Preliminary Results From Stable Isotope Investigations In The Kupa Drainage Basin (Western Croatia)

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Abstract

For the very first time stable isotope data of river waters from Western Croatia are presented. During a campaign lasting from October 27 to November 21, 2010 sixty-seven water samples from sites along the three hundred kilometres long course of the Kupa River, and along selected tributary rivers of its catchment of about ten thousand square kilometres, respectively. We want to emphasize that hydrological conditions during the sampling period were influenced by heavy rain falls midst of October.

Our interpretation of isotope ratios in river water is mainly based on the relation between weighted mean $\delta^{18}O$ and the altitude obtained from stations of the Global Network of Isotopes in Precipitation (GNIP), revealing an approximate vertical $\delta^{18}O$ gradient of -0,30‰ per 100 m, as reported by Vreča et al. (2006). In addition, the $\delta^{18}O$ data from the GNIP station Zavižan predominantly indicate precipitation from the Adriatic coast, in contrary to the GNIP station Zagreb, the precipitation of which is influenced by more continental air masses.

The catchment of upper Kupa River in the Gorski Kotar rises up to 1500 metres above sea level (a.s.l.). Upper Kupa is mainly charged by springs from big karst reservoirs, in which a residence time of groundwater of up to one year has to be considered. We interpret the $\delta^{18}O$ values of Čabranka River (about -8,07‰) as signals from maritime precipitation in this karstified catchment area. The $\delta^{18}O$ value of upper Kupa River diminishes along its course from -8,09‰ near Osilnica to -9,06‰ west of Karlovac. After the inflow of tributaries south of Karlovac the oxygen isotope ratio of Kupa River water reveals a significant change because $\delta^{18}O$ values of Dobra-, Korana- and Mrežnica River are lower (-10,45‰ to -9,58‰).

The catchment of Dobra River and Korana River rises between 400 and 880 metres a.s.l. We interpret the lower $\delta^{18}O$ values of river waters from the drainage basins at those low mean altitudes as basically not caused by an altitude effect, but caused by precipitation out of more continental air masses.

Keywords: *Western Croatia, Kupa catchment, river water, stable isotopes.*

1 Introduction

In Europe only few studies have been published on isotopic composition of river waters. Over a five-year period, from 2003 to 2007, water samples from Weser River in Germany (46.200 km^2 basin area in total) were collected on a monthly basis from 46 sites to characterize temporal and spatial isotope patterns of river waters as indicators of groundwater contribution, and for confirmation of modelling results (Koeniger et al., 2009). In 2007 the International Commission for the Protection of the Danube River initiated a sampling campaign along the 2857 km long River Danube covering an overall catchment area of 817.000 km^2 with an average discharge of about 6.500 m^3/s at its mouth, and 96 sampling points were selected (Rank et al., 2009). The isotopic composition of hydrogen and oxygen in river water was mainly determined by the isotopic composition in precipitation water in the drainage area (altitude effect, continental effect, seasonal variations, storms etc.). Evaporation effects in the Danube Basin played only a minor role. Compared to these studies, the investigated catchment in Croatia is relatively small because the area of the Kupa Basin is 10.052 km^2 only (Frančišković-

Bilinski, 2007). The length of Kupa River is 296 km from Kupa Spring at an altitude of 380 m a.s.l. down to Sisak at 93 m a.s.l., where it contributes Sava River.

Hydrochemistry, stream sediments, pollution and fluvial geomorphology of the Kupa River catchment have been intensively studied (e.g.: Frančišković-Bilinski et al., 2005; Frančišković-Bilinski, 2006, 2007, 2008; Bilinski, 2008; Bilinski et al., 2010; Frančišković-Bilinski et al., 2011). For karst groundwater protection in the Kupa River catchment also isotope ratios were measured (Kapelj et al., 2002; Biondić et al., 2006). For special investigations of karst hydrogeology in the Kupa catchment stable isotopes were used (Stadler et al., 2010, 2011; Häusler & Stadler, 2011; Frančišković-Bilinski et al., 2012; see Figure 1).

Figure 1. Kupa catchment in Western Croatia (modified from www.mapsorama.com/satellite-map-of-croatia)

2 Climatic and hydrogeologic setting

The isotope composition of river waters in Western Croatia is depending on several parameters such as relief, hydrogeology and the origin of air moisture more maritime or more continental. The storage of karst water or rapid surface run off depends on the distribution of permeable and impermeable formations. In addition to the mean altitude of the recharge areas, the stable isotopes also reflect climatic influences.

