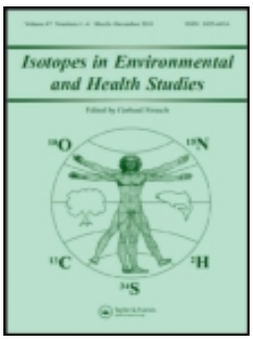

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The isotope altitude effect reflected in groundwater: a case study from Slovenia

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This paper presents the stable isotope data of oxygen (δ^{18}O) and hydrogen (δ^{2}H) in groundwater from 83 sampling locations in Slovenia and their interpretation. The isotopic composition of water was monitored over 3 years (2009–2011), and each location was sampled twice. New findings on the isotopic composition of sampled groundwater are presented, and the data are also compared to past studies regarding the isotopic composition of precipitation, surface water, and groundwater in Slovenia. This study comprises: (1) the general characteristics of the isotopic composition of oxygen and hydrogen in groundwater in Slovenia, (2) the spatial distribution of oxygen isotope composition (δ^{18}O) and d-excess in groundwater, (3) the groundwater isotope altitude effect, (4) the correlation between groundwater d-excess and the recharge area altitude of the sampling location, (5) the relation between hydrogen and oxygen isotopes in groundwater in comparison to the global precipitation isotope data, (6) the groundwater isotope effect of distance from the sea, and (7) the estimated relation between the mean temperature of recharge area and δ^{18}O in groundwater.

Keywords: altitude effect; hydrogen-2; oxygen-18; groundwater; Slovenia; water cycle

1. Introduction

1.1. *Aim of the study*

Despite a large number of routine isotope analyses on individual water sources in Slovenia, there has not yet been comprehensive research into the isotopic characteristics of groundwater, nor has any detailed interpretation of groundwater's isotopic composition, based on its origin, ever been made. This survey covers groundwater sampled in the main aquifer types occurring in Slovenia, which turned out to be very diverse in their chemical and isotopic characteristics. The aim of this study was to observe:

(1) the general characteristics of the stable isotopic composition of oxygen (δ^{18}O) and hydrogen (δ^{2}H) in groundwater in Slovenia,
(2) the spatial distribution of oxygen isotope composition (δ^{18}O) and d-excess in groundwater in Slovenia,
(3) the groundwater isotope altitude effect,
(4) the correlation between groundwater d-excess and the recharge area altitude of the sampling location,

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(5) the relation between hydrogen and oxygen isotopes in groundwater in comparison with the global precipitation isotope data,
(6) the groundwater isotope effect of distance from the sea,
(7) the correlation between the mean annual air temperature of the recharge area and the measured groundwater isotopic composition.

1.2. *Isotopes in the global water cycle*

Stable isotopes, as a result of their conservative behaviour in water and the large variability of their isotope ratios, are powerful tools for studying the global water cycle. The stable isotopes of oxygen and hydrogen (^{18}O and ^{2}H) in water are applied for tracing water in its various stages of migration [1] and are used for identifying recharge areas (source and movement) of groundwater,[2] which reflects the stable isotope content of precipitation. Variations of $\delta^{18}O$ and $\delta^{2}H$ in atmospheric water vapour, which starts from isotope fractionation during evaporation from the ocean and condensates during the formation of rainfall, occur almost exclusively in the atmospheric and the earth's surface part of the water cycle. During those phase changes, i.e. evaporation and condensation of water, the heavy water molecules remain preferentially in, or pass into, the liquid (solid) phase. During infiltration of precipitation below the unsaturated zone, the isotopic composition remains practically unchanged during subsurface movement and storage, except at higher temperatures ($> 60°C$), where isotopic exchange of oxygen with the rock matrix can occur.[3]

Hydrogen isotopes are fractionated proportionally to oxygen isotopes,[2] where the linear relation between $\delta^{18}O$ and $\delta^{2}H$ on the global scale is expressed as the global meteoric water line (GMWL), defined as $\delta^{2}H = 8\delta^{18}O + 10$ (‰).[4] Rozanski et al. [5] and Gourcy et al. [6] reported a refined empirical regression line for the long-term (1961–2000) annual-weighted means of $\delta^{18}O$ and $\delta^{2}H$ values, collected in the Global Network of Isotopes in Precipitation (GNIP), as $\delta^{2}H = (8.07 \pm 0.02)\delta^{18}O + (9.9 \pm 0.01)$. It is known that the ratio between the isotopic composition of oxygen and hydrogen varies locally, owing to differences in climate and geographic characteristics, which are presented as a local meteoric water line (LMWL). Vreča et al. [7] calculated LMWLs for precipitation in Ljubljana: $\delta^{2}H = (8.1 \pm 0.1)\delta^{18}O + (9.8 \pm 0.7)$; Portorož Airport: $\delta^{2}H = (8.05 \pm 0.22)\delta^{18}O + (9.35 \pm 1.55)$ and Kozina: $\delta^{2}H = (7.7 \pm 0.3)\delta^{18}O + (9.6 \pm 0.7)$. In the literature, the nearest LMWLs to Slovenia are: Zagreb, Croatia with $\delta^{2}H = 7.8\delta^{18}O + 5.7$;[8] Northern Italy with $\delta^{2}H = 7.74\delta^{18}O + 9.4$; Central Italy with $\delta^{2}H = 7.0\delta^{18}O + 5.6$; Southern Italy with $\delta^{2}H = 6.94\delta^{18}O + 7.31$;[9] and the Eastern Mediterranean meteoric water line (EMMWL) with $\delta^{2}H = 8\delta^{18}O + 22$.[10] An interpretation of meteoric water lines can help to determine the source of air masses, together with the deuterium excess (d-excess), defined as d-excess $= \delta^{2}H - 8\delta^{18}O$ (‰), according to Dansgaard.[11] The d-excess is believed to be related mainly to the meteorological conditions in the source region from which the sample is derived, i.e. the relative humidity in the atmosphere above the ocean, the wind regime, surface roughness of the ocean, as well as its temperature.[12] In addition, d-excess reflects the prevailing conditions during the evolution and interaction of air masses mixing *en route* to the precipitation site.[13] It is measured from the relative proportions of $\delta^{18}O$ and $\delta^{2}H$ contained in water and can be depicted visually as an index of deviation from the GMWL. Vapour generated over a closed basin with restricted communication such as the Mediterranean Sea is characterised by a higher d-excess value (~ 20 ‰),[10] compared with Atlantic air masses with a lower d-excess value (~ 10 ‰).[13,14]

Dansgaard [11] also observed the geographic distribution in the isotopic composition of precipitation in relation to many environmental parameters, e.g. latitude (latitude effect), altitude (altitude effect), distance from coast (continental effect), the amount of precipitation (amount effect) and surface air temperature (temperature effect). The altitude effect is caused by increasing elevation in mountain regions as a result of the continuous pseudo-adiabatical cooling of the air mass to

below the dew point in an orographic precipitation system where heavier isotopes precipitate preferentially.[2,11,15–17] Hydrological applications of isotopic measurements derive usually from the knowledge of the altitude effect, which is one of the numerous applications of environmental isotope techniques in hydrology often used to calculate the mean altitude of the recharge area of aquifers.[9] The altitude effect is temperature-related, and values of ^{18}O mentioned in the literature vary between -0.1 and -0.6 ‰ $\delta^{18}O/100$ m.[2,18] The continental effect is present when meteoric water evaporates from the sea to the atmosphere, and the vapour masses move inland. Isotopic fractionation occurs in moving air masses, resulting in the depletion of heavy isotopes.[17] Coastal precipitation is isotopically enriched relative to colder, inner continental regions, which receive isotopically depleted precipitation with strong seasonal differences.[2,17] For example, in Irish precipitation over Europe, from the Irish coast to the Ural mountains, an average depletion of 7 ‰ in $\delta^{18}O$ is observed.[1]

1.3. *Stable isotope composition of precipitation in Slovenia*

In Slovenia, the precipitation station at Ljubljana and occasionally a few other stations are included in the GNIP, organised jointly by the Isotope Hydrology Section of the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WHO).[6] The precipitation quantity monitoring programme is performed in the framework of the regular activities of the Slovenian environmental agency, but monitoring of the isotopic composition is not included in the regular monitoring. It has been performed by the Jožef Stefan Institute in Ljubljana at the Ljubljana meteorological station (since 1981), Portorož Airport (since 2000) and Kozina (2000–2003).

