most part of the region. Quaternary sediments form thick and highly permeable aquifers within these lowlands [51,52]. In between the lowlands, there is a hilly region (in some places mountainous), composed mainly of low permeable deposits ranging in age from the Palaeozoic to Quaternary, while only smaller areas are occupied by permeable carbonate deposits of the Triassic age, which represent an important aquifer. The altitudes of these lowlands vary from approximately 120 m a.s.l. in the west to approximately 80 m a.s.l. in the east. In the mountainous region, the altitudes can reach 1000 m a.s.l.

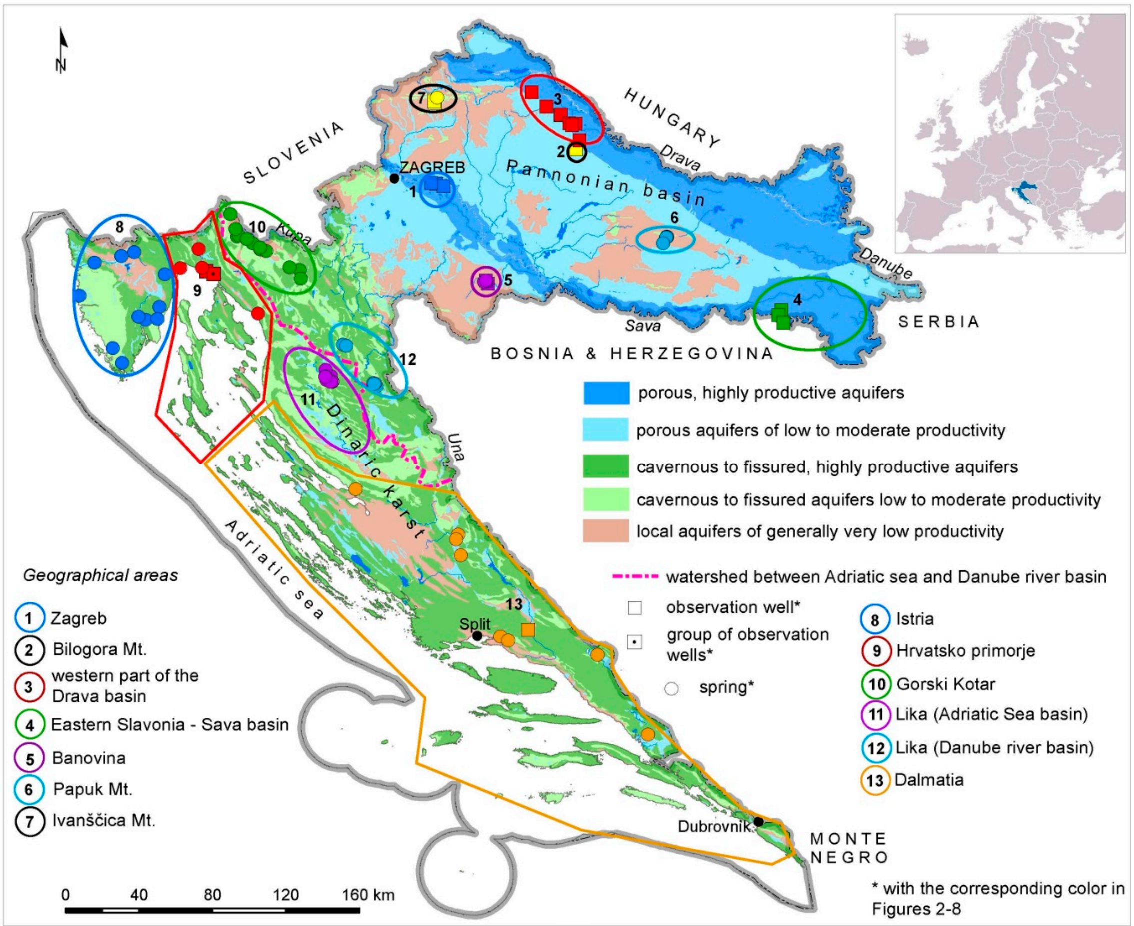

Figure 1. Aquifer types in Croatia, geographical areas (schematic), and the locations of the isotope composition measurements. The colours of the sampling points and the frame colours of the geographical areas correspond to the colours of the points in Figures 2–8.

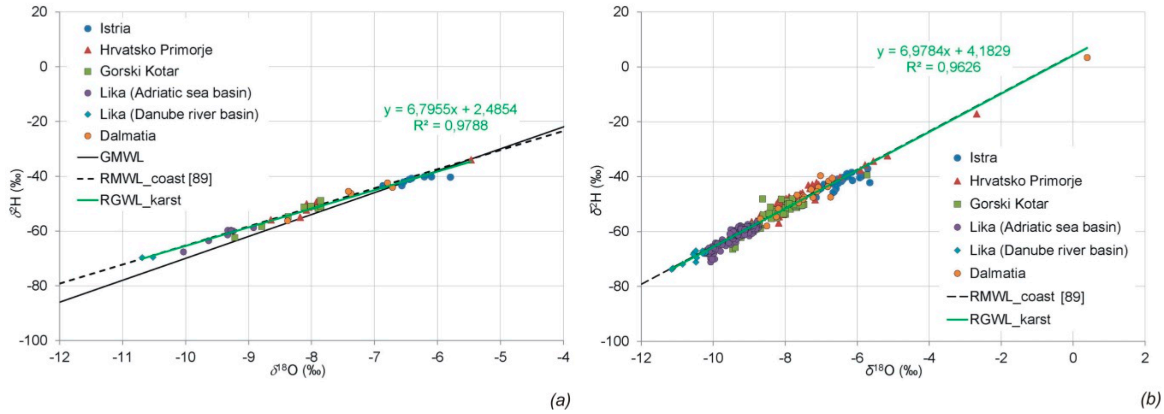

Figure 2. The regional meteoric water line of the coastal part of Croatia (RMWL_coast) and the stable isotope composition of the spring water in the Dinaric karst in Croatia: (**a**) the mean values of the stable isotopes and (**b**) the single values of the stable isotopes.

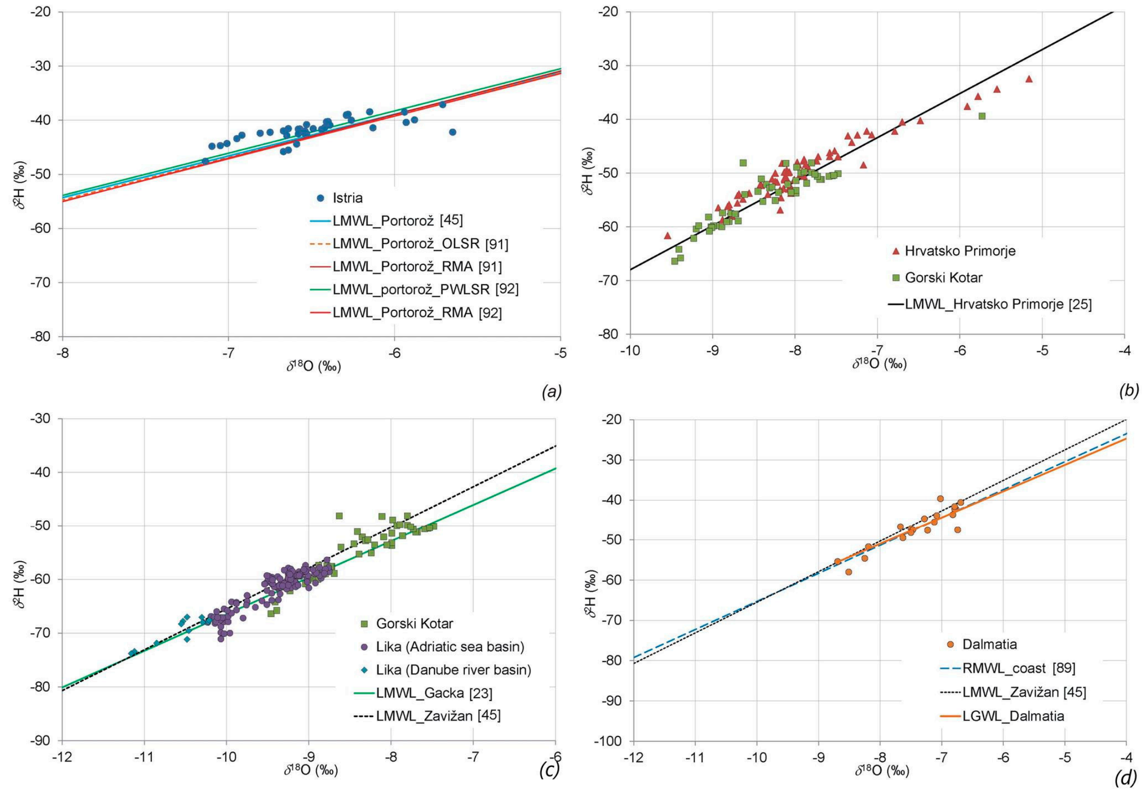

Figure 3. Local meteoric water lines (LMWLs) and the single values of the groundwater stable isotopes in the Dinaric karst in Croatia: (**a**) Istria, (**b**) Hrvatsko Primorje and Gorski Kotar, (**c**) Gorski Kotar and Lika, and (**d**) Dalmatia.