The drainage pattern of Kupa River and its sub-basins comprises different dendritic as well as karstic patterns, which basically reflect the permeability of the hard rock formations in the watershed. River morphology and drainage pattern therefore are good indicators of karstified and non karstified catchment areas. Where impermeable Paleozoic rocks prevail in the sub-basins of the Kupa catchment, surface run off prevails, and after heavy precipitation even smaller rivers become torrents. Relief and climate therefore control the quantity and regional distribution of precipitation, both of which significantly influence the signals of stable isotopes in precipitation and discharge of the rivers. For official hydrological and meteorological data we refer to the statistical yearbook 2011 of the Central Bureau of Statistics of the Republic of Croatia (www.dzs.hr/Eng/Publication/stat_year). The drainage patterns are classified according to the stream ordering after A. N. Strahler (1958, 1964), where a river segment with no tributaries is designed as a first-order stream ("1"), and two first order streams join to form a second-order stream ("2") and so on.

2.1 Climate

Most of Croatia has a moderately warm, rainy climate characterised by a mean monthly **temperature** ranging between -3°C and +18°C in the coldest month. Only the highest parts of mountains (above 1200 m) of Lika and Gorski Kotar have a snowy forested climate with a mean temperature below -3°C in the coldest month. However, in contrast to the interior, where the warmest month of the year has a mean temperature of less than 22°C, the area along the Adriatic coast has a mean temperature of more than 22°C in the warmest month. The mean annual air temperature in the coastal regions ranges from 12°C to 17°C. Mean annual quantity of **precipitation** in Croatia ranges from 600 mm to 3500 mm. The lowest quantities of precipitation on the Adriatic are found on the outer islands (under 700 mm). Moving from that region towards the Dinara mountain range, the mean annual precipitation increases to a maximum quantity of up to 3500 mm on the peaks of Gorski Kotar (Risnjak and Snježnik). In the northern Adriatic, Lika and Gorski Kotar there are no dry periods but there are two precipitation maxima, with the first one occurring in the cold part of the year and the second one in the transitional period between spring and summer. In the southern and middle Adriatic the yearly precipitation pattern is maritime in character, with dry summers and maximum precipitation in the cold months of the year. The prevalent **wind directions** in the interior of Croatia are the northeast and, to a lesser extent, southwest. In the Adriatic prevalent in the cold months are the north-eastern wind "bura" from the north-east and sirocco from the south, while in the summer it is landward breeze mostly from the west. To sum up the climate of the Kupa Basin is continental with Mediterranean influence.

2.2 Hydrology

In Figure 2 we present the drainage pattern of the Kupa Basin with its major tributary rivers referred to in this paper. It clearly reveals that the hydrogeologic catchment exceeds the orographic ones by far. The average discharge of Kupa in Croatia is 201 m^3/s. Korana tributes 29 m^3/s, Dobra 35 m^3/s, Mrežnica 27 m^3/s and Glina 18 m^3/s (http://www.watersee.net/kolpakupa-river.html). Seven gauge stations along the Kupa River document its yearly range of discharge and reveal two maxima, one in spring and one in autumn. The lowest discharge is during summer months (June, July, and August) with a minimum in July. According to Trninić (2010) the Kupa River annual runoff analysis for the hydrologic stations near Hrvatsko and Kamanje (period: 1957-2008) shows a decreasing trend.