Stable isotope composition in precipitation in Slovenia was already the topic of many researchers like Krajcar-Bronić et al.,[19,20] Vreča et al.,[7,8,21–23] Ogrinc et al. [24] and others. The stable isotopic composition of oxygen and hydrogen has been implemented in groundwater studies as well by Doctor et al.,[25,26] Brenčič and Vreča,[27] Brenčič and Poltnig,[28] Ogrinc et al.,[24] Kanduč et al.,[29] Urbanc et al. [30] and others. Calculation of altitude and continental effects for Slovenia with mean values of $\delta^{18}O$ in surface water in Slovenia was conducted by Pirc et al.[31]

2. Study area

2.1. *Geomorphology*

Slovenia, covering around 20,273 km^2, is heterogeneous in its geomorphologic, geological, hydrological and climate characteristics. The country is positioned in contact with four relief units: the Alps, the Dinaric Mountains, the Adriatic Sea basin and the Pannonian basin. Several types of morphology can be found. Plains are formed by accumulation of sediments of major rivers with altitudes ranging up to 400 m. In the mountains of northern Slovenia, peaks and ridges reach up to and above the forest line (above 1700 m a.s.l.), with the highest peak in the Julian Alps (up to 2864 m a.s.l.). The low plateau in southern Slovenia reaches 700 m a.s.l., and the high plateau in southern and northern Slovenia over 1000 m.[32]

2.2. *Geology*

The Slovenian territory has been a site of complex geological processes from the Palaeozoic period to the present, with all main types of rocks present: sedimentary, metamorphic and igneous. By far the most abundant are sedimentary rocks that make up the largest part (around 93 %) of

the Slovenian territory. Among the sedimentary rocks, Mesozoic to Palaeocene carbonate rocks (limestone and dolomite) are representative of this area, especially in the southern and north-western parts of the country.[33,34] Karst covers almost half of the Slovenian surface territory.[35] Palaeogene flysch rocks make up large parts of south-western Slovenia, while the eastern and central parts of Slovenia are rich in Neogene clastic sedimentary rocks (sandstone, marl and siltstone). Quaternary clastic sedimentary rocks (around 10 %), such as gravel and sand, cover river basins from the central part to the north-eastern part of Slovenia. Igneous rocks (around 3 %) make up smaller parts of Slovenia, mainly the north-eastern and northern parts, as well as a belt across the central part of the country. The latter mentioned igneous rocks are of Oligocene to mid-Miocene age. Small areas of igneous rocks can also be found in the belt through central Slovenia. The oldest, metamorphic rocks are not so abundant in Slovenia. Palaeozoic (or perhaps even Precambrian) metamorphic rocks (around 4 %) are found in smaller areas of the north-eastern and northern parts of Slovenia.[33,34]

2.3. *Hydrogeology*

In Figure 1 the aquifers are categorised on the basis of their porosity geometry as intergranular, fissured and karstic aquifers. Groundwater in large intergranular aquifers on plains is related to the balance and hydrodynamics of large rivers. The amount of dynamic groundwater reserves in those aquifers is approximately 18.3 $m^3 s^{-1}$, while in karstic and fractured porosity aquifers it is approximately 31 $m^3 s^{-1}$.[36] In sandstone and shale, as well as in igneous and metamorphic rocks, usually less significant aquifers of local and limited groundwater resources occur.[37] For water management in accordance with European legislation, the Slovenian territory is divided into 21 groundwater bodies and 165 aquifer systems.[38]

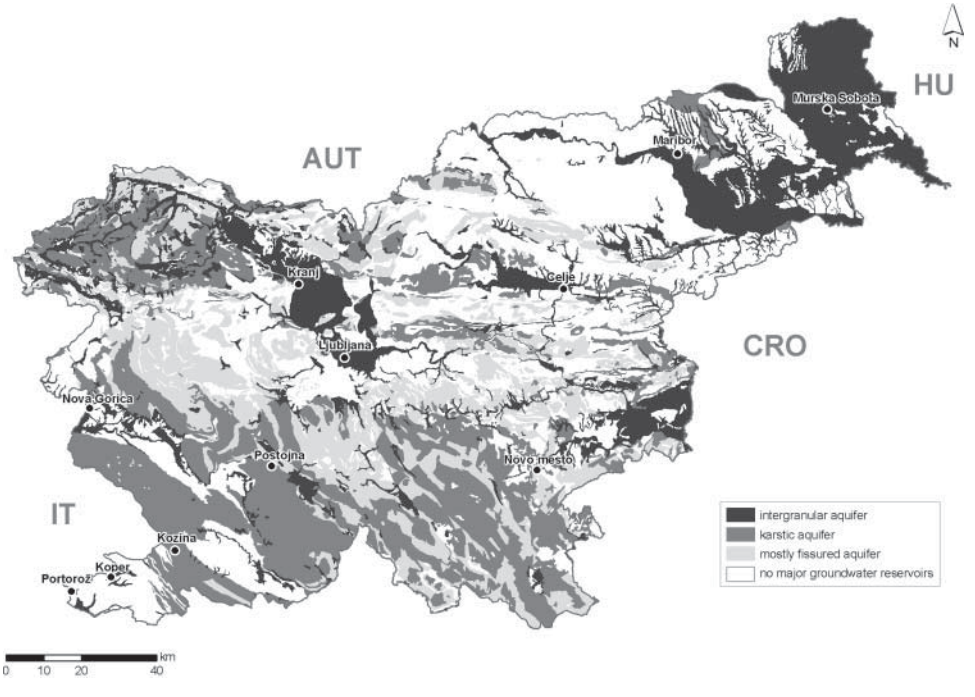

Figure 1. Simplified hydrogeological map of the study area.

2.4. *Climate*

Owing to its specific geographic diversity, Slovenia is influenced by several climate types. There is a mixing of: (a) continental climate, which influences the majority of the country, (b) Alpine climate, which prevails in the mountains in the north-western part of the country and (c) the coastal Mediterranean climate that influences the south-western part of the country.[39] In most parts of the country, except in mountains and along the coast, a moderate, warm, humid climate prevails. The coldest month is January, with a mean temperature around −3°C, and the warmest is July, with a mean temperature around 22°C. The mean amount of annual precipitation increases from the east (800–1000 mm/yr), over the central part (1000–1300 mm/yr), to the south and west (up to 2800 mm/yr). For the south-western part of the country, a sub-mediterranean climate is typical, with a mean temperature above 4°C for the coldest month and above 22°C for the warmest month. The mean amount of precipitation ranges from 1200 to 1700 mm/yr. In the mountains (Julian Alps, Karavanke Mountains, Kamnik-Savinja Alps, Pohorje Mountains and Snežnik Mountain), the mean temperature is around −3°C in the coldest month and around 10°C in the warmest month (above 2000 m under 10°C). The amount of precipitation varies widely and sometimes reaches 3500 mm/yr (Julian Alps and Kamnik-Savinja Alps).[33,40]

Four major types of air masses influence the weather in Slovenia [41]: (1) maritime polar air masses, which originate in the Northern Atlantic and North Sea, (2) maritime tropical air masses, which originate predominantly in the Azores area, (3) continental tropical air masses, originating in northern Africa and Asia Minor and (4) continental polar air masses, which originate in Scandinavia, Finland, Russia and also the Pannonian Plain.

3. Materials and methods

3.1. *Groundwater sampling*

The sampling network (Figure 2) was designed in such a way that:

- sampling locations were distributed evenly over the entire Slovenian territory,
- sampling locations were representative of the main aquifer porosity types, defined by the aquifer lithology.

The groundwater sampling campaign was carried out from 2009 to 2011, at a total of 83 sampling locations. Water was sampled at 50 springs, 5 boreholes, 4 private wells, 15 pumping stations and 9 surface waters. The last ones were sampled where access to spring water was not possible. Sampling was performed during hydrological conditions of base flow, and water from each location was sampled twice, in spring and in autumn. Sampling locations were sampled at altitudes ranging from 50 to 1790 m a.s.l.