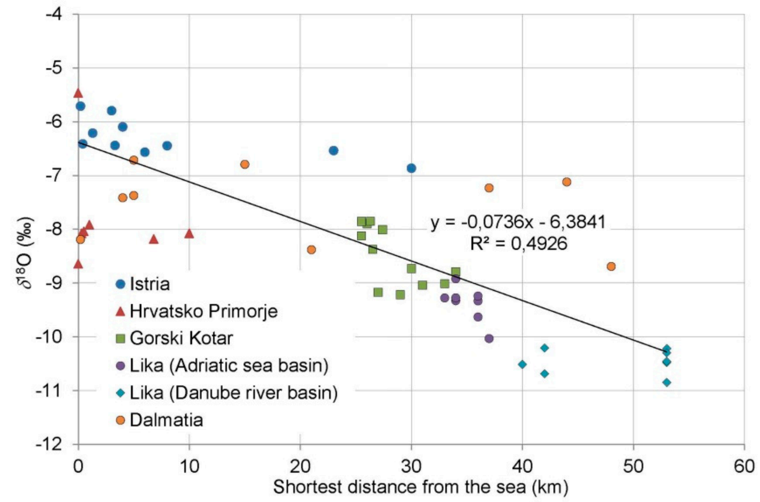

Figure 4. The mean δ^{18}O vs. the shortest distance from the sea.

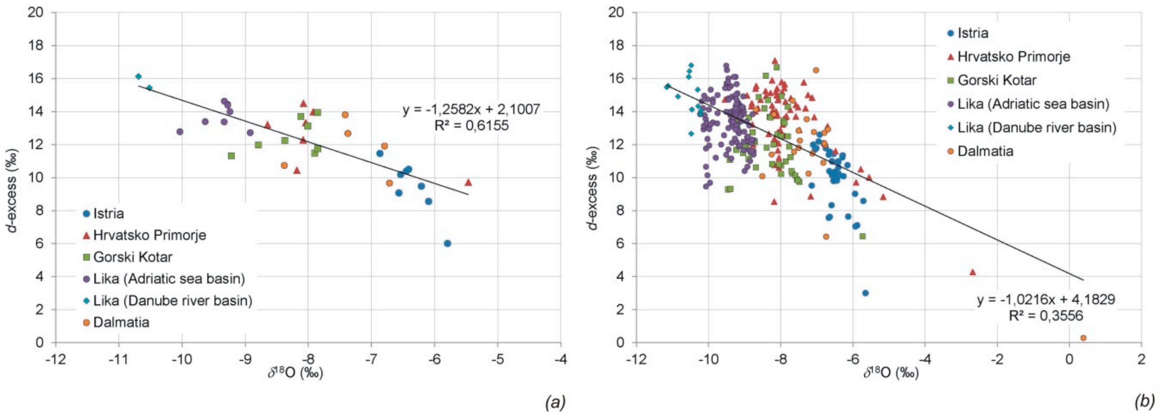

Figure 5. Linear relationship between δ^{18}O and *d*-excess of karst groundwater: (**a**) the mean values and (**b**) the single values.

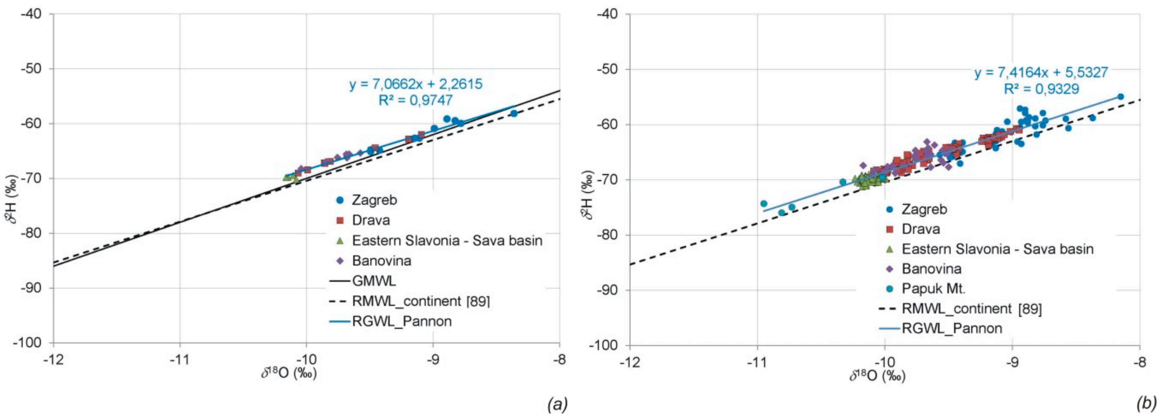

Figure 6. The regional meteoric water line of the continental part of Croatia (RMWL_continent) and the stable isotope composition of spring water in the Pannonian part in Croatia: (**a**) the mean values of stable isotopes and (**b**) the single values of stable isotopes.

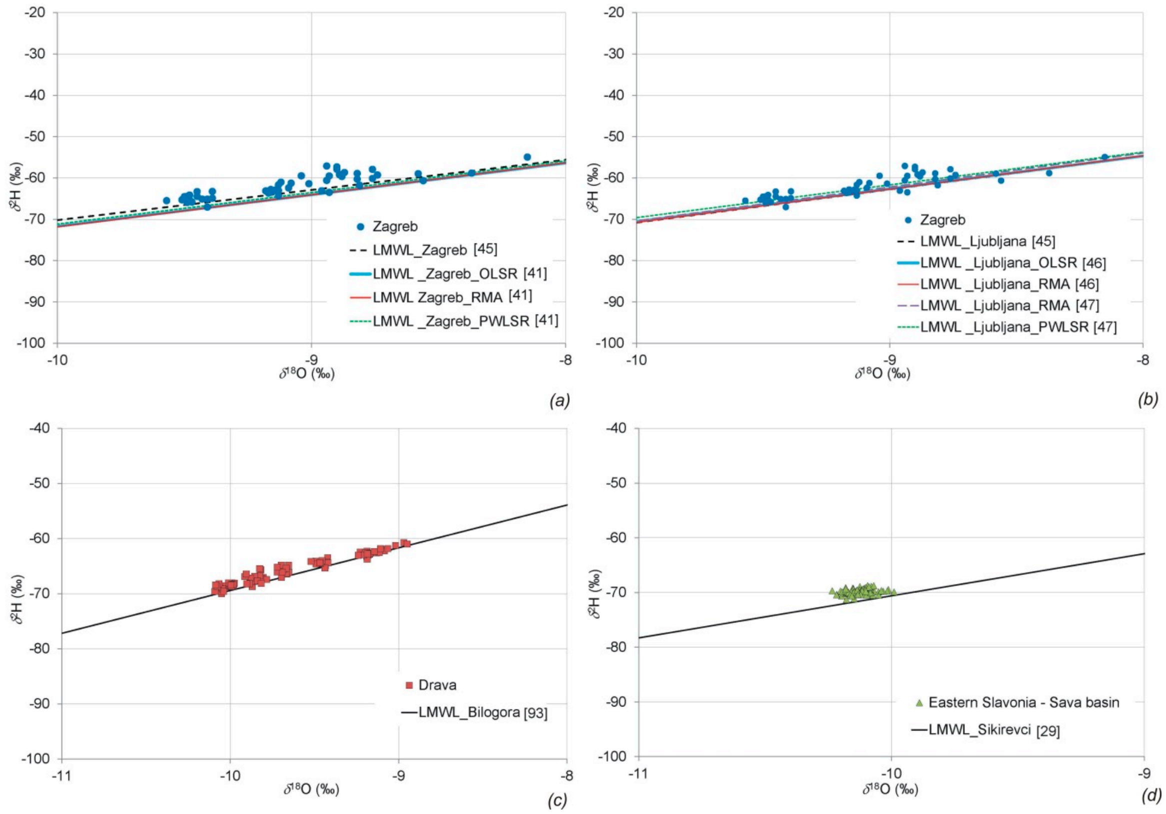

Figure 7. LMWLs and the single stable isotope composition of groundwater in the Pannonian part of Croatia: (**a**) groundwater in the Zagreb aquifer and LMWL Zagreb, (**b**) groundwater in the Zagreb aquifer and LMWL Ljubljana, (**c**) the Drava Basin, and (**d**) Eastern Slavonia—the Sava basin.