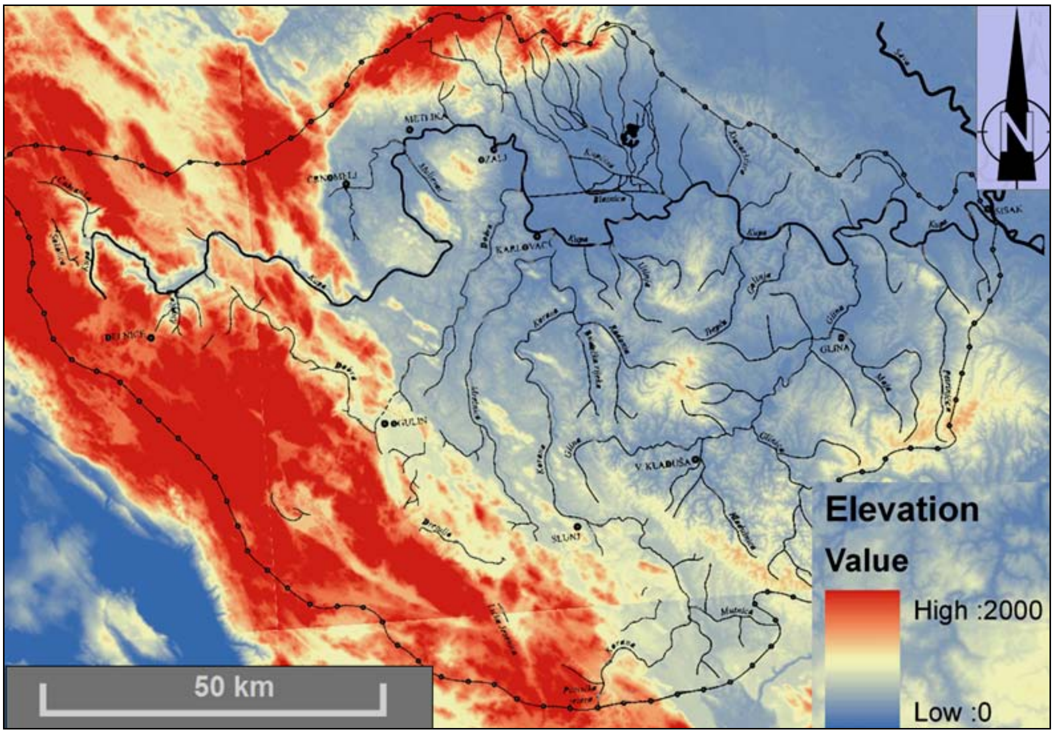

Figure 2. Catchment of Kupa River, which partly extends to Slovenia in the northwest and to Bosnia-Herzegovina in the southeast. Elevation in meter above sea level.
Chain dotted line = Kupa catchment (modified from Frančišković-Bilinski et al., 2005; digital elevation model courtesy of NASA: asterweb.jpl/nasa.gov).

2.3 Geology and drainage pattern

The Kupa catchment discharges the southeast-striking Outer Dinarides, comprising Paleozoic to Cenozoic formations, which are overlain by Miocene deposits. South-westward tectonic shortening resulted in major syn- and anticlines, and caused local thrusting of Permian and Triassic formations over Jurassic formations (Hrvatski Geološki Institut, 2009). Basically Paleozoic formations consist of clastic rocks, which are impermeable, and Triassic to Jurassic carbonate rocks, which are karstified. The rivers tributing Kupa River mainly flow in north-eastern direction, perpendicular to the folded Paleozoic to Cenozoic formations. In the Table 1 we briefly characterize the hydrogeology of the river catchment investigated.

For the watershed of Kupa River we distinguish between karstic, dendritic, parallel and centripetal drainage patterns. Karstic drainage typically is characterized by sinkhole ponds, sinkhole throats (dolines), caverns and caves, and therefore subsurface discharge prevails. The degree of dissection as indicated by the drainage density in the karstified Kupa watershed (Figure 2) is very low. Dendritic and parallel drainage patterns indicate surface dominated river flow. Southeast oriented parallel drainage pattern prevails in the northern catchment of Žumberak-Samobor mountain range. Except for the Glina sub-basin with a medium drainage density, the drainage density of all other dendritic and parallel drainage patterns is low. This is also true for the centripetal drainage pattern of the depression Draganićka šuma east of Karlovac, where streams converge centrally.

River	Length of river	Basin area	Geology and drainage pattern
Čabranka	17,5 km	135 km^2	Karstified limestones and dolomites of Triassic, Jurassic and Cretaceous age, locally overthrusted by Permian clastic rocks. Very low density drainage pattern with karstic drainage and few dendritic tributaries from both Slovenian and Croatian side.
Kupa	296 km	10032 km^2	Karstified Triassic to Cretaceous formations, partly overlain by Permian clastic formations in its upper flow. Important karstic springs from Gorski Kotar charge upper Kupa River. Long southeast-oriented sections of River follow the Dinaric fold structures. Very low density drainage pattern perpendicular Kupa River.
Dobra	104 km	900 km^2	Huge upper catchment of Dobra River west of Ogulin comprises karstified Jurassic limestones and dolomites. Smaller catchment of lower Dobra River comprises flysch (Paleocene-Eocene), and overthrusted Triassic dolomites as well as Permian clastic deposits. Karstic drainage in upper catchment and very low density drainage pattern along entire river course.
Korana	134 km	2595 km^2	Very big catchment comprising Cretaceous ophiolites in its upper course, and clastic Upper Miocene formations in its lower course. Very low density drainage pattern with karstic drainage in upper catchment, and few dendritic tributaries in both upper and lower catchment.
Mrežnica	63 km	64 km^2	The small catchment comprises karstified Jurassic limestones and dolomites and therefore reveals a karstic drainage pattern.
Glina	100 km	1426 km^2	Big catchment with a complex sequence of Permian clastic deposits, Triassic formations, metamorphosed Jurassic deposits, and Jurassic ophiolites. Its western tributaries discharge hills covered by Plio-/Pleistocene deposits. Glina basin reveals a pronounced dendritic, medium density drainage pattern.

Table 1. Length of river, size of catchment and general characterization of the geology and drainage pattern of Kupa River and its tributaries (Figure 10).