Before sampling, the groundwater from observation objects was pumped till the measured physical parameters became stabilised. The water temperature, pH and specific electrical conductivity were measured *in situ*, using a WTW pH/conductivity measuring instrument pH/Cond 340i SET. A 0.1–l water sample was sealed in a polyethylene bottle for the isotopic analysis of $\delta^{18}O$ and $\delta^{2}H$ in water.

3.2. *Analytical methods*

Isotopic analyses for $\delta^{18}O$ and $\delta^{2}H$ in water samples were performed at the Hydroisotop GmbH laboratory in Schweitenkirchen, Germany. The oxygen isotopic composition ($\delta^{18}O$) was determined by the analysis of CO_2 equilibrated with sample water.[42] The isotopic composition of

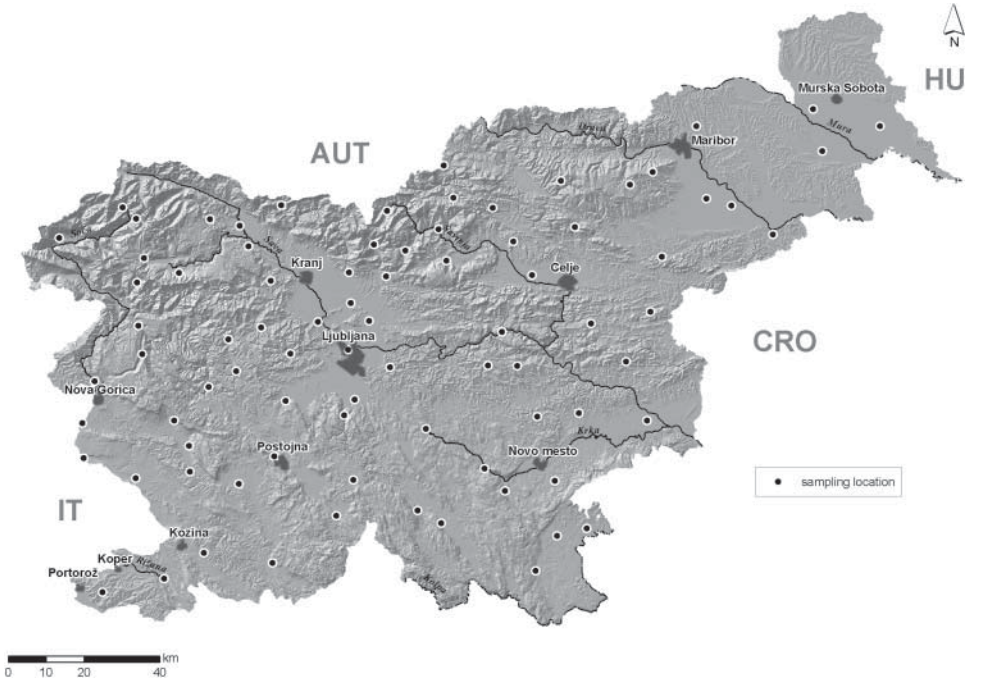

Figure 2. Distribution of sampling locations.

hydrogen (δ^2H) was determined using H_2 equilibrated with the water sample using Pt-catalyst.[43] The isotopic composition of water samples was determined with dual inlet Finnigan MAT 250 and Finnigan MAT 251 isotope ratio mass spectrometers. Results are expressed in δ-notation as δ^{18}O and δ^2H, i.e. as relative deviations in per mil (‰) of the isotope ratio from the standard V-SMOW for δ^{18}O and δ^2H.[44] Maximum reported analytical uncertainty is $\pm$0.15 ‰ for δ^{18}O and $\pm$1.5 ‰ for δ^2H, respectively. Values for d-excess were calculated by the laboratory from the δ^{18}O and δ^2H values in sampled water. Resulting errors of the d-excess are in the order of $\pm$1.5 ‰.

3.3. *Groundwater dynamics*

The main purpose of conducting the sampling twice at each sampling location was to obtain the typical value for stable isotope compositions of oxygen and hydrogen at the individual sampling location. There is a significant additional uncertainty to the reported mean values when there are limited samplings.

During the study only young groundwater, which was closely related to recent precipitation events, was sampled. This was verified by the tritium activities of the sampled groundwater and precipitation. The histogram in Figure 3 presents the distribution of tritium in groundwater with a mean value of 6.2 TU, and the arrow at 8.9 TU shows the mean value of tritium over the last few years (2002–2006) in precipitation for Ljubljana.[45] Since the tritium values in the sampled groundwater are close to the values measured in the precipitation, it is expected that the sampled groundwater is quite young, not exceeding 10 years.

3.4. *Determination of sampling location recharge areas*

For every groundwater sampling location, the characteristics of its recharge area were studied in detail. The recharge area of each sampling location was determined according to the type of

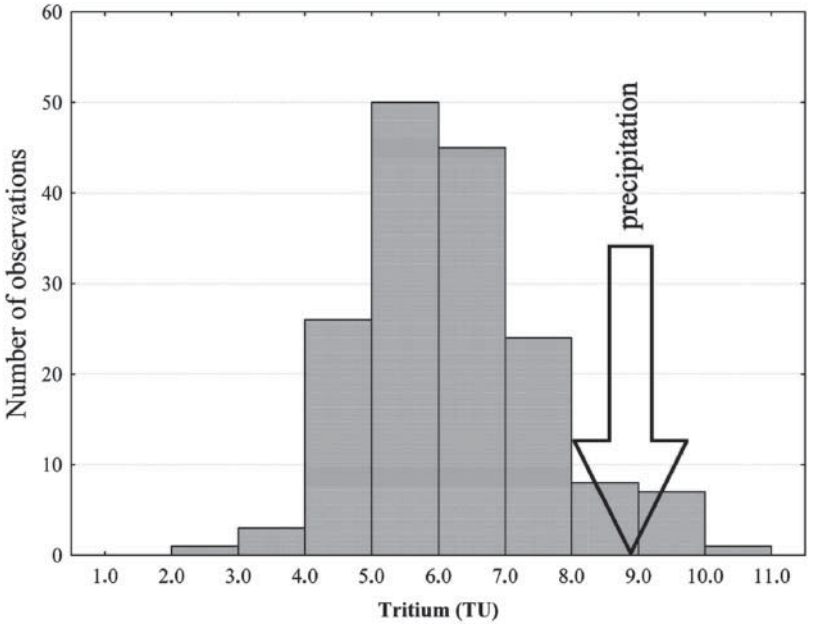

Figure 3. Frequency distribution histogram for tritium in Slovenian groundwaters.

aquifer where the water was sampled. In the karstic and fissured aquifers, the lithological and hydrogeological structure of the aquifer, the topology of the terrain, active water protection areas, past tracer tests, past hydro-contours, orographic watersheds and borders of groundwater bodies and aquifer systems were examined in detail. The recharge areas of the sampling locations in intergranular aquifers were determined regarding the main hydrogeological characteristics of the aquifer: groundwater flow velocity and groundwater direction. For certain groundwater bodies, the results of hydrogeological modelling were used. The one year isochrone was used as the outer border of the recharge area.

The recharge areas of the sampling locations in aquifers with minor groundwater reservoirs (poorly permeable or impermeable rocks) were determined mostly regarding the topography of the terrain.

All the recharge areas of the chosen sampling locations were processed in ArcGIS Version 9.2.[46] Mean altitudes for all sampling locations were calculated by ArcGIS spatial analyses based on raster layers of the Slovenian Digital Elevation Model of cell size 12.5×12.5 m.[47]

4. Results and discussion

4.1. *Stable isotopic composition of groundwater*

Basic information about the sampling locations and mean values of $\delta^{18}O$, $\delta^{2}H$ and d-excess measured in groundwater are presented in Table 1.

Isotope histograms show that groundwater isotope data for Slovenia is close to normally distributed (test of normality for skewness and kurtosis). Variations of data for $\delta^{18}O$ and d-excess are presented with histograms in Figures 4 and 5.

Table 1. Basic information about sampling locations and mean isotopic composition of sampled groundwater based on the two samplings.