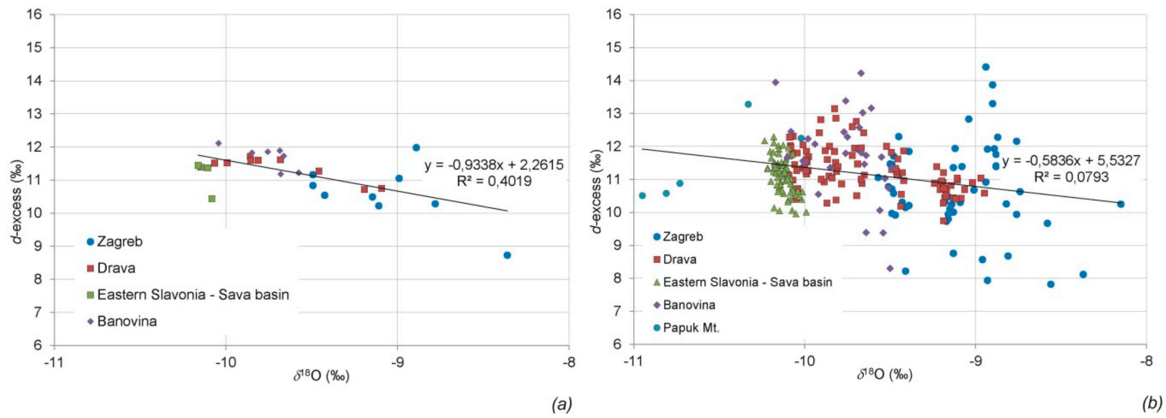

Figure 8. Relationship between δ^{18}O and *d*-excess in the analysed groundwater in the Pannonian part of Croatia: (**a**) the mean values and (**b**) the single values.

The karst area of Croatia is mainly composed of carbonate rocks of the Mesozoic age. Carbonate rocks, especially limestone, have developed conduit and fissured porosity, which accumulate and transfer a significant amount of groundwater. Besides the existence of numerous geomorphological phenomena, the basic characteristics of the karst area are the absence of surface water, a high velocity of groundwater flow, groundwater discharge at the springs of over ten m^3/s, significant groundwater amounts that discharge into the sea, and the strong impact of the sea on coastal aquifers. There are frequent occurrences here of karst poljes with springs on one side and ponors on the other; this sometimes also means that the same water sinks and reappears multiple times on several levels [poljes] before it reaches the final erosion base [53–55]. The altitudes of these areas vary from approximately 1900 m a.s.l. in the high mountains to 0 m a.s.l. at the coast.

Croatia is divided into two main climate regions—Continental and Mediterranean—with some variations within those climate zones [56]. According to Köppen's classification, most of Croatia has a moderately warm rainy climate (C), whereas only the highest mountain areas have a snow-forest climate (D). The Dalmatian coast and islands have a Mediterranean climate (Cs), while in other parts of Croatia there are different types of moderately warm and humid climates (Cf) which differ according to the warmth of summer months (hot, warm or fresh summers) and annual precipitation. The lowest mean annual air temperature occurs at the highest mountains and reaches 2–3 °C. In the lowlands of northern Croatia, the average air temperature is around 11 °C, while in the Adriatic area, it ranges from 13 °C in the north to 17 °C in the far south. Summer is the driest season along the coast, and winter is the rainiest season, with twice the amount of precipitation as in the summer. The continental part of Croatia has a different climate. The mean annual precipitation in Croatia ranges from about 300 mm to just above 3500 mm. The majority of precipitation is caused by south-western and western air circulation (cyclogenetic area of the Mediterranean), while a significantly smaller amount of precipitation is caused by relatively dry air masses coming from the northeast. The lowest annual precipitation, approximately 300 mm, can be found on the outer islands of the southern Adriatic. On the islands and coasts of central and northern Dalmatia and on the western coast of Istria, about 800 to 900 mm of precipitation can be expected. In continental Croatia, the mean annual precipitation decreases from west to east. In the western part (wider Zagreb area), it ranges from 1000 to 1500 mm, while in Eastern Slavonia, the mean annual precipitation reaches only 600 to 700 mm. Due to orographic influence, the greatest amount of precipitation can be found along the Dinaric Mountain Range, which extends from NW to SE, separating the coastal area from continental Croatia. In this area, the mean annual precipitation reaches 3000 to 3500 mm. The karst aquifers formed below this massif drain towards both regional basins, the Adriatic Sea basin in the south and the Danube basin in the north.

The hydrogeological structures, relief indents, and different climatological influences result in different isotopic signatures of the groundwater in Croatian regions.

2.2. Data and Methods

The first step in analysing the isotopic composition of groundwater was to collect as much measured data as possible. For this study, the data sources were mainly the HGI-CGS database, unpublished reports, and published articles. Groundwater samples for the analysis of stable isotopes and tritium in groundwater were collected in different periods from 1997 to 2014 (Tables 1 and 2).

The stable isotope compositions were analysed at the Jožef Stefan Institute (Ljubljana, Slovenia) from 1997 to 1999. They were measured on a Varian MAT 250 mass spectrometer [46]. From 2001 to 2005, the measurements were conducted at Joanneum Research (Graz, Austria). An isotope ratio mass spectrometer (IRMS) was used for the measurements. The stable isotope composition of the water from 2005 to 2014 was determined at SILab [Stable Isotope Laboratory at the Physics Department, School of Medicine, University of Rijeka, Rijeka, Croatia]. An HDO Equilibration Unit (ISO Cal, Phoenix, AZ, USA) attached to the dual inlet port of a DeltaPlusXP (Thermo Finnigan, Waltham, MA, SAD) IRMS was used [23].

The results of the stable isotope composition are expressed as the δ-values per mill (‰) relative to the standard: $\delta_{S/R} = (R_{Sample}/R_{Reference}) - 1$ [14,57–59]. R_{Sample} and $R_{Reference}$ mark the isotope ratio ($R = {}^{2}H/{}^{1}H$ and $R = {}^{18}O/{}^{16}O$) in the sample. The analytical precision of the determined δ-values was better than ±0.1‰ for $\delta^{18}O$ and ±1‰ for $\delta^{2}H$.

Tritium activity concentrations were mostly analysed at the Department of Experimental Physics of the Ruđer Bošković Institute (RBI) in Zagreb. The gas proportional counting (GPC) technique was used until 2007 [60,61]. Since 2010, samples have been measured only using the liquid scintillation counting technique following electrolytic enrichment (LSC-EE), while during 2008 and 2009, both techniques were used [47,62–65]. The GPC technique was replaced by the LSC-EE technique for the following reasons: (i) the tritium activity approached natural pre-bomb levels (<5–10 TU), so the measurement of samples without tritium enrichment was not sufficiently precise and (ii) the GPC technique did not satisfy the requirements for a low detection limit and a high throughput of samples. In the RBI reports from 1997 to 1999, the results were expressed in Bq/L and later in TU and Bq/L. The detection limit was 2.5 TU, and the measurement uncertainty was between 2 and 5 TU, depending on the activity concentration [41]. The tritium activity concentrations in some samples collected from 2005 to 2008 were determined at the Isotope Hydrology Section Laboratory at the IAEA [26]. Tritium activity concentrations in the samples collected in 2013 and 2014 were measured at Hydrosys Labor Ltd. in Budapest, Hungary. The analytical method was based on the MSZ 19387:1987 standard. The results are expressed in TU.

For locations featuring a large amount of measured data, the descriptive statistics of stable isotopes and tritium activity concentrations (minimum and maximum values, arithmetic mean, and standard deviation) were used to describe the isotopic data of groundwater variability in the territory of Croatia. In several locations, there was only one measured datum, which was also used in the analysis. Data divided into two categories were used to create the attached diagrams. The term "mean values" is used when the displayed values represent the calculated arithmetic mean of all values measured so far at a particular measuring point. Individual results of all performed measurements were used on diagrams made based on "single values". The first step in the analysis was to compare the δ^2H and δ^{18}O isotopic compositions of groundwater for each site considering the global meteoric water line (GMWL), as well as the local meteoric water lines (LMWLs).

If δ^2H is plotted versus δ^{18}O, the data group form a linear trend line, which can be described by its slope and intercept. The global meteoric water line (GMWL) defines the general relation between δ^2H and δ^{18}O in the precipitation on a global scale and is described by $\delta^2H = 8 \times \delta^{18}O + 10$ [83–85]. For regional and local areas, the slope and intercept can differ from the GMWL, so for hydrogeological research, the regional/local meteorological water line (RMWL/LMWL) can be more appropriate. A comparison of RMWL/LMWL with GMWL shows local deviations from the world average. A direction coefficient (slope) of LMWL with a value greater than 8 indicates multiple moisture circulation, whereas a direction coefficient of less than 8 indicates greater moisture loss through evaporation [86].

There are different ways to calculate slope and intercept. Ordinary least squares regression (OLSR) is most commonly used for this purpose. Recently, reduced major axis (RMA) regression has been used. These methods do not, however, take into account the amount of precipitation. A new precipitation weighted least square regression (PWLSR) method and precipitation-weighted regressions (PWRMA) method have been applied more recently [87,88]. In this paper, the regional meteoric water lines (RMWL) for the continental and coastal parts of Croatia [89] are used alongside other published LMWLs [20,26,27,41,45–47,90–93] (Table 3).