The catchment of the rivers **Utinja-Golinja** comprises Upper Cretaceous carbonatic and volcanic formations, which are overlain by carbonatic and volcanoclastic formations of Miocene age. The dense net of small rivulets discharging this region indicates that the base rock formations act as an aquitard and therefore surface run off prevails. Utinja-Golinja Rivers reveal a low density drainage pattern with rivulets perpendicular to Kupa River. The upper catchment of **Petrinjčica River** lies in Zrinska Gora comprising flysch deposits of Paleocene to Eocene age. North of Mačkovo Selo Petrinjčica River flows through Miocene clastic and volcanic rocks. In total the river shows a parallel and low density drainage pattern. The synoptic view on the investigated sub-basins and their characterization by means of stable isotopes is presented in Figure 10.

The Kupa watershed is a good example where drainage patterns reflect the permeability of hard rock formations and major flow directions either follow the general south-east striking of the syn- and anticlines of the Outer Dinarides or faults perpendicular to them. The low drainage density is also characterized by a low bifurcation ratio and therefore low stream orders (Frančišković-Bilinski et al., 2011). According to the Strahler scheme most of the perennial river networks in the Kupa Basin form a second-order stream (or 2nd order basin) only, comprising at least two single tributaries. Third order streams such as Glina, formed by several second-order streams, are rare.

3 Methods

In order to understand the interpretations of stable isotopes in river waters we briefly introduce the isotope methods used. The stable isotope composition of samples was measured at the University of Vienna, Department for Environmental Geosciences. The used set up of a Picarro Inc. Isotopic Water Analyzer combined with a CTC HTC-Pal autosampler (LEAP Technologies) is similar to the one described by Gupta et al. (2009). The Picarro “Cavity Ring-Down Spectroscopy” (CRDS) uses a near-infrared laser to determine hydrogen and oxygen isotope ratios out of liquid water samples (Picarro Inc.). CRDS is a direct absorption technique (Berden et al., 2001) that offers results for pure water samples highly comparable in precision with classical mass spectroscopy (Brand et al., 2009). Using the Picarro CRDS measurement precision of $\delta^{18}O$ is ±0,1‰, and measurement precision of $\delta^{2}H$ is ±0,5‰.

$\delta^{18}O$ values depend on several effects such as altitude effect, continental effect, and temperature effect, and in addition we have to take in mind the climatic influence, because maritime air masses are generally moist, containing considerable amounts of water vapour, while continental air masses are usually drier (Vreča et al., 2006). Basically the relation between the $\delta^{18}O$- and $\delta^{2}H$ values plots around the Local Meteoric Water Line (LMWL) as published by Vreča et al. (2006) from the Velebit Mountains (Figure 3). Compared to the LMWL, the Global Meteoric Water Line (GMWL) lies below the LMWL, which indicates more maritime air moisture in river waters of the Kupa catchment. When applying the concept of deuterium excess (d), which is defined as $d = \delta^{2}H - 8\delta^{18}O$, and which is believed to be mainly related to the meteorological conditions at the source region from where the sample water is derived, the deuterium-excess of about 17‰ for Zavižan high altitude station is the highest one in Croatia (Vreča et al., 2006). Despite the fact that we do not know the annual variation of the d-excess of the studied river waters in the Kupa Basin, their values match the deuterium-excess of Zavižan meteorological station very well.

Due to the fact that no time series analyses of stable isotopes from high alpine meteorological stations in the Kupa catchment are available, we refer to Vreča et al. (2006) for interpretation of isotopic characteristics of precipitation. Where we interpret stable isotopes of precipitation in river waters depending on the altitude effect, the higher values (e.g. $\delta^{18}O$ of -8,0‰) represent precipitation at lower altitude, and the lower values (e.g. $\delta^{18}O$ of -10,0‰) indicate precipitation at higher altitude of the recharge area. The interpretation of stable isotope values of river waters is based on the relation between weighted mean δ18O values and the altitude obtained from the Croatian GNIP stations Zavižan and Zagreb, revealing an approximate vertical gradient of 0,30‰ per 100 m, as reported by Vreča et al. (2006).

4 Results

In order to characterize stable isotopes of sub-basins we divide the Kupa catchment into the following sub-basins (compare to Figure 10):

- Čabranka River
- Upper Kupa River west of Brod na Kupi
- Upper Kupa River from Brod na Kupi to Karlovac
- Dobra River
- Discharge from Žumberak/Samobor to depression Draganićka šuma
- Mrežnica River
- Korana River
- Lower Kupa River from Karlovac to Petrinja
- Utinja and Golinja River
- Glina River
- Petrinjčica River