Sampling location	Mean altitude (m)	Distance from the Adriatic Sea (km)	Object type	Mean values (‰)		
				$\delta^{18}O$	$\delta^{2}H$	d-excess
B-9, Brestovica	247	34	Borehole	−7.70	−48.4	13.1
Berglez	797	134	Spring	−8.90	−60.3	10.9
BLP-2, Nedelica	170	244	Borehole	−9.04	−63.3	9.1
Bohinjska Bistrica	1298	87	Surface water	−9.34	−61.3	13.4
Brekovice	557	71	Spring	−8.93	−58.8	12.6
C-4, Domžale	314	104	Pumping station	−8.26	−56.5	9.6
Čemažarjev izvir	886	96	Spring	−9.45	−62.5	13.1
Čepovan-1/94	862	64	Pumping station	−8.25	−52.6	13.4
Črna	1321	129	Spring	−9.82	−66.6	12.0
DAC-3, Skopice	155	157	Borehole	−8.90	−61.5	9.6
Debevčev mlin	717	116	Spring	−8.80	−57.9	12.5
Dobličica	553	121	Pumping station	−10.46	−72.4	11.3
Dobravca	506	105	Spring	−8.60	−58.4	10.4
Dobrova	689	157	Surface water	−10.31	−69.4	13.1
Framski slap	1099	187	Spring	−10.65	−71.1	14.0
GI-1, Gornji Ig	807	84	Pumping station	−9.69	−65.0	12.4
Gljun	1541	92	Surface water	−9.44	−61.7	13.7
Godec	987	143	Spring	−9.76	−64.1	13.9
Gradišče	196	232	Pumping station	−8.80	−60.2	10.1
Grajsko zajetje	559	83	Spring	−8.89	−59.5	11.6
Grešnikov hrib	462	101	Spring	−8.87	−59.3	11.6
Hotešk	826	71	Surface water	−8.46	−53.1	14.5
Hubelj	1006	51	Spring	−8.78	−52.6	17.6
Ilirska Bistrica	778	52	Spring	−8.05	−49.9	14.5
Iščica	686	88	Spring	−9.43	−63.6	11.8
Jelševa Loka	779	162	Spring	−9.81	−65.7	12.8
Jurčičev izvir	340	94	Spring	−8.56	−57.8	10.7
Kamniška Bistrica	1534	120	Spring	−10.11	−67.0	13.8
Korentan	645	50	Spring	−8.09	−49.9	14.7
Krajcarica	1203	99	Spring	−10.33	−67.7	15.0
Krka	493	101	Spring	−9.20	−62.3	11.3
Kropa	958	130	Spring	−9.68	−62.5	14.9
Krupa	369	127	Spring	−9.62	−64.6	12.4
Lipnica	1101	101	Spring	−8.85	−57.8	12.9
Lipnik	1245	103	Spring	−9.38	−63.1	12.0
LMV-1, Ljubljana	307	95	Pumping station	−8.59	−60.4	8.3
Lučnica	1306	124	Spring	−9.39	−62.0	13.1
Malenščica	646	62	Spring	−8.86	−58.6	12.3
Mali Obrh	898	71	Spring	−9.16	−61.9	11.4
Maver	426	147	Spring	−9.72	−63.3	14.4
Mazej	733	148	Spring	−9.46	−65.4	10.3
Metliški Obrh	315	135	Spring	−9.60	−66.0	10.8
Mitovšek	808	131	Spring	−10.01	−66.0	14.0
Močilnik	702	74	Spring	−8.62	−56.4	12.6
Mošenik	1265	114	Spring	−10.34	−69.2	13.5
Mrzlek	825	54	Spring	−8.27	−54.5	11.6
NG-4	52	43	Borehole	−7.12	−44.7	12.2
Obrh Rinža	709	97	Pumping station	−10.07	−68.2	12.3
Odolina	675	34	Surface water	−8.01	−49.9	14.2
OV-29, Brunšvik	253	195	Private well	−9.38	−64.5	10.5
P-1, Pliskovica	317	32	Borehole	−6.96	−44.5	11.1
Padiščak	148	7	Spring	−6.91	−40.9	14.4
Pasji rep	425	42	Surface water	−7.17	−45.2	12.2
Pevčevo	1081	180	Spring	−10.74	−73.1	12.8
Podroteja	786	63	Spring	−8.86	−57.0	13.9
Potok pri dvorcu Visoko	637	84	Surface water	−8.75	−56.7	13.3

(*Continued*)

Table 1. Continued.

Sampling location	Mean altitude (m)	Distance from the Adriatic Sea (km)	Object type	Mean values (‰)		
				$\delta^{18}O$	$\delta^{2}H$	d-excess
Pšata	805	110	Spring	−8.74	−60.0	9.9
Radeščica	678	116	Spring	−10.18	−70.2	11.2
Rakitnica	868	92	Pumping station	−9.75	−65.1	12.8
Rižana	556	23	Spring	−7.89	−50.4	12.7
Savica	1785	89	Surface water	−9.61	−61.8	15.1
Sevšek	825	130	Spring	−9.82	−65.6	12.9
Soča	1749	101	Surface water	−10.50	−71.3	12.7
Strahinec	296	204	Private well	−9.07	−61.3	11.3
Ščetar	266	140	Spring	−9.59	−65.4	11.2
Šempeter 0840	275	146	Private well	−8.32	−56.9	9.6
Šumec	901	148	Spring	−11.41	−77.9	13.3
Težka voda	476	129	Spring	−10.22	−70.1	11.6
Tominčev izvir	527	112	Spring	−9.74	−65.3	12.6
TR-1/99, Trebelno	427	129	Pumping station	−9.83	−67.1	11.5
Trate	680	152	Spring	−9.95	−65.2	14.3
Trebija	657	77	Spring	−8.97	−58.3	13.4
V-3A, Lukavci	186	228	Pumping station	−9.31	−64.3	10.1
V-6, Skorba	238	200	Pumping station	−9.23	−62.9	10.9
Velika Toplica	446	177	Pumping station	−10.20	−68.5	13.0
Veliki Vrh, Bloke	793	78	Spring	−10.11	−67.6	12.8
VG-10, Mala Goba	715	123	Pumping station	−9.46	−64.2	11.5
Vidovič	277	206	Private well	−8.89	−60.7	10.3
Vipava	824	47	Spring	−8.60	−53.8	15.0
Vo-1, Vodice	339	104	pumping station	−8.35	−56.9	9.9
Vt-1, Tinsko	464	168	Pumping station	−9.39	−64.0	11.1
Zadlaščica	1511	82	Spring	−9.34	−60.8	13.9
Žegnan studenec	1466	167	Spring	−10.89	−71.1	16.0

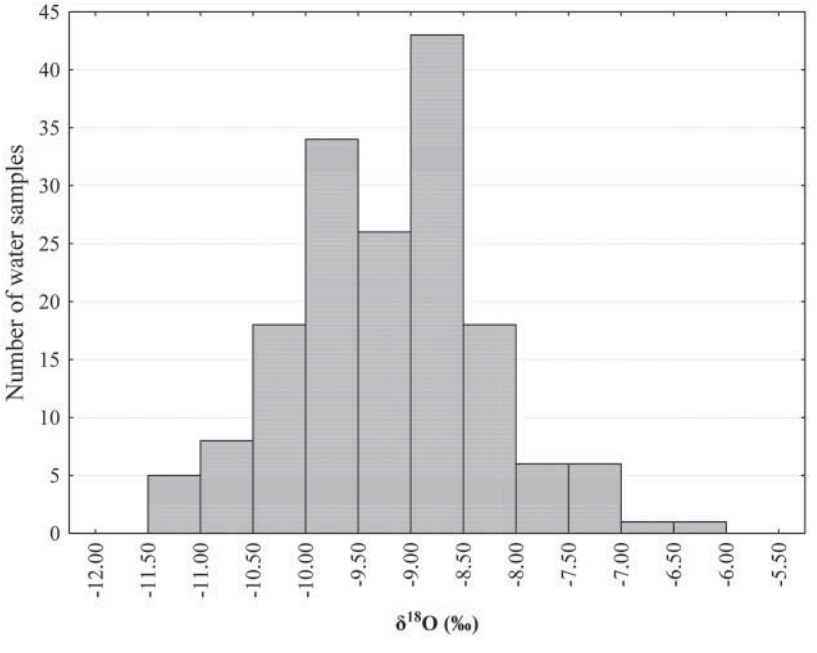

Figure 4. Frequency distribution histogram for $\delta^{18}O$ (V-SMOW) in Slovenian groundwaters.