Table 1. Information on the measurement points in the Pannonian part of Croatia. Legend: measurement point type (OW—observation well, S—spring), lithology (G—gravel, S—sand, L—limestone; D—dolomite).

Sampling Location	Measurement Point Type	Longitude (°)	Latitude (°)	Z (m a.s.l.)	Screen Bottom (m a.s.l.)	Lithology	Geographical Area	Sampling Time	Number of Stable Isotope Samples	Number of ^{3}H Samples	Data Source
ČDP-9/1	OW	16.07	45.76	107.75	31.8	G	western part of the Sava basin (Zagreb area)	2001–2003	7	7	[28,66]
ČDP-9/2	OW	16.07	45.76	107.75	62.8	G		2001–2003	7	7	[28,66]
ČDP-9/3	OW	16.07	45.76	107.75	88.8	G		2001–2003	7	7	[28,66]
ČDP-23/1	OW	16.13	45.75	103.79	18.8	G		2001–2003	7	7	[28,66]
ČDP-23/2	OW	16.13	45.75	103.79	47.8	G		2001–2003	7	7	[28,66]
ČDP-23/3	OW	16.13	45.75	103.79	86.2	G		2001–2003	7	7	[28,66]
PP-18/20	OW	16.04	45.77	108.25	87.8	G		2001–2003	7	3	[28,66]
PP-18/40	OW	16.04	45.77	108.25	67.9	G		2001–2003	7	3	[28,66]
PP-18/90	OW	16.04	45.77	108.25	19.3	G		2001–2003	7	3	[28,66]
JP-10	OW	16.04	45.77	107.88	70.1	G		2001–2003	7	4	[28,66]
SPB-J	OW	17.06	45.93	175.00	79.0	G, S	Bilogora Mt.	2013	1	2	[66,67]
GR-1D	OW	16.75	46.21	143.04	99.1	G	western part of the Drava basin	2013–2014	7		[66,68]
KP-12A	OW	16.85	46.14	138.50	115.5	G		2013–2014	11	2	[66,68]
KP-12	OW	16.85	46.14	138.00	49.0	G		2013–2014	12	2	[66,68]
SO-1	OW	16.95	46.10	126.00	112.0	G, S		2013–2014	12	2	[66,68]
O-6	OW	16.95	46.10	126.00	54.0	G, S		2013–2014	12		[66,68]
VIRJE	OW	17.01	46.06	125.00	115.0	G, S		2013–2014	12		[66,68]
SPB-8	OW	17.05	46.06	117.50	49.5	G, S		2013–2014	11	2	[66,68]
SPB-10	OW	17.03	46.05	126.50	62.5	G, S		2013–2014	7		[66,68]
ĐN-3	OW	17.08	45.98	141.00	92.7	G, S		2013–2014	7		[66,68]
SPB-4	OW	18.47	45.13	83.00	16.3	G, S	Eastern Slavonia—Sava basin	2012–2013	17		[29,66]
SPB-7	OW	18.45	45.10	85.50	16.2	G, S		2012–2013	17	1	[29,66]
SPB-9	OW	18.45	45.10	85.00	9.5	G, S		2012–2013	17	1	[29,66]
V-13	OW	18.48	45.07	87.00	55.8	G, S		2012–2013	17	1	[29,66]
SPBPv	OW	16.44	45.27	182.70		L		2006–2007	4	1	[66,69]
B-1	OW	16.42	45.29	178.60		L		2006–2007	4	1	[66,69]
B-2	OW	16.42	45.29	178.60		L		2006–2007	4	1	[66,69]
B-3	OW	16.42	45.29	178.60	145.6	L	Banovina	2006–2007	4	1	[66,69]

Table 1. *Cont.*

Sampling Location	Measurement Point Type	Longitude (°)	Latitude (°)	Z (m a.s.l.)	Screen Bottom (m a.s.l.)	Lithology	Geographical Area	Sampling Time	Number of Stable Isotope Samples	Number of ^{3}H Samples	Data Source
Bojanića vrelo	S	16.43	45.29			L		2006–2007	4	1	[66,69]
Grabovac	S	16.41	45.28			L		2006–2007	4	1	[66,69]
Pašino vrelo	S	16.43	45.29			L		2006–2007	4	1	[66,69]
Veličanka	S	17,64	45,50	512.00		D	Papuk Mt.	2002	1	1	[66,70]
Dubočanka	S	17.68	45.50	490.00		D		2002	1	3	[66,70,71]
Tisovac I	S	17.69	45.50	495.00		D		2002, 2013	1	3	[66,70,71]
Tisovac II	S	17.69	45.50	487.00		D		2002, 2013	1	3	[66,70,71]
Tisovac III	S	17.68	45.49	465.00		D		2002, 2013	1	3	[66,70,71]
Subthermal spring	S	17.66	45.47	287.00		D		2013		2	[66,71]
LO-1	OW	16.06	46.17	322.00	Open hole to 140 m	D	Ivanščica Mt.	2013		1	[66,72]
LO-4	OW	16.06	46.16	280.00		D		2013		1	[66,72]
LO-5	OW	16.06	46.17	305.00	Open hole to 214–244 m	D		2013		1	[66,72]
Škrabutnik	S	16.08	46.19	447.00		D		2013		1	[66,72]

Table 2. Information on the measurement points in the karst part of Croatia. Legend: measurement point type (OW—observation well, S—spring, M—mine).

Sample ID	Measurement Point Type	Longitude (°)	Latitude (°)	Z (m a.s.l.)	Geographical Area	Sampling Time	Number of Stable Isotope Samples	Number of ^{3}H Samples	Data Source
Bubić jama	S	14.16	45.14	20.0	Istria	1998	2	2	[66,73]
Bulaž	S	13.89	45.38	18.0		1998, 2001–2003	9	7	[66,73,74]
Fonte Gajo	S	14.07	45.07	5.0		1998	2	2	[66,73]
Gradole	S	13.70	45.34	5.0		1998, 2001–2003	9	7	[66,73,74]
Rakonek	S	14.02	45.09	5.0		1998	2	2	[66,73]
Rudničke vode	M	14.15	45.08	2.0		1998	2	2	[66,73]
Sv. Ivan	S	13.98	45.40	48.0		1998, 2001–2003	9	7	[66,73,74]
Šišan	S	13.92	44.86	49.0		1998	2	2	[66,73]
Funtana	S	13.61	45.18	2.0		1998	1	2	[66,73]
Karpi	S	13.85	44.93	50.0		1998	1	2	[66,73]
Vela Učka	S	14.19	45.30	926.0		1998	2	2	[66,73]
Rječina	S	14.42	45.42	325.0	Hrvatsko Primorje	1997–1998, 2001–2003, 2012–2013	23	12	[12,66,73,74]
Zvir	S	14.45	45.33	5.0		1997–1998, 2001–2003, 2012–2013	23	13	[12,66,73,74]
Kristal	S	14.30	45.33	0.0		2001–2003	7	7	[66,74]
Novljanska Žrnovnica	S	14.85	45.12	1.5		1997, 1999	6	4	[66,75]
Martinšćica	OW *	14.48	45.32	2.0		1999	5	4	[66,75]
Perilo	OW *	14.54	45.31	1.0		1999	4	4	[66,75]
Čabranka	S	14.64	45.60	552.0		1997–1999, 2001–2003	10	10	[66,74,76]
Kupa	S	14.69	45.49	320.0		1997–1999	5	5	[66,76]
Kupica	S	14.85	45.43	250.0		1997–1999	5	5	[66,76]
Kupari	S	14.70	45.50	310.0		1997–1999	5	5	[66,76]
Mala Belica	S	14.80	45.46	290.0		1997–1999	5	5	[66,76]