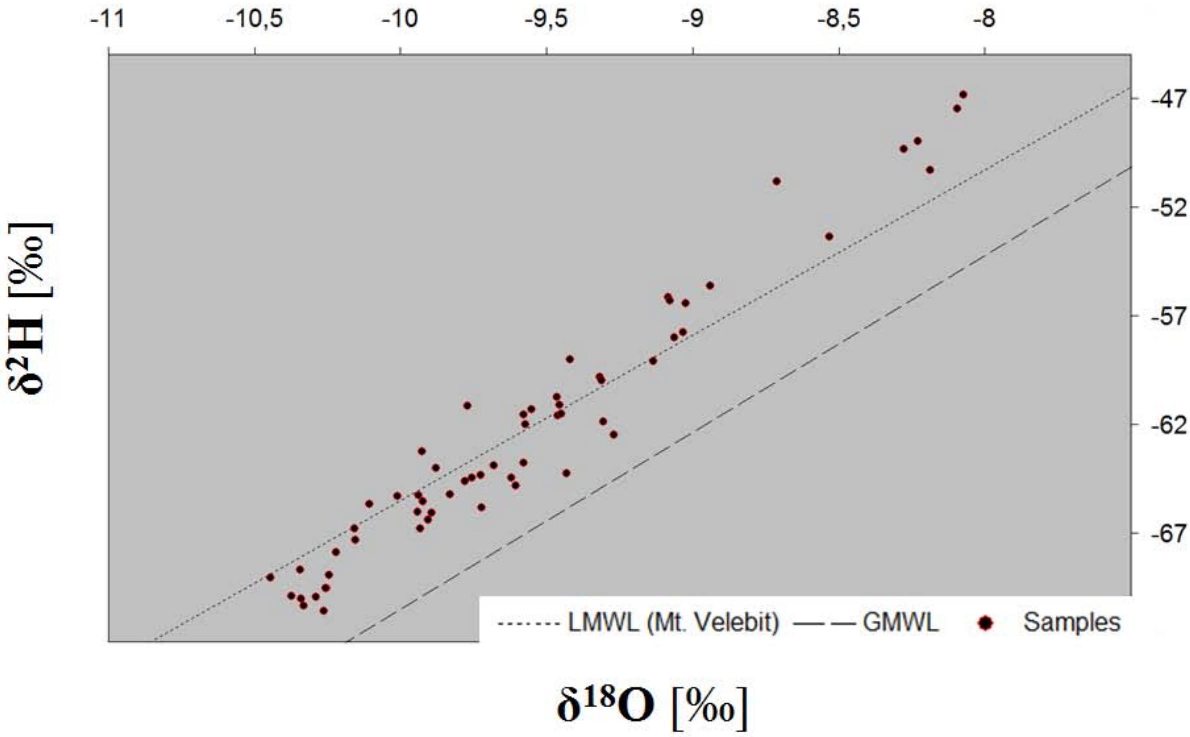

Figure 3. Relation between $\delta^{18}O$ and $\delta^{2}H$ values of river waters in the Kupa catchment with indication of local meteoric water line (LMWL) as published by Vreča et al. (2006) from the Velebit Mountains. Global Meteoric Water Line (GMWL) for comparison.

Table 2 contains the results of stable isotope ratios measured according to sampling locations (sample-ID) from the river sources down Kupa River and its tributaries, respectively. However, the listing of samples within one sub-basin does not necessarily reflect the results of measurements in flow direction. In more detail we characterize stable isotope ratios of river waters in the Kupa catchment, from Čabranka Spring and Kupa Spring west of Brod na Kupi, and their catchment in the Gorski Kotar at about 700 m above sea level, down to Karlovac (106 m), Petrinja (97 m) and Sisak (93 m). Figure 4 gives an overview of river catchments investigated in upper Kupa Basin. First the stable isotopes of river waters are described from the catchment of Čabranka River and of upper Kupa River west of Brod na Kupi (Figure 5), further from Kupa River east of Brod na Kupi down to Karlovac, and from the catchment of Dobra River, respectively (Figure 6).

Čabranka River

Čabranka River originates from karst springs in the Croatian-Slovenian border region. Its major sources in Western Croatia are Čabranka Spring and Zamost Spring discharging Gorski Kotar to the north. Close to the confluence with Kupa River, water of Čabranka River is characterized by $\delta^{18}O$

values of about -8,10‰, varying from -8,07‰ (sample 1-3) to -8,19‰ (sample 1-1), which is within the measurement accuracy. Its recharge area basically is Crna gora, the mountains bordering Slovenia with altitudes up to 1200 m a.s.l., and the green karst mountains of north-western Gorski Kotar (Figure 5).