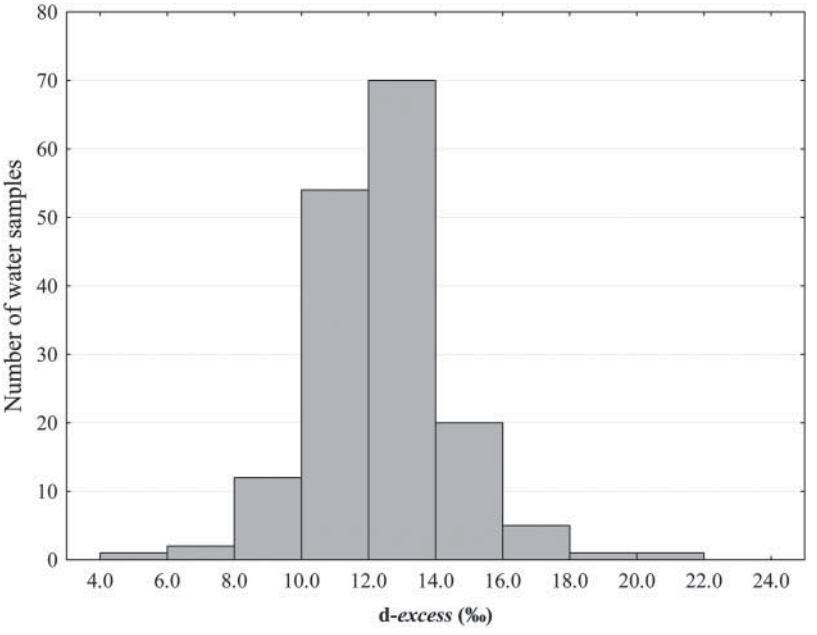

Figure 5. Frequency distribution histogram for d-excess in Slovenian groundwaters.

Basic descriptive statistics, i.e. mean, minimum and maximum values were calculated to describe the variation of measured data in groundwater. Values of $\delta^{18}O$ and $\delta^{2}H$ were used to calculate d-excess values. The mean value of $\delta^{18}O$ in groundwater is -9.21 ‰, minimum -11.43 ‰ and maximum -6.49 ‰. The mean value of $\delta^{2}H$ is -61.2 ‰, minimum -78.6 ‰ and maximum -40.6 ‰. The mean calculated value of d-excess is 12.4 ‰, minimum 6.0 ‰ and maximum 21.4 ‰.

4.2. *Spatial distribution of mean isotopic composition of sampled water*

The spatial distribution of the mean values of $\delta^{18}O$ and d-excess in the sampled groundwater for each groundwater body is presented in Figure 6. We observed the highest ^{18}O enrichment in the groundwater samples at low elevation in the coastal area. The inner continental waters that receive isotopically depleted precipitation as well as groundwater sampled at high elevations in the northern part of the country (Alps region) are depleted in ^{18}O. Similar observations were noticed with $\delta^{2}H$ values in the sampled water.

The values of d-excess in groundwater in Slovenia suggest that the sampled groundwater is mainly recharged by Atlantic-derived precipitation (westerly circulation), while Mediterranean-derived precipitation seems to be of minor importance as a precipitation source in the sampled groundwater.

4.3. *Comparison of isotopic composition in groundwater with precipitation*

The mean isotopic composition of oxygen (and hydrogen) in long-term measurements of precipitation at the meteorological stations at Ljubljana, Portorož Airport and Kozina [7] was compared with isotopic composition measured in Slovenian groundwaters (Table 2).

The biggest difference in isotopic composition was observed between the groundwater and precipitation measured at the Portorož Airport and Kozina stations, due to the proximity of the

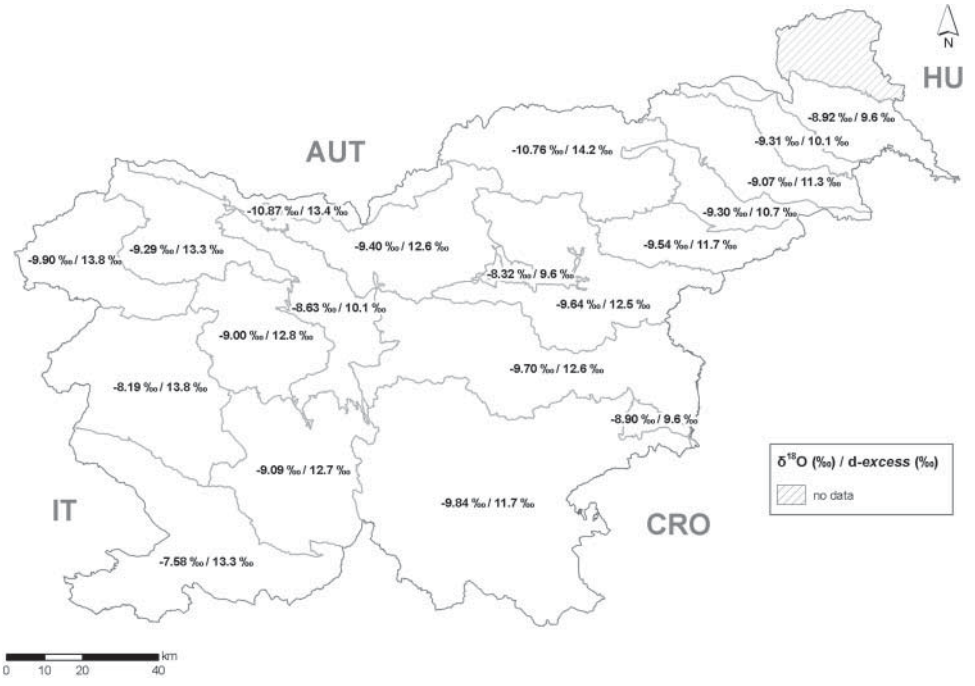

Figure 6. Spatial distribution of mean $\delta^{18}O$ (V-SMOW) in sampled water.

Table 2. Mean values of isotopic composition of Slovenian precipitation (meteorological stations Ljubljana, Portorož Airport, and Kozina) [7] and groundwaters.

	Precipitation Ljubljana (‰)	Precipitation Portorož Airport (‰)	Precipitation Kozina (‰)	Groundwaters Slovenia (‰)
$\delta^{18}O$ (‰ V-SMOW)	−8.60	−6.30	−7.80	−9.21
$\delta^{2}H$ (‰ V-SMOW)	−59.0	−40.0	−50.0	−61.2
d-excess (‰)	9.5	10.3	12.3	12.4

Adriatic Sea, where precipitation was more enriched in heavy oxygen (and hydrogen) isotopes compared with the isotopic composition measured in the groundwater. The isotopic composition of the precipitations measured at the Portorož Airport and Kozina stations is more local and the time series of measurements is shorter than for the precipitation measured at the Ljubljana station, which is more representative due to its central location and the longer time series of measurements. Values of d-excess around 10 ‰ can be attributed to air masses coming mostly from the Atlantic (precipitation at Ljubljana and Portorož Airport), whereas higher values of d-excess suggest the additional greater influence of Mediterranean air masses (precipitation at Kozina and in Slovenian groundwater). Vreča et al. [22] suggest that precipitation at the Kozina station is more complex to interpret due to its geographical positions where there is a mixing of continental and Mediterranean air masses, and the presence of the strong northerly Bora wind.