Table 2. *Cont.*

Sample ID	Measurement Point Type	Longitude (°)	Latitude (°)	Z (m a.s.l.)	Geographical Area	Sampling Time	Number of Stable Isotope Samples	Number of ^{3}H Samples	Data Source
Velika Belica	S	14.76	45.48	290.0	Gorski Kotar	1997–1998	4	4	[66,76]
Zeleni vir	S	14.90	45.42	350.0		1997–1999	5	5	[66,76]
Gerovčica spring	S	14.68	45.53	320.0		1997–1999	5	5	[66,76]
Gomirje	S	15.13	45.33	377.0		2002	1		[66]
Mala Lešnica	S	14.85	45.44	238.0		2002	1		[66]
Vitunjčica	S	15.14	45.29	349.0		2002	1		[66]
Kamačnik	S	15.06	45.35	415.0		2002	1		[66]
Majerovo vrelo	S	15.36	44.81	462.0	Lika (Adriatic Sea basin)	1996, 2005–2008	28	21	[26,66,77]
Tonkovića vrelo	S	15.37	44.79	457.0		1996, 2005–2008	27	18	[26,66,77]
Pećina	S	15.33	44.80	456.0		1996, 2005–2008	29	21	[26,66,77]
Klanjac	S	15.37	44.79	458.0		2005, 2008	14		[26,66]
Grab	S	15.32	44.85	454.0		2008	10		[26,66]
Jaz	S	15.32	44.81	456.0		2005, 2008	10		[26,66]
Knjapovac	S	15.36	44.79	459.0		2005–2006, 2008	13		[26,66]
Marusino vrelo	S	15.32	44.81	456.0		2005–2006, 2008	14		[26,66]
Korenička Rijeka spring	S	15.65	44.78	695.0	Lika (Danube River basin)	2006	1	1	[66,78]
Kameniti vrelac	S	15.66	44.77	690.0		2006	1	1	[66,78]
Koreničko vrelo	S	15.67	44.77	700.0		2006	1	1	[66,78]
Makarevo vrelo	S	15.66	44.78	695.0		2006	1	1	[66,78]
Mlinac	S	15.66	44.78	700.0		2006	1	1	[66,78]
Stipinovac	S	15.46	44.97	696.0		2006	1	1	[66,78]

Table 2. *Cont.*

Sample ID	Measurement Point Type	Longitude (°)	Latitude (°)	Z (m a.s.l.)	Geographical Area	Sampling Time	Number of Stable Isotope Samples	Number of ^{3}H Samples	Data Source
Malo vrelo Ličke Jesenice	S	15.44	44.97	481.0		2007–2008	3	3	[66,79]
Veliko vrelo Ličke Jesenice	S	15.46	44.97	479.0		2007–2008	3	3	[66,79]
Vrilo Velebita	S	15.54	44.26	0.0	Dalmatia	1999	1		[66,80]
Vrulja Modrič	S	15.54	44.26	0.0		1999	1		[66,80]
Jadro	S	16.52	43.54	40.0		2001	4	4	[66,81]
Žrnovica	S	16.57	43.52	90.0		2001	4	4	[66,81]
B-22A	OW	16.71	43.58	335.0		2001	4	4	[66,81]
Krka	S	16.24	44.04	225.0		2001	1	1	[66,82]
Lopuško vrelo	S	16.22	44.02	230.0		2001	1	1	[66,82]
Kosovčica spring	S	16.25	43.94	250.0		2001	1	1	[66,82]
Modro oko	S	17.51	43.06	1.5		2005	2		[66]
Opačac	S	17.18	43.45	266.2		2005	2		[66]

* group of observation wells.

Table 3. Local meteoric water lines (LMWLs) used in this paper.

Name of RMWL/LMWL in This Paper	Station (Altitude m a.s.l.)	Observation Period	$\delta^2H/\delta^{18}O$ Correlation Equation	R or rmSSE *	N	Data Source
RMWL_continent	Bilogora (202), Zagreb (158), Sirač (161), Plitvička jezera (580), Sikirevci (82), Veliki Grđevac (148), Medicinska škola Varaždin (173), Sokolovac (207), Jastrebarsko (152), Duga Resa (130), Virovitica (122), Slavonski Brod (92), Bedekovčina (160), Sošice (560), Pogana jama (980), Grdanjci (185) i Karlovac (126)	2008–2013	$\delta^2H = (7.4 \pm 0.005) \times \delta^{18}O + (4.1 \pm 0.5)$	0.99	524	[89]
RMWL_coast	Labin (263), Vežica (219), Zadar (2), Opatija (0), Kastav (333), Rijeka_Medicinski fakultet (12), Kukuljanovo (281), Ponikve (20), Ičići (1), Vrh, Pehlin (278), Jadranovo (0), Kraj (72), Mali Lošinj (1.9), Zadar GNIP (5), Komiža-Vis GNIP (6), Dubrovnik GNIP (52), Split (42) i Murter (16.6)	2008–2013	$\delta^2H = (7.0 \pm 0.08) \times \delta^{18}O + (4.4 \pm 0.5)$	0.96	655	[89]
LMWL_Portorož	Portorož—Airport (2)	2001–2003	$\delta^2H = (7.7 \pm 0.4) \times \delta^{18}O + (7.3 \pm 2.2)$	0.96	35	[45]
LMWL_Portorož_OLSR	Portorož—Airport (2)	2000–2006	$\delta^2H = (7.82 \pm 0.23) \times \delta^{18}O + (7.84 \pm 1.57)$	0.97	74	[91]
LMWL_Portorož_RMA	Portorož—Airport (2)	2000–2006	$\delta^2H = (8.05 \pm 0.22) \times \delta^{18}O + (9.35 \pm 1.55)$	0.97	74	[91]
LMWL_Portorož_PWLSR	Portorož—Airport (2)	2007–2010	$\delta^2H = (7.8 \pm 0.27) \times \delta^{18}O + (8.52 \pm 1.85)$	0.96	71	[92]
LMWL_Hrvatsko Primorje	Kukuljanovo (281), Pehlin (278), Škalnica (526), Gumance (688), Ilirska Bistrica (1043), Snežnik (1300)	2010–2012	$\delta^2H = (8.2 \pm 0.1) \times \delta^{18}O + (14.0 \pm 1)$	0.98	88	[25]
LMWL_Zavižan	Zavižan—Velebit Mt. (1594)	2001–2003	$\delta^2H = (7.6 \pm 0.4) \times \delta^{18}O + (10.5 \pm 4.0)$	0.95	35	[45]
LMWL_Gacka	Ličko Lešće (457), Gospić (656)	2005–2006	$\delta^2H = 6.8 \times \delta^{18}O + 1.5$			[23]
LMWL_Ljubljana	Ljubljana (299)	2001–2003	$\delta^2H = (8.0 \pm 0.2) \times \delta^{18}O + (9.2 \pm 1.8)$	0.99	36	[45]
LMWL_Ljubljana (Bežigrad)_OLSR	Ljubljana (299)	1981–2006	$\delta^2H = (7.95 \pm 0.08) \times \delta^{18}O + (8.9 \pm 0.71)$	0.99	290	[46]

Table 3. *Cont.*

Name of RMWL/LMWL in This Paper	Station (Altitude m a.s.l.)	Observation Period	$\delta^2H/\delta^{18}O$ Correlation Equation	R or rmSSE *	N	Data Source
LMWL_Ljubljana (Bežigrad)_RMA	Ljubljana (299)	1981–2006	$\delta^2H = (8.06 \pm 0.08) \times \delta^{18}O + (9.84 \pm 0.71)$	0.99	290	[46]
LMWL_Ljubljana (Reaktor)_RMA	Ljubljana	2007–2010	$\delta^2H = (8.19 \pm 0.22) \times \delta^{18}O + (11.52 \pm 1.97)$	0.98	46	[47]
LMWL_Ljubljana (Bežigrad)_PWLSR	Ljubljana (299)	2007–2010	$\delta^2H = (7.94 \pm 0.21) \times \delta^{18}O + (9.76 \pm 1.91)$	0.99	46	[47]
LMWL_Zagreb	Zagreb (157)	2001–2003	$\delta^2H = (7.3 \pm 0.2) \times \delta^{18}O + (2.8 \pm 1.8)$	0.99	34	[45]
LMWL_Zagreb_OLSR *	Zagreb (157)	1980–2018	$\delta^2H = (7.65 \pm 0.06) \times \delta^{18}O + (4.79 \pm 0.55)$	1.0047	389	[41]
LMWL_Zagreb_RMA *	Zagreb (157)	1980–2018	$\delta^2H = (7.74 \pm 0.06) \times \delta^{18}O + (5.57 \pm 0.55)$	1.0019	389	[41]
LMWL_Zagreb_PWLSR *	Zagreb (157)	1980–2018	$\delta^2H = (7.64 \pm 0.06) \times \delta^{18}O + (5.24 \pm 0.54)$	1.00	389	[41]
LMWL_Bilogora	Bilogora (202)	2010–2013	$\delta^2H = 7.75 \times \delta\ ^{18}O + 8.11$	0.99	19	[93]
LMWL_Sikirevci	Sikirevci (85)	2012–2014	$\delta^2H = 7.69 \times \delta^{18}O + 6.29$	0.99	21	[29]

* rmSSE: average of the root mean square sum of squared errors [85].

Most LMWLs are defined by the least squares regression method; the exceptions are the LMWLs for Ljubljana and Portorož [47,91,92] and Zagreb [41]. Previous studies of different approaches to calculate the LMWL have led to the conclusion that all regression lines have similar values for both the slope and the intercept [41,47,91,92]. This indicates that the LMWLs defined by the OLSR method can be used for comparisons with the measured isotopic composition of groundwater in Croatian regions. The absence of a significant difference between the PWLSR slope and both the OLSR and RMA slopes indicates a relatively homogeneous distribution of monthly rainfall, as well as little small monthly rainfall with a minor excess of deuterium [41,88].