Sample ID	Site description	River	GPS coordinates	m a.s.l.	Sampling date	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	d (‰)
0 – 1	Some hundred m downstream Radonja source	Radonja	N 45°18'06.4" E 15°46'28.4"	177	27.10.2010	-10,45	-69,08	14,50
0 – 2	Muljava, about 100 m upstream hunting house	Muljava	N 45°19'03.8" E 15°46'53.9"	125	27.10.2010	-10,34	-68,71	14,03
0 – 3	Knežević Kosa, at bridge	Radonja	N 45°20'44.1" E 15°40'41.3"	131	27.10.2010	-10,15	-67,33	13,90
0 – 4	Tušilović, big bridge at the main state road D1	Radonja	N 45°22'25.1" E 15°36'38.4"	123	27.10.2010	-10,10	-65,68	15,16
0 – 5	Donji Budački	Budačka Rijeka	N 45°20'46.0" E 15°36'42.6"	130	27.10.2010	-10,16	-66,80	14,46
1 – 1	Zamost, at the bridge over Gerovč, at the road to Hrvatsko	Gerovčica	N 45°31'35.0" E 14°41'24.3"	299	10.11.2010	-8,19	-50,31	15,19
1 – 2	Road Zamost-Hrvatsko, near bridge over Kupe, upstr. of Čabr.	Kupa	N 45°31'29.4" E 14°42'00.3"	291	10.11.2010	-8,53	-53,39	14,86
1 – 3	Road Zamost-Hrvatsko, at the bridge over Kupa, upstr. from K.	Čabranka	N 45°31'32.9" E 14°41'57.5"	288	10.11.2010	-8,07	-46,86	17,73
1 – 4	Hrvatsko, parking place, Kupa downstream Čabr.	Kupa	N 45°31'59.9" E 14°42'06.8"	286	10.11.2010	-8,09	-47,50	17,25
1 – 5	Crni Lug, near the lake down of motel of N.P. Risnjak	Sovin Jarak	N 45°25'04.5" E 14°41'11.8"	667	10.11.2010	-8,23	-48,98	16,86
1 – 6	Mala Lešnica, road towards Kupica spring, at bridge	Kupica	N 45°26'20.7" E 14°51'06.9"	227	10.11.2010	-8,94	-55,64	15,89
1 – 7	Iševnica, at hydropower plant, ~50 m before inflow to Kpc.	Iševnica	N 45°27'00.2" E 14°51'13.3"	220	10.11.2010	-9,42	-59,02	16,32
1 – 8	Brod na Kupi, at Kupica-Kupa confluence	Kupica	N 45°27'49" E 14°51'22"	249	10.11.2010	-9,08	-56,17	16,50
1 – 9	Brod na Kupi, at Kupica-Kupa confluence	Kupa	N 45°27'53" E 14°51'22"	246	10.11.2010	-8,28	-49,33	16,89
1 – 10	Golik, downstream from Brod na Kupi	Kupa	N 45°28'22.2" E 14°52'55.6"	209	10.11.2010	-8,71	-50,84	18,85
1 – 11	Donja Dobra, bridge at beginning of road along Dobra	Dobra	N 45°26'54.4" E 14°58'38.7"	438	10.11.2010	-10,01	-65,30	14,77
1 – 12	Damalj, bathing place in front of weekend houses	Kupa	N 45°25'21.4" E 15°10'53.2"	152	10.11.2010	-9,08	-56,33	16,28
1 – 13	Prilišće, near the spring by Kupa River	Kupa	N 45°28'16.7" E 15°21'24.0"	127	10.11.2010	-9,02	-56,43	15,75
2 – 1	Letovanić, near the wooden church	Kupa	N 45°30'27.6" E 16°11'57.2"	95	11.11.2010	-9,32	-59,83	14,71
2 – 2	Odra (Sisačka), at bridge of main road Zagreb-Sisak	Odra	N 45°29'55.4" E 16°21'06.3"	96	11.11.2010	-9,46	-61,10	14,55
2 – 3	Sisak, downstream bridge, at the right bank	Kupa	N 45°28'43.8" E 16°22'18.6"	94	11.11.2010	-9,57	-62,00	14,57
2 – 4	Sisak, Zibel beach	Kupa	N 45°28'35.5" E 16°21'34.4"	96	11.11.2010	-9,72	-64,33	13,47
2 – 5	Petrinja, town beach	Kupa	N 45°26'40.6" E 16°16'07.4"	97	11.11.2010	-9,46	-61,59	14,12
2 – 6	Petrinja, about 100 m upstream town beach, near the bridge	Petrinjčica	N 45°26'34.5" E 16°16'18.1"	98	11.11.2010	-9,72	-65,82	11,95
2 – 7	Marinbrod, about 200 m from the main road	Glina	N 45°23'19.7" E 16°08'20.6"	102	11.11.2010	-9,88	-64,03	14,99
2 – 8	Glina, at the bridge, exit from Glina towards Topusko	Glina	N 45°20'10.1" E 16°04'58.9"	110	11.11.2010	-9,90	-66,38	12,85
2 – 9	Donje Taborište, at the bridge on the road Glina-Pokupsko	Golinja	N 45°27'08.1" E 16°00'12.6"	121	11.11.2010	-9,30	-61,89	12,54
2 – 10	Pokupsko, beach	Kupa	N 45°28'35.8" E 15°59'50.3"	101	11.11.2010	-9,45	-61,53	14,07

Table 2. Description of sampling sites with number of water sample (sample ID), GPS coordinates, elevation of sampling stations in m above sea level (a.s.l.), sampling date, and measured values of stable isotopes O-18 and H-2 as well as calculated deuterium-excess (d) from Kupa- and Rječina drainage basins.