4.4. *The groundwater isotope altitude effect*

Figure 7 presents the relation between $\delta^{18}O$ in groundwater and the altitude of the recharge area for all corresponding sampling locations. The distribution of $\delta^{18}O$ values in groundwater decreases

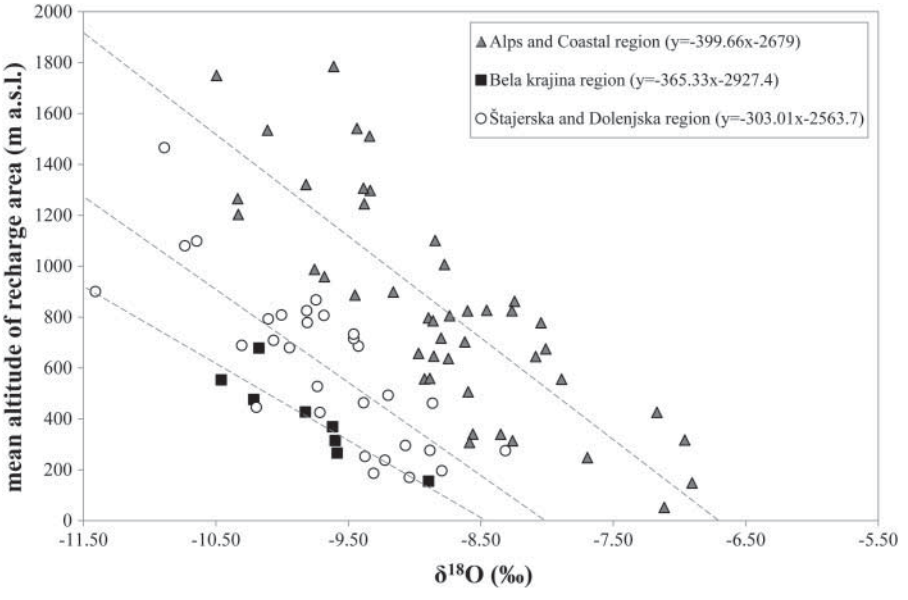

Figure 7. δ^{18}O (V-SMOW) vs. altitude (altitude effect) for all water samples.

gradually with the increasing elevation of the determined recharge area. Additionally, a grouping of sampling locations regarding individual areas in Slovenia is observed.

The study area was divided into three regions with different groundwater isotope characteristics reflecting different precipitation formation history: (1) Alps and Coastal region, (2) Dolenjska and Štajerska region and (3) Bela krajina region (Figure 8).

In Figure 8 we can observe that the southwest–northeast direction of each group is generally in accordance with the prevailing precipitation trajectory. In Slovenia, most of the important precipitation air masses that exceed a rain quantity of $50\,l\,m^{-2}$ generally come from the south-west.[48] Statistical evaluation shows that 35 % of the intensive rain air masses come from the south-west, 34 % from south-southwest and 18 % from south.

A major role is also played by relief characteristics, which determine orographic precipitation formation processes, and are reflected further in the oxygen and hydrogen isotope composition in precipitation. In this frame, the orographic barriers of the Trnovo–Banjšice plateau on the west and the Dinaric Gorski Kotar massif on the east side of the study area play an important role, inducing strong orographic precipitation in south-west wind situations.[49]

The radar picture of a precipitation event in July 2009 (Figure 9) [50] shows a typical meteorological situation where the south-west part of Slovenia (Alps and Coastal region) receives more rain than the south-eastern part.

For all three regions, the isotope altitude effect was calculated by adding the trend line on the scatter plot of mean altitudes of the recharge areas, compared with the mean values of δ^{18}O in the water. δ^{2}H variations in groundwater match equally well, as expected.

A statistically significant correlation exists between δ^{18}O in groundwater and the mean altitude of the recharge area in the Alps and Coastal region. The altitude effect (total 45 sampling locations) is $-0.25\,‰\,\delta^{18}\mathrm{O}/100\,\mathrm{m}$ ($r = -0.81, p < 0.001$) and $-2.25\,‰\,\delta^{2}\mathrm{H}/100\,\mathrm{m}$ ($r = -0.7$, $p < 0.001$).

A statistically significant correlation was observed also for the Štajerska and Dolenjska region. The altitude effect (total 30 sampling locations) is $-0.27\,‰\,\delta^{18}\mathrm{O}/100\,\mathrm{m}$ ($r = -0.79, p < 0.001$) and $-1.84\,‰\,\delta^{2}\mathrm{H}/100\,\mathrm{m}$ ($r = -0.71, p < 0.001$).

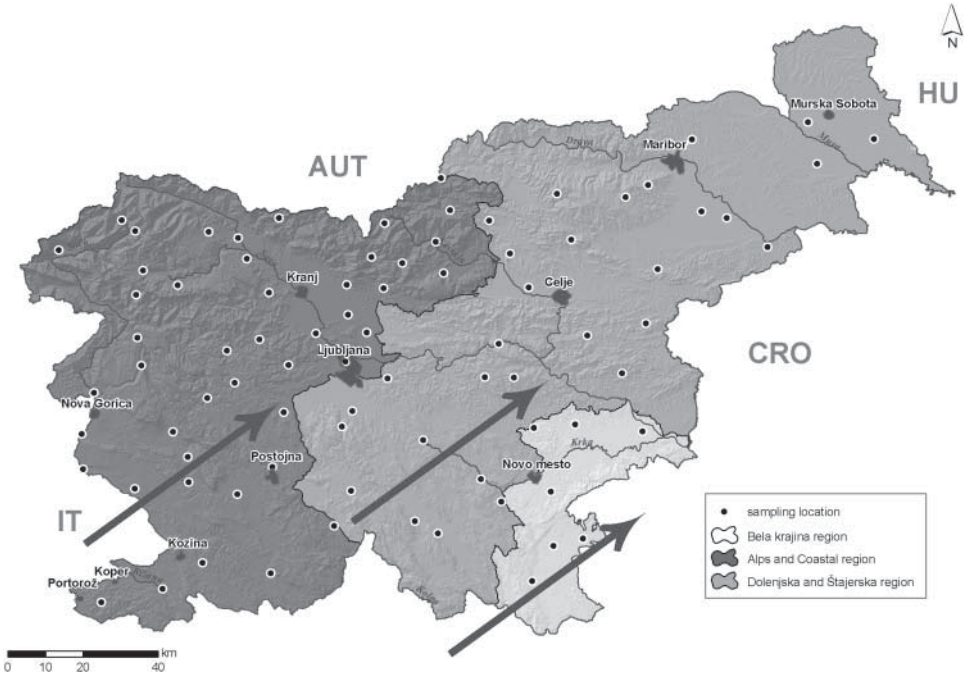

Figure 8. Spatial distribution of studied area in three regions with prevailing precipitation trajectory directions.

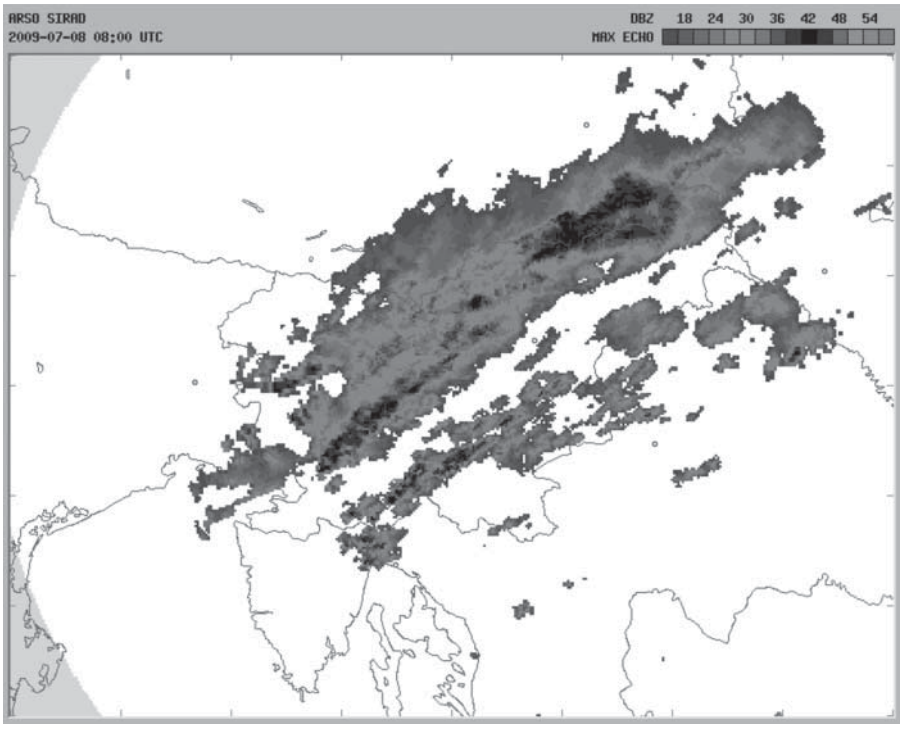

Figure 9. Radar picture showing a typical precipitation pathway (8 July 2009) [50].