Deuterium excess (*d*-excess) is defined as d (‰) = $\delta^2H - 8 \times \delta^{18}O$ [83]. This is an isotope parameter that indicates the deviation of local samples from the GMWL and is an indicator of climate sensitivity at the source of humidity, as well as along the trajectory of air masses into the atmosphere [94]. In other words, *d*-excess reflects the prevailing conditions during the evolution and interaction or mixing of air masses en route to the precipitation site [86].

Tritium activity concentrations in the groundwater samples were used to estimate an approximate mean groundwater age (MRT). The qualitative interpretations in this study are made as follows [9]: <0.8 TU indicates sub-modern water (recharged prior to 1950s), 0.8 to ≈ 4 TU indicates a mix of sub-modern and modern water, 5 to 15 TU indicates modern water, 15–30 TU indicates some "bomb" tritium, and >30 TU indicates that a recharge occurred in the 1960s to 1970s.

3. Results and Discussion

The statistical isotopic data of groundwater samples from the observation wells and springs are presented in Tables S1a, S2a, S3a and S4a. On the sampling sites where the composition of stable isotopes was measured only once, groundwater isotopic data are shown in Tables S1b, S2b, S3b and S4b. The tables can be found in Supplementary Files.

3.1. Stable Isotope Composition of Groundwater in the Karst Area of Croatia

The mean $\delta^{18}O$ values in the drinking karst groundwater range from −10.9‰ to −5.5‰. Similarly, the lowest mean δ^2H was −71.9‰, and the highest δ^2H was −34.0‰ (Table S1a, Figure 2a). The most positive δ-values were measured in the spring below the sea surface (submarine spring, vrulja Modrič), reflecting the influence of sea water (Figure 2b). A slightly more negative value of stable isotopes was measured in the groundwater sample of the coastal spring Kristal in the summer of 2001 (Figure 2b). Since the sampling was done in summer, during the dry season, the influence of the sea was very pronounced, as observed by the isotopic composition of the groundwater. The $\delta^{18}O/\delta^2H$ values for all karst springs are distributed along the regional meteoric water line of the coastal part of Croatia (RMWL_cost in Table 3) and indicate a meteoric origin. This also applies to springs belonging to the Danube River basin that are approximately 50 km away from the sea. Consequently, most precipitation that exerts an influence on groundwater recharge in the karst area comes from the precipitation supplied by the south wind in the direction of the Adriatic sea (more often in the cold than in the warm part of the year).

A comparison of RMWL with GMWL shows local deviations from the world average. The slope of RMWL_coast has a value less than 8 (Table 3), indicating greater moisture losses through evaporation. Evaporation moisture losses occur due to low rainfall, during very hot summers, or for both reasons simultaneously [95], which is characteristic of this part of Croatia.

The $\delta^{18}O/\delta^2H$ values form the regional karst groundwater line (RGWL_karst), which is described by following equations—$\delta^2H = 6.8 \times \delta^{18}O + 2.5$ (n = 38, R^2 = 0.98), for the mean values of the stable isotopes (Figure 2a), and $\delta^2H = 7.0 \times \delta^{18}O + 4.2$ (n = 340, R^2 = 0.96), for the single values of the stable isotopes (Figure 2b). Both lines have very similar slopes and intercepts to RMWL_coast.

Depending on their affiliation with their geographic areas, individual groups of springs are clearly located along the RMWL_coast. However, some spring groups fit better with LMWLs. The single values of stable isotopes of karst groundwater from Figure 2b and LMWLs are shown in Figure 3.

Figure 3a shows the isotopic composition of the spring water in Istria and the LMWLs defined by Vreča et al. [45,91,92] (Table 3). The $\delta^{18}O/\delta^{2}H$ data of the spring water fit very well with the LMWLs determined by the isotopic precipitation composition in Portorož, Slovenia. This is unsurprising, since Portorož is less than 50 km away from central Istria and climatically belongs to the same area. The figure shows several LMWLs that are determined using different methods. All regression lines have similar values (within uncertainties) for both the slope and the intercept values [92]. The slopes of LMWLs obtained using data for the period 2007–2010 and the PWLSR method are close to those of the LMWLs using the OLSR and RMA method for the periods of 2001–2003 and 2000–2006.

The majority of the springs that belong to the Gorski Kotar (Kupica, Mala Belica, Gerovčica, Vela Učka, Zvir, Velika Belica, Kupa, and Kupari) in the Danube River basin and Hrvatsko Primorje (Vela Učka, Rječina, Zvir Perilo, and Martinščica) in the Adriatic Sea basin (Table 2) are situated in the zone between approximately $\delta^{18}O$ = −8.6‰ and $\delta^{18}O$ = −7.9‰, as well as $\delta^{2}H$ = −55.9‰ and $\delta^{2}H$ = −48.9‰ (Figure 3b). Although some of these springs are located along the coast (Zvir, Perilo, and Martinscica) and some at several hundred meters above sea level (Rječina, Vela Učka, Kupica, Mala Belica, Gerovčica, Velika Belica, Kupa, and Kupari), their $\delta^{18}O$ values have small variations. Their isotopic compositions are mainly influenced by the climatic conditions in the recharge area of the aquifer, which are approximately the same (found in close proximity to one another) for the considered springs.

The mean residence time (MRT) of groundwater was calculated for the stable isotope $\delta^{18}O$ using the lumped parameter approach and applying the exponential model, the combined exponential-piston model, and the dispersion model to the isotopic input (rainfall) and output (spring) datasets during 2011–2013 [12]. The MRTs of 3.24 and 3.6 months for the Rječina spring and 7.2 months for the Zvir spring suggest the presence of recent groundwater recharge from precipitation, as well as fast groundwater flow. The cumulative age distributions show that the proportion of water younger than 1xMRT at both springs was more than 50% and that the proportion of water younger than 2xMRT was almost 90%.

The high mean δ-values $\delta^{18}O$ = −5.9‰ to −5.2‰ and $\delta^{2}H$ = −37.6‰ to −32.5‰ in Hrvatsko Primorje refer to the coastal spring Kristal in Opatija (Figures 1 and 3b). The water is brackish, and during low water hydrological conditions, the proportion of seawater is considerable, which is reflected in the composition of the stable isotopes in the water.

Figure 3c shows the isotopic composition of the spring water in Gorski Kotar and Lika, as well as the LMWLs defined by Vreča et al. [45] and Mandić et al. [23] (Table 3). The figure clearly shows that the LMWL defined by Mandic et al. [23] fits well with groundwater samples at all Lika springs and at the springs located in the eastern part of Gorski Kotar. At the same time, LMWL_Zavižan [45] fits better with the springs in the westernmost part of Gorski Kotar, whose recharge area is situated at a high altitude, as well as the Zavižan.

The lowest δ-values were recorded on the springs that belong to the Lika area in the Danube River basin (Table 2, Figure 3c). Although these springs are located in the Danube River basin, it is evident that aquifer recharge is carried out by precipitation, which is influenced by the Mediterranean air mass. In this area (but east of Malo vrelo Ličke Jesenice and Veliko vrelo Ličke Jesenice), the composition of the stable isotopes was once measured at six springs (Koreničká Rijeka spring, Kameniti vrelac, Koreničko vrelo, Makarevo vrelo, and Mlinac i Stipinovac) in the Una river basin (Table 2, Figure 1). The measured $\delta^{18}O$ values were in the range of −10.9‰ to −10.2‰ and −71.9‰ to −67.1‰ for $\delta^{2}H$ (Table S1b), which is very similar to the mean isotopic composition of Malo vrelo Ličke Jesenice and Veliko vrelo Ličke Jesenice.

At the same time, at springs that belong to the Lika area in the Adriatic Sea basin (Majerovo vrelo, Klanjac, Tonkovića vrelo, Grab, Marusino vrelo, Jaz, and Knjapovac—in Table 2), the mean $\delta^{18}O$ values were in the range of −10.2‰ to −8.0‰, as well as −71.0‰ to −50.0‰ for $\delta^{2}H$ (Table S1a). All springs, including those in the Danube River basin and those in the Adriatic Sea basin, are situated at similar altitudes (Table 2), so the differences between the stable isotope compositions of the springs belonging to the Danube River basin and the springs belonging to the Adriatic Sea basin could be caused by the "continental effect", also referred to as the distance-from-coast effect [39]. However, in this case, the distance from the sea is likely not the reason because the differences are very small, (approximately 20 kilometres) (Figure 4). Although the springs are at similar altitudes, the altitudes of their recharge areas are different. Higher altitudes in the catchment area of the springs in the Danube River basin likely have a much greater impact than the distance from the coast. As the altitude of the terrain increases, the δ^{18}O and δ^{2}H in precipitation becomes increasingly more depleted. This effect correlates to air temperature, which drops due to an increase in altitude [39]. The δ^{18}O effect generally varies between −0.1‰ and −0.6‰/100 m of altitude and often decreases with an increase in altitude [96].