2 – 11	Lijevo Sredičko, near Fishermen house	Kupa	N 45°31'54.6" E 15°53'22.5"	103	11.11.2010	-9,58	-61,58	15,06
2 – 12	Jamnička Kiselica, at bridge	Kupa	N 45°32'55.0" E 15°51'28.5"	104	11.11.2010	-9,55	-61,31	15,11
2 – 13	Donja Kupčina, at the road extension at Kupa-Kupa channel	Kupčina	N 45°32'00.5" E 15°47'26.3"	105	11.11.2010	-8,51	-58,96	9,11
2 – 14	Blatnica, at road extension	Kupa	N 45°31'00.9" E 15°43'59.6"	104	11.11.2010	-9,47	-60,77	14,96
2 – 15	Karlovac – Vodostaj, left Kupa bank, close to Korana inflow	Kupa	N 45°30'04.7" E 15°34'37.1"	106	11.11.2010	-9,31	-59,99	14,50
2 – 16	Brežani, at bridge	Utinja	N 45°28'33.0" E 15°41'33.0"	108	11.11.2010	-9,60	-64,82	12,01
3 – 1	Towards the Rječina source, about 2 km upstream Kukuljani	Rječina	N 45°24'34.5" E 14°25'29.5"	286	12.11.2010	-7,27	-42,07	16,09
3 – 2	Kukuljani, near the bridge and bus terminate	Rječina	N 45°24'08.8" E 14°25'04.0"	278	12.11.2010	-7,35	-42,53	16,31
3 – 3	Martinovo selo, at mill	Rječina	N 45°23'10.9" E 14°26'25.2"	256	12.11.2010	-7,29	-41,54	16,78
3 – 4	Pašac, under big artificial waterfalls	Rječina	N 45°21'26.5" E 14°26'52.2"	134	12.11.2010	-7,17	-40,47	16,91
3 – 5	Rijeka – Delta, parking	Rječina	N 45°19'32.7" E 14°26'53.4"	2	12.11.2010	-7,00	-41,00	15,01
3 – 6	Rijeka – Zvir (sample provided by water supply company)	Zvir	N 45°20'03.2" E 14°27'05.6"	8	12.11.2010	-6,82	-39,07	15,52
3 – 7	Vrbovsko – Kamačnik, Dobra upstream Kamačnik	Dobra	N 45°22'06.3" E 15°04'16.1"	379	12.11.2010	-10,22	-67,90	13,86
3 – 8	Vrbovsko – Kamačnik, Kamačnik before inflow to Dob.	Kamačnik	N 45°22'01.4" E 15°04'18.1"	380	12.11.2010	-9,77	-61,15	17,01
3 – 9	Vrbovsko – Kamačnik, Dobra downstream Kamačnik inflow	Dobra	N 45°22'00.8" E 15°04'24.0"	379	12.11.2010	-9,93	-63,24	16,17
3 – 10	Jurovo, beach	Kupa	N 45°37'36.0" E 15°18'11.4"	133	12.11.2010	-9,03	-57,76	14,51
3 – 11	Ozalj, beach upstream of hydropower plant	Kupa	N 45°36'54.3" E 15°28'24.8"	121	12.11.2010	-9,06	-58,00	14,49
4 – 1	Brodarci, at right bank, about 50 m upstream	Kupa	N 45°32'04.1" E 15°32'18.7"	117	16.11.2010	-9,27	-62,48	11,67
4 – 2	Priselci, near Donje Pokuplje, about 200 m before confluence	Dobra	N 45°33'07.2" E 15°31'11.7"	121	16.11.2010	-9,94	-66,02	13,52
4 – 3	Near Levkušje – Zorkovac road, on right river bank	Kupa	N 45°34'40.5" E 15°31'12.6"	121	16.11.2010	-9,13	-59,12	13,96
4 – 4	Grdun, beach at Papalina restaurant	Dobra	N 45°33'02.1" E 15°28'12.3"	127	16.11.2010	-9,92	-65,54	13,85
4 – 5	Gornje Stative, Držić's artificial waterfall	Dobra	N 45°30'01" E 15°27'18"	121	16.11.2010	-9,94	-65,27	14,24
4 – 6	Novigrad, at bridge	Dobra	N 45°28'39.4" E 15°26'56.1"	135	16.11.2010	-9,89	-66,07	13,09
4 – 7	Jarče Polje, at the source by the road towards Protulipa	Dobra	N 45°26'43.1" E 15°24'12.9"	139	16.11.2010	-9,83	-65,22	13,42
4 – 8	Lipa – Protulipa, downstream artificial waterfall	Dobra	N 45°24'28.6" E 15°23'37.0"	146	16.11.2010	-9,78	-64,64	13,59
4 – 9	Puškarić Selo, at mill, about 2 km upstream Đula abyss	Dobra	N 45°16'07.3" E 15°11'54.9"	345	16.11.2010	-9,68	-63,91	13,54
4 – 10	Sabljaci, in front of house no.10	Sabljaci Lake	N 45°13'54.9" E 15°13'43.5"	344	16.11.2010	-9,58	-63,76	12,87
4 – 11	Lešće, artificial waterfall near thermal bath, downstr. Lešće HP	Dobra	N 45°22'32.9" E 15°21'17.7"	167	16.11.2010	-9,76	-64,45	13,59
4 – 12	Zvečaj, at Zeleni kut restaurant	Mrežnica	N 45°22'47.8" E 15°25'24.1"	163	16.11.2010	-10,24	-68,93	13,02