The groundwater isotopic composition in Bela krajina region is more uniform within a limited area, and variations in isotopic values are small. The correlation is statistically significant, with an altitude effect (total 8 sampling locations) of -0.33 ‰ $\delta^{18}O/100$ m ($r = -0.89$, $p < 0.01$) and -2.40 ‰ $\delta^{2}H/100$ m ($r = -0.89$, $p < 0.01$).

The calculated isotope altitude effects derived from groundwater samples are comparable to the estimated altitude effects in precipitation from the past researches in Slovenia and neighbouring countries. For example for the Slovenian coastal part, the isotope altitude effect is -0.3 ‰ $\delta^{18}O/100$ m,[8] for the central part of Slovenia -0.2 ‰ $\delta^{18}O/100$ m,[28] for Slovenia and Croatia -0.37 ‰ to -0.26 ‰ $\delta^{18}O/100$ m,[51] in Germany -0.21 ‰ $\delta^{18}O/100$ m,[52] and in Italy close to -0.2 ‰ $\delta^{18}O/100$ m.[9]

4.5. *The d-excess versus altitude*

The d-excess in meteoric water depends on the elevation as well (positive correlation). This suggests that precipitation which is recharging the aquifer could be influenced by site-specific secondary effects such as partial re-evaporation and isotope exchange of raindrops on their travel to the ground, due to the longer distance between the cloud base level and the ground, (high) relative humidity, and other factors described in more detail in Cruz-San et al.,[53] Peng et al. [54] and others. Figure 10 shows the statistically significant correlation between d-excess in groundwater and the altitude of the recharge area ($r = 0.57$ and $p < 0.01$).

4.6. *Isotopic composition of sampled water compared with meteoric water lines*

Mean values of $\delta^{18}O$ and $\delta^{2}H$ in groundwater are plotted on a $\delta^{18}O$-$\delta^{2}H$ graph (Figure 11) compared with various precipitations' meteoric water lines; GMWL, EMMWL and LMWLs for Ljubljana, Zagreb (Croatia) and Italy (Northern, Central and Southern). As expected, a close linear relationship between $\delta^{18}O$ and $\delta^{2}H$ is seen.

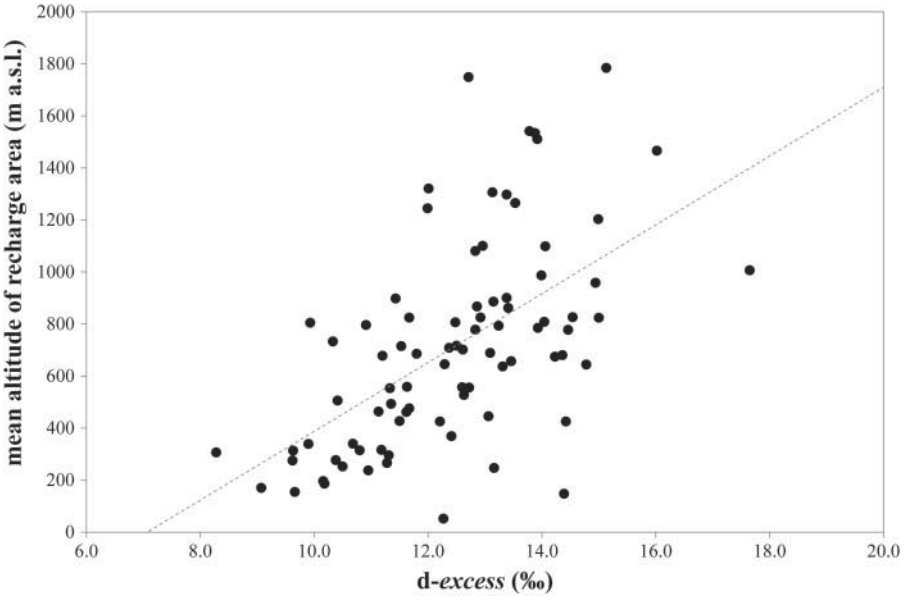

Figure 10. Mean d-excess vs. mean altitude of recharge area.

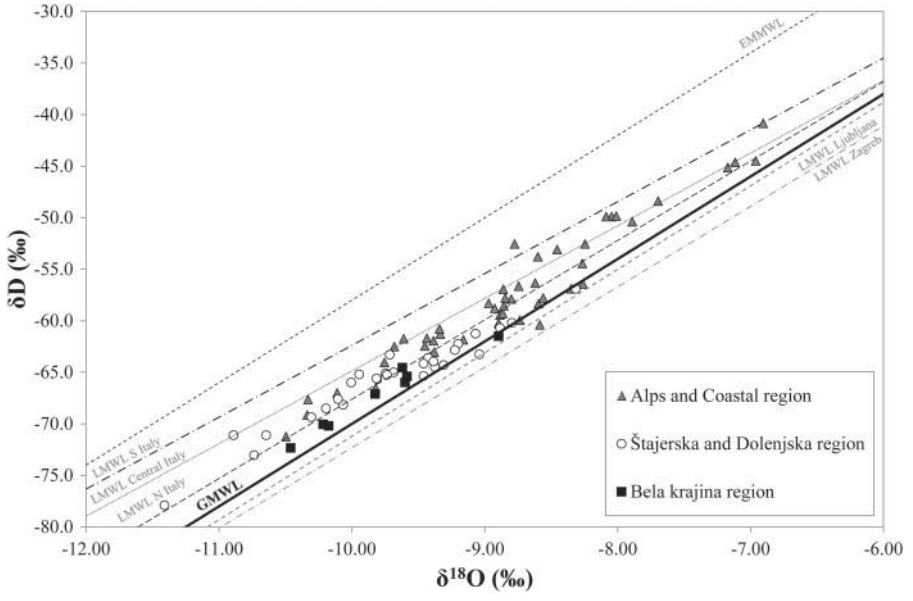

Figure 11. Mean values of δ^{18}O (V-SMOW) vs. δ^{2}H (V-SMOW) plot for water samples compared to GMWL, EMMWL and a few LMWLs.

The comparison of δ^{18}O and δ^{2}H values in the sampled water shows that the majority of water samples fall between GMWL and EMMWL. Water samples from the Alps and Coastal regions lie between the GMWL and EMMWL lines, while LMWLs for Italy (North, Central and South) lie in between, suggesting some influence from the air masses coming from the Mediterranean Sea. Water from the Štajerska and Dolenjska region lies between the LMWL of Central Italy and Ljubljana, where the influence of the Mediterranean is less visible. A similar situation occurs in the case of waters from the Bela krajina region, where samples are plotted between the GMWL and LMWL of North Italy.

4.7. *The groundwater isotope effect of distance from the sea (isotope continental effect)*

In order to trace the variation change of δ^{18}O (and δ^{2}H) in precipitation during transit over the Slovenian territory in groundwater, we considered the main direction of the precipitation's progress. Because of the orographic influence of the Alps, the main precipitation pathway to the Slovenian territory passes from the Atlantic Ocean over the Mediterranean and onwards to the north-east. In order to evaluate this effect, the direct (air) distance from the south-west at the Coast (Adriatic Sea) to the north-east Prekmurje region was considered. Only nine sampling locations, with a similar mean altitude of their recharge areas, were considered in this direction (Figure 12). The calculated groundwater isotope effect of distance from the sea for Slovenian ground waters is approximately -8.3 ‰ δ^{18}O/1000 km ($r = -0.89$, $p < 0.001$).