The mean δ^{18}O values of spring water in Dalmatia vary between −6.7‰ and −8.7‰ and −40.0‰ and −58.0‰ for δ^{2}H (Figure 3d), which is, according to Kapelj et al. [21], within the range of the stable isotope composition of groundwater in middle Dalmatia. The composition of stable isotopes in groundwater, especially in the spectrum of depleted values, shows similarity to LMWL_Zavižan [45] and thus reflects the influence of the recharge area at high altitudes (e.g., Zavižan—Velebit Mt. 1594 m a.s.l., Dinara Mt. 1830 m a.s.l.). However, the stable isotopes data of measured groundwater define a local groundwater line (LGWL_Dalmatia) that better matches the RMWL_coast (Figure 3d). It is described using equation $\delta^{2}H = 6.6 \times \delta^{18}O + 1.7$ (n = 21, $R^2 = 0.97$). The difference between the slope values of the lines for RGWL_coast and LGWL_Dalmatia is generally about 0.42‰ and between the axis intercept values is about 2.74‰. These differences between LMWL_Zavižan and LGWL_Dalmatia are 1.02‰ for slope values and 8.84‰ for intercept values. Kapelj et al. [21] analysed the mean altitude of the spring catchment areas and found the δ^{18}O gradient to be between −0.2‰ and −0.4‰/100 m, which corresponds to the value of −0.3‰/100 m determined by Vreča et al. [46] using stable isotope data for precipitation at several stations in Croatia and Slovenia, as well as that of Mandić et al. [23], who used stable isotope data for the groundwater at Lika springs Majerovo vrelo, Tonkovic vrelo, and Pećina. Using data on the stable isotopes in precipitation at several stations in the Učka area (Rijeka hinterland), Hunjak [89] determined a δ^{18}O gradient of −0.19‰/100 m. However, these relationships cannot be applied to all springs analysed in this paper because they have different catchment areas that differ in their temperature changes and wind directions, which both significantly affect the composition of stable isotopes in precipitation and thus in groundwater.

The *d*-excess values of karst groundwater were determined to be between 6‰ and 17‰ (Table S1, Figure 5). *d*-values lower than 6‰ were found in three individual samples (coastal Kristal spring, vrulja Modrič, and Šišan spring in Istria), which are under the influence of sea water. In many cases, *d*-excess is found to increase with altitude [39,45]. Atlantic air masses typically have *d*-excess values around 10‰, while Mediterranean air masses are characterized by higher *d*-excess values of approximately 12‰ [14]. The catchment areas of the springs in Lika, Gorski Kotar, and Hrvatsko Primorje are at relatively high altitudes, and due to the influence of high altitudes and Mediterranean air masses, their *d*-excess values are high and reach 17‰ (Figure 5b). The lowest *d*-excess values are determined in springs in Istria whose catchment areas are at relatively low altitudes and are partly affected by Atlantic air masses.

3.2. Stable Isotope Characteristics of Groundwater in the Pannonian Area of Croatia

δ^{18}O values of groundwater ranged from −11.0‰ to −8.2‰ and from −76.0‰ to −57.0‰ for δ^{2}H (Table S2, Figure 6). The lowest δ^{18}O and δ^{2}H values were measured in the spring water on Papuk Mt (Figure 6b). As an increase in altitude leads to depleted isotope values, it is expected that among all the analysed groundwater samples, these springs will have the lowest isotopic values as their recharge areas are situated at the highest altitudes, reaching 825 m a.s.l. The highest values of stable isotopes were measured in groundwater in the Zagreb area where they range from −9.5‰ to −8.2‰ for δ^{18}O and from −65.0‰ to −57.0‰ for δ^{2}H (Figure 6b). The altitude of the groundwater recharge in this area reaches up to 200 m a.s.l. As shown in Figure 6b, the stable isotope values of groundwater samples from Eastern Slavonia—the Sava basin, Banovina, and the Drava River valley—are located between the stable isotope values of groundwater on Papuk Mt. and the Zagreb area. The groundwater recharge areas in the Drava river valley reach approximately 250 m a.s.l. and 290 m a.s.l. in the Banovina area. The catchment area of groundwater captured by observation wells in Eastern Slavonia—the Sava basin—is mostly north of the wells [29], possibly also on the slopes of the Slavonian highlands up to altitudes of about 250 m a.s.l.

The groundwater isotopic values in the Pannonian part of Croatia lie slightly above the RMWL_continent and indicate a meteoric origin (Figure 6). Considering that only a small fraction of precipitation actually reaches groundwater in these types of aquifers, the meteoric signal in groundwater is muted. The regional groundwater line (RGWL_Pannon) is developed from groundwater $\delta^{18}O/\delta^{2}H$ values. It is described by the following equations—$\delta^{2}H = 7.1 \times \delta^{18}O + 2.3$ (n = 30, $R^2 = 0.97$), for the mean values of the stable isotopes (Figure 6a), and $\delta^{2}H = 7.4 \times \delta^{18}O + 5.5$ (n = 255, $R^2 = 0.93$), for the single values of the stable isotopes (Figure 6b).

As in the case of karst groundwater, the groundwater in certain areas in the Pannonian part of Croatia is compared with LMWLs (Figure 7a–d). The single values of stable isotopes of groundwater in the Pannonian part of Croatia from Figure 6b and LWWLs are shown in Figure 7. The isotopic composition of the studied groundwater in the Zagreb area fits better with LMWL_Ljubljana [45–47] than with LMWL_Zagreb [41,45]. This was previously identified by Marković et al. [24], Horvatinčić et al., [27], and Parlov et al. [30]. The different methodologies used to calculate the LMWLs for Ljubljana [45–47] showed slightly better matching of the groundwater isotopic composition with the LMWL determined using the PWLSR method (Figure 7b). Considering that the precipitation weighted least square regression (PWLSR) method takes into account the precipitation amount and that the analysed groundwater is relatively close to the surface of the terrain and to the Sava River (which has an impact on groundwater recharge), the result is unsurprising. The values of the stable isotopes are scattered and show seasonal influence, which points to a relatively short mean residence time of the groundwater in this area. The aquifer is directly exposed to precipitation because there are no covering deposits, as well as to the influence of the Sava River because the observation wells are located in its immediate vicinity. Figure 7c shows the composition of the stable isotopes in the groundwater in the Drava River valley. The LMWL was developed on the basis of the measured values of the stable isotopes on Bilogora Mt. [93], south of the observed wells. The isotopic composition of the groundwater lies slightly above the LMWL_Bilogora. Stable isotopes were analysed over a wide area and at different depths of the aquifer (Table 1), and their values are grouped according to these elements (Figure 7c). The depleted isotope composition is characteristic of groundwater from the deeper parts of the aquifer system and the enriched isotopes are characteristic of the shallower parts of aquifers.

Figure 7d shows the composition of the stable isotopes of groundwater in the aquifer system in Eastern Slavonia—the Sava basin—as well as the LMWL that was made on the basis of the stable isotope values of the precipitation, which were measured in the immediate vicinity of the analysed wells [29]. The stable isotope composition data in groundwater are slightly above the LMWL and are grouped into almost a single point. Since groundwater is accumulated in the aquifer system in which the mean residence time is several decades (as evidenced by ^{3}H activity concentrations), the water is homogenized so that the differences in the stable isotope composition of the precipitation—which recharge the groundwater—completely disappear.

The mean *d*-excess values of groundwater were determined to be between 8.7‰ and 12.1‰ (Table S2, Figure 8a), while the single values range from 7.8‰ to 14.4‰ (Figure 8b). Higher values of *d*-excess are attributed to the influence of Mediterranean precipitating air masses [41,45]. Bottyán et al. [97] estimated that the moisture sources of precipitation in Hungary come from the Mediterranean region (57.0%), local moisture (14.8%), the Atlantic region (14.2%), Northern Europe (7.4%), and Eastern Europe (6.6%). Most of the *d*-excess values in the groundwater samples range from 10‰ to 12‰. This is especially pronounced in the groundwater samples in Eastern Slavonia—the Sava basin—, where the mean residence time of the groundwater is relatively long [29] and, accordingly, the range of *d*-excess values is relatively narrow—i.e., the differences in climatic conditions (the source of humidity and contribution of air masses) during aquifer recharge are muffled in the groundwater samples. Opposite to this, *d*-excess is found in a wide range of values in the analysed groundwater samples in the Zagreb and Banovina area. Since higher values of *d*-excess are characteristic for winter months and lower values for summer months [14,41,45] (as evident in the groundwater samples), it can be concluded that the mean residence time of groundwater is relatively short.