Not much information is available about the precipitation values of the isotope continental effect in neighbouring countries. In present day European precipitation, the continental effect is around -2.0 ‰ δ^{18}O/1000 km [5] and in France -3.2 ‰ δ^{18}O/1000 km.[55]

We believe that the considerable isotope effect observed in Slovenia is a result of the specific relief conditions in Slovenia. Mountain barriers near the coastal area cause intensive precipitation, resulting in heavy depletion of heavy oxygen and deuterium from the air mass. The final result is a great continental isotope effect in the precipitation at a relatively short distance, which is reflected further in the groundwater isotope composition.

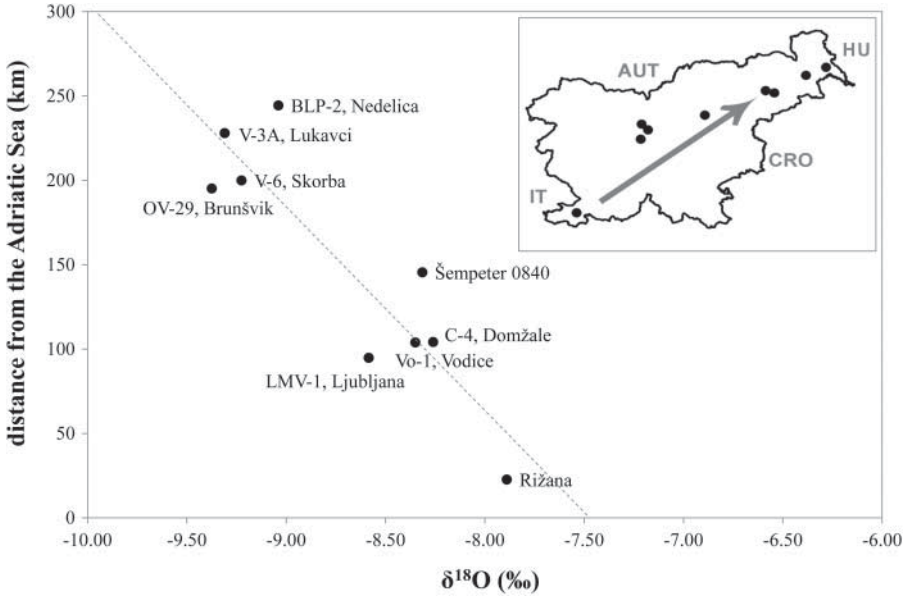

Figure 12. Mean δ^{18}O (V-SMOW) vs. distance from the sea.

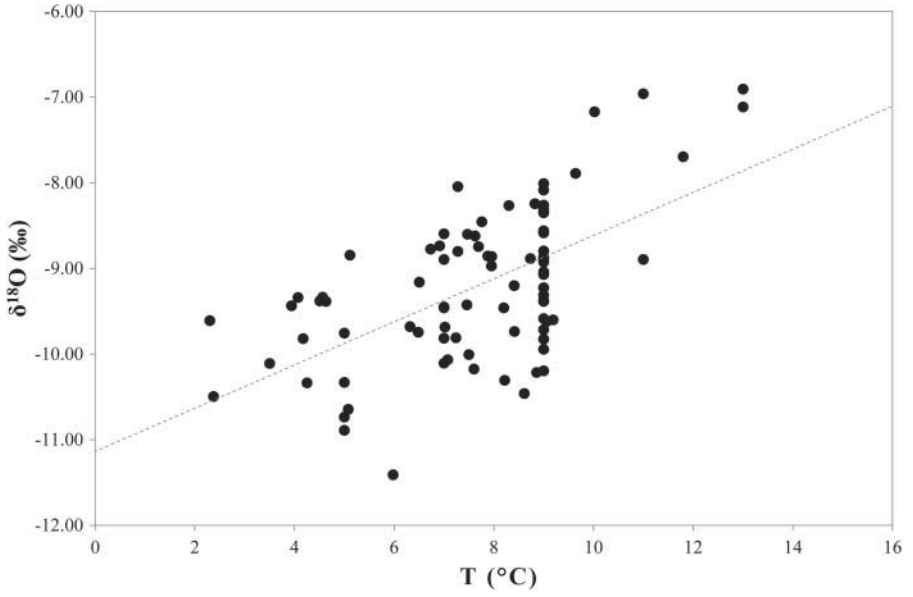

Figure 13. δ^{18}O (V-SMOW) vs. recharge area mean annual air temperature.

4.8. *δ^{18}O in groundwater and air temperature*

Since there is a relationship between the altitude and the mean air temperature, and since previously conducted tritium analyses have confirmed the young groundwater age, we can expect to find a correlation between the groundwater isotopic composition and the mean air temperature. A correlation between δ^{18}O in groundwater and the mean annual temperature of the recharge area is observed (Figure 13), as has been reported by other authors.[56] For definition of the mean air temperature of the sampling location recharge area, a map of the spatial distribution of air

temperatures with a resolution of 1–2 km was used.[57] The mean annual temperature of each sampling location has been estimated in ArcGIS according to its estimated recharge area. The graph in Figure 13 shows mean $\delta^{18}O$ values in ground water compared with mean annual temperature. There is a positive correlation between these two parameters ($r = 0.56$, $p < 0.001$). The mean values of $\delta^{18}O$ in groundwater from colder areas are more depleted in $\delta^{18}O$ than those in lowlands as a consequence of the isotope altitude effect. The isotope temperature gradient is estimated at around 0.25 ‰ $\delta^{18}O/°C$, which coincides with estimated temperature gradients in precipitation of 0.11 ‰ $\delta^{18}O/°C$ at the Portorož Airport station and 0.30 ‰ $\delta^{18}O/°C$ at Ljubljana station.[8]

5. Conclusion

Research into the isotopic composition of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) in Slovenian groundwater over the past 3 years shows important differences in their isotopic values, owing to the altitude and location of their recharge areas.

Values for $\delta^{18}O$ in Slovenian groundwater vary between −11.43 and −6.49 ‰, for $\delta^{2}H$ between −78.6 and −40.6 ‰, and for d-excess between 6.0 and 21.4 ‰.

Our results present the spatial distribution of the measured parameters in Slovenia. Most enriched in ^{18}O is groundwater at low elevation in coastal areas, while groundwater at high altitudes and in the inner part of the country (with increasing distance from the seaside) is isotopically depleted in ^{18}O. Similar observations are seen with $\delta^{2}H$ in sampled water.

From groundwater isotopic data as well as the geographic and climatic diversity of the study area, three different isotopic altitude effect zones could be defined, following the precipitation intensity pattern. The isotope altitude effect for the Alps and Coastal region is −0.25 ‰ $\delta^{18}O/100$ m, for the Štajerska and Dolenjska regions −0.27 ‰ $\delta^{18}O/100$ m, and for the Bela krajina region −0.33 ‰ $\delta^{18}O/100$ m.

In addition, we observed the variability of d-excess in groundwater compared with the sampling location recharge areas. Groundwater in lowlands/valleys has a lower d-excess value than groundwater in high mountain regions, which could be the result of isotopic fractionation during orographically uplifted air masses or of other processes.

A good correlation between $\delta^{18}O$ and $\delta^{2}H$ is observed for all the sampling locations. The values of the isotopic composition of the sampled waters plot mostly between GMWL and EMMWL. This suggests that the groundwater reflects the isotopic composition of precipitation discharging mostly from Atlantic air masses and also some influence from the Mediterranean basin indicated by the higher d-excess values (> 10 ‰).

Comparison between $\delta^{18}O$ values in the groundwater and the distance from the Adriatic Sea to the Prekmurje region (southwest-northeast direction) indicates the presence of a strong ^{18}O isotope effect, with a value of around −8.3 ‰ $\delta^{18}O/1000$ km. The magnitude of the estimated effect is greater than the precipitation isotope continental effects found in neighbouring countries. We interpret this as the result of the specific Slovenian topography where air masses are influenced by relatively high altitude mountains not far from the coastal area.

Based on the relation between the mean annual air temperature of the recharge area and the isotope composition of the sampled groundwater, the groundwater from colder areas is isotopically more depleted than the groundwater in lowlands, which is a consequence of the isotope altitude effect. The groundwater isotope temperature gradient was estimated and is around 0.25 ‰ $\delta^{18}O/°C$.

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