3.3. Tritium Activity in Groundwater

Spatial distribution of an approximate groundwater age estimated by tritium is shown in Figure 9. The mean ^{3}H activity concentrations in the groundwater mostly vary between 4 TU and 10 TU (Tables S3 and S4). In karst aquifers, the ^{3}H activity of the groundwater in the rainy seasons and the mean tritium activity concentrations indicate modern water [9]. For the karst springs Pećina, Majerovo vrelo, and Tonkovića vrelo (areas of the Lika in the Adriatic Sea basin), the groundwater age was estimated using the ^{3}H activity concentration in groundwater and the lumped parameter model [26]. A similar MRT was defined for all three springs and was estimated to be approximately 12 years.

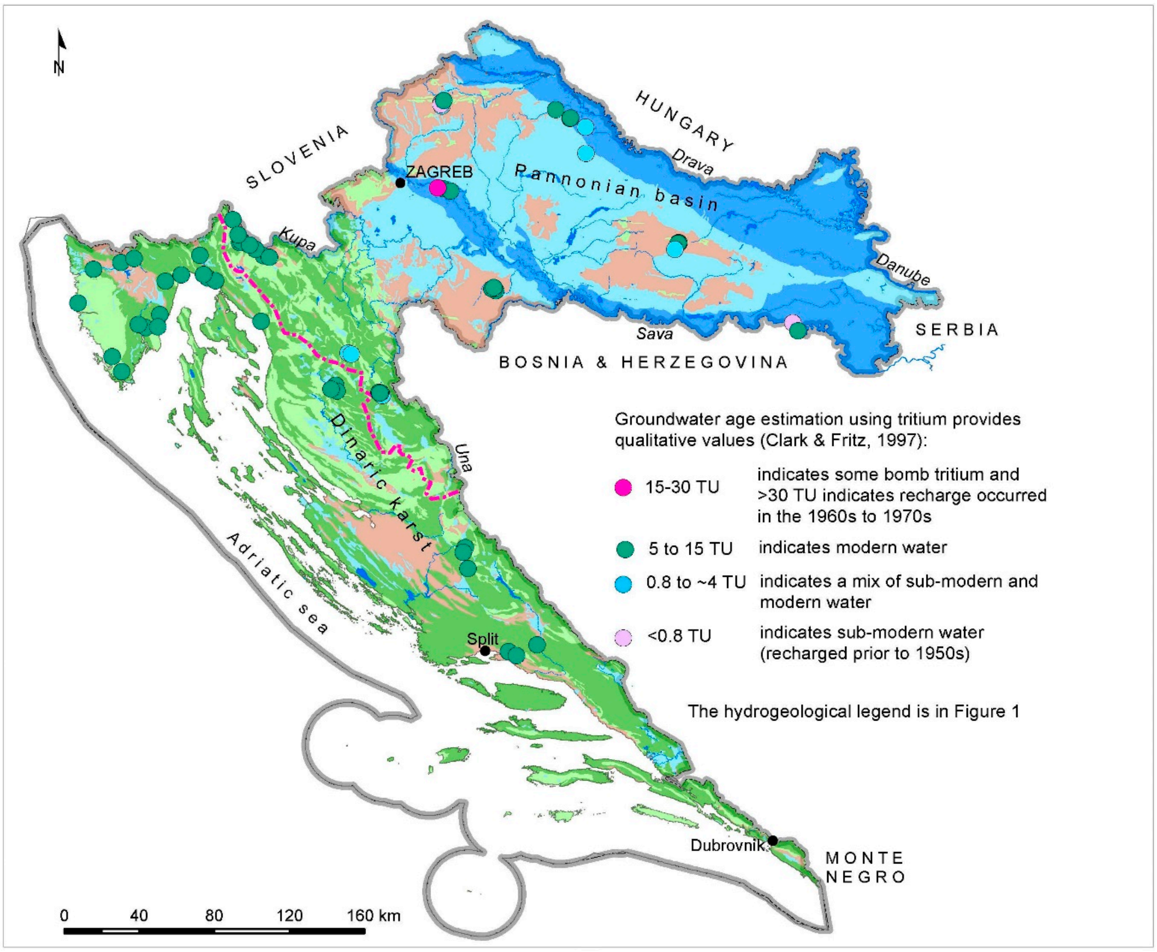

Figure 9. Spatial distribution of an approximate groundwater age using tritium activity.

Modern water is also indicated in the groundwater from alluvial aquifers close to the Sava River (Table S4). The highest ^{3}H activity concentrations were measured in the groundwater in the Zagreb area, as well as in the Sava River, which flows through Zagreb. This result is consistent with the well-known fact that the aquifer is recharged by the Sava River in the Zagreb area [29,52,98,99]. The observation wells are located close to the Sava River. The high ^{3}H activity concentrations in the groundwater samples are explained by the release of tritiated water from Krško Nuclear Power Plant, 30 km upstream from Zagreb [27,100]. This indicates the infiltration of surface water from the Sava

River into the Quaternary alluvial aquifer. Modern water is indicated in the groundwater accumulated in the porous aquifer and observed close to the Sava River in Eastern Slavonia—the Sava basin—during high water periods (Table 2, Figure 9). In the shallow part of the aquifer system in the western part of the Drava basin (Table 1), modern groundwater is also indicated (Table S4).

The values between 0.8 and 4 TU indicate a mix of sub-modern and modern water. These values were measured in the karst aquifers during summer under base flow conditions (Table S3). A mix of sub-modern and modern water is also indicated in the deep porous aquifer of Bilogora Mt. (label 2 in Figure 1), as well as in the deeper part of the alluvial aquifer system in the western part of the Drava basin (Table S4). ^{3}H activity concentrations less than 0.8 TU were measured in the deep alluvial aquifer in Eastern Slavonia as well as in the deep carbonate aquifer on Ivanščica Mt and in the thermal spring on Papuk Mt (Table S4). In Eastern Slavonia—the Sava basin—, but approximately one km away from the Sava river, ^{3}H activity concentrations were measured only once under conditions of high water and accurately reflects the dynamics of groundwater flow in a semi-confined aquifer. Groundwater is recharged north of the sampled observation well and through relatively thick covering deposits, so the mean residence time of groundwater is relatively long [29]. The aquifer is recharged from the Sava River only in its immediate vicinity and only during high water [29], as evidenced by the measurement of tritium activity.

4. Conclusions

This paper presents an analysis of stable isotope data and tritium activity concentrations in Croatian groundwater at approximately 100 sites. Data were collected between 1997 and 2014. The stable isotope composition was compared with different regional and local meteoric water lines. The primary findings of the study are as follows:

- The composition of groundwater stable isotopes in the Pannonian area of Croatia fits well with the regional meteoric water line for the continental portion of Croatia (RMWL_continent), based on which we conclude that RMWL_continent can be accepted for all future research on the composition of stable isotopes in northern Croatia.
- Although the regional meteoric water line for the coastal part of Croatia (RMWL_coast) was developed according to stable isotopic compositions of precipitation, especially at measuring sites located on the Adriatic coast, it is evident that the line fits well with the composition of the stable isotopes of all analysed karst groundwater. Thus, we conclude that the recharge of the karst aquifers is mainly driven by precipitation introduced by winds blowing from the south of the region as shown by the *d*-excess, which has a strong Mediterranean influence.
- The composition of the groundwater stable isotopes in the karst part of Croatia agrees well with RMWL_coast, based on which we conclude that RMWL_coast can be used as an accurate reference for all future research on the composition of stable isotopes in the karstic part of Croatia.
- The composition of stable isotopes in the Pannonian part of Croatia forms a unique regional line of Pannonian groundwater.
- The composition of stable isotopes in the karst part of Croatia forms a unique regional line of karst groundwater.
- This article offers a unique summary of data measured over a long period of time and provides a large picture of the stable isotope data found in Croatia. Especially valuable are the insights into the correspondence between the stable isotope data of precipitation and groundwater through LMWLs and local groundwater lines over a large span of time. The fact that this correspondence is best in the karst area is perhaps not a great surprise (since karst areas are known to have the shortest mean residence time), but that the Mediterranean influence is spreading far beyond mountains of a high altitude and corresponds strongly with isotopic groundwater data are findings that will help in further research.

- According to its isotopic composition, almost all the investigated groundwater used in Croatia for various purposes, primarily as drinking water, is modern water, making such water relatively vulnerable to the potential sources of pollution found in the environment. The groundwater that is accumulated in semi-confined aquifers in eastern Croatia is in a better position, as well as the groundwater in the deep carbonate aquifers in northern Croatia, whose age can reach several decades.
- The number of geographical and temporal data points is very large (approximately 100 groundwater measurement locations and 50 precipitation measurement locations, as well as approximately 1000 measurements of the stable isotopes and tritium activity concentrations in groundwater and more than 1000 measurements of the stable isotopes in precipitation), which is significant for all conclusions made.

The present analysis of data on the isotopic composition of groundwater may be useful for future comparisons with other data in different or identical locations to obtain better knowledge on the isotopic composition of groundwater in Croatia and in nearby countries.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/12/7/1983/s1 and include isotope data in Tables S1–S4.

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