Table 2. Continued.

4 – 13	Belavići, left bank, above waterfall, down pontoon bridge	Mrežnica	N 45°25'09.5" E 15°28'41.3"	145	16.11.2010	-10,34	-70,04	12,69
4 – 14	Belajske Poljice, under weekend houses	Korana	N 45°25'40.1" E 15°33'44.7"	141	16.11.2010	-10,25	-69,53	12,51
4 – 15	Mala Švarča, town beach	Mrežnica	N 45°27'42.5" E 15°31'39.1"	141	16.11.2010	-10,37	-69,89	13,10
4 – 16	Mostanje, about 1 km downstr. Mrežnica inflow, at new bridge	Korana	N 45°28'02.8" E 15°34'20.1"	139	16.11.2010	-10,26	-70,60	11,49
4 – 17	Mostanje, close to bridge over Korana, 100 m upstream inflow	Korana	N 45°27'51.4" E 15°33'57.9"	141	16.11.2010	-10,26	-69,56	12,48
4 – 18	Mostanje, at the bridge over Mrežnica, 100 m upstr. confl.	Mrežnica	N 45°27'57.4" E 15°33'35.3"	135	16.11.2010	-10,33	-70,33	12,31
4 – 19	Karlovac, Fogin's beach	Korana	N 45°29'05.0" E 15°33'35.6"	137	16.11.2010	-10,29	-69,95	12,36
5 – 1	Klinča Selo, near petrol station at bridge on D1 state road	Okićnica	N 45°41'24.4" E 15°43'40.5"	151	21.11.2010	-9,62	-64,47	12,49
5 – 2	Petrovinski Novaki, at the bridge on D1 state road	Volavčica	N 45°38'47.3" E 15°37'18.7"	137	21.11.2010	-9,43	-64,24	11,20
5 – 3	Čeglje, between two bridges near petrol station and mill	Kupčina	N 45°37'01.3" E 15°35'52.0"	135	21.11.2010	-9,93	-66,81	12,65

Table 2. Continued.

Figure 4. Overview of catchments presented in Figure 5 (Čabranka River; upper Kupa River west of Brod na Kupi) and in Figure 6 (upper Kupa River east of Brod na Kupi and Dobra River) (modified from ESRI, ArcGIS, National Geographic Map).

Upper Kupa River from Kupa Spring to Brod na Kupi

Kupa Rivulet originates at an altitude of 320 m a.s.l. west of village Razloge, and flows about five kilometres in northern direction through the forested Risnjak National Park until its junction with Čabranka River. Its $\delta^{18}O$ value of -8,53‰ at sampling point 1-2 indicates a significantly higher catchment from Gorski Kotar National Park (up to 1526 m a.s.l.), compared to Čabranka River. This influence of higher altitudes is also obvious at river sampling point 1-5 near Crni Lug in Gorski Kotar National Park, where a $\delta^{18}O$ value of -8,23‰ was measured, indicating water from higher altitudes of Risnjak National Park. The catchment of Kupica Spring is characterized by an oxygen isotopic composition ($\delta^{18}O$) of -8,94‰ (sample 1-6), and Kupica Rivulet down to Brod na Kupi, tributing Kupa

River, by δ^{18}O of -9,08‰ (sample 1-8). The water of Curak River (1-7) with a δ^{18}O value of -9,42‰ is a mixture of water from the karstified catchment of Skradski vrh, and surface run off from clastic Paleozoic formations south of Zeleni Vir, a complex discharge system, which was recently studied by Stadler (2011), and by Häusler & Stadler (2011). Water of Kupa River east of Brod na Kupi (sample 1-10) with a δ^{18}O value of -8,71‰ represents a mixture of river waters from all of the above described catchments at differing altitudes (Figure 5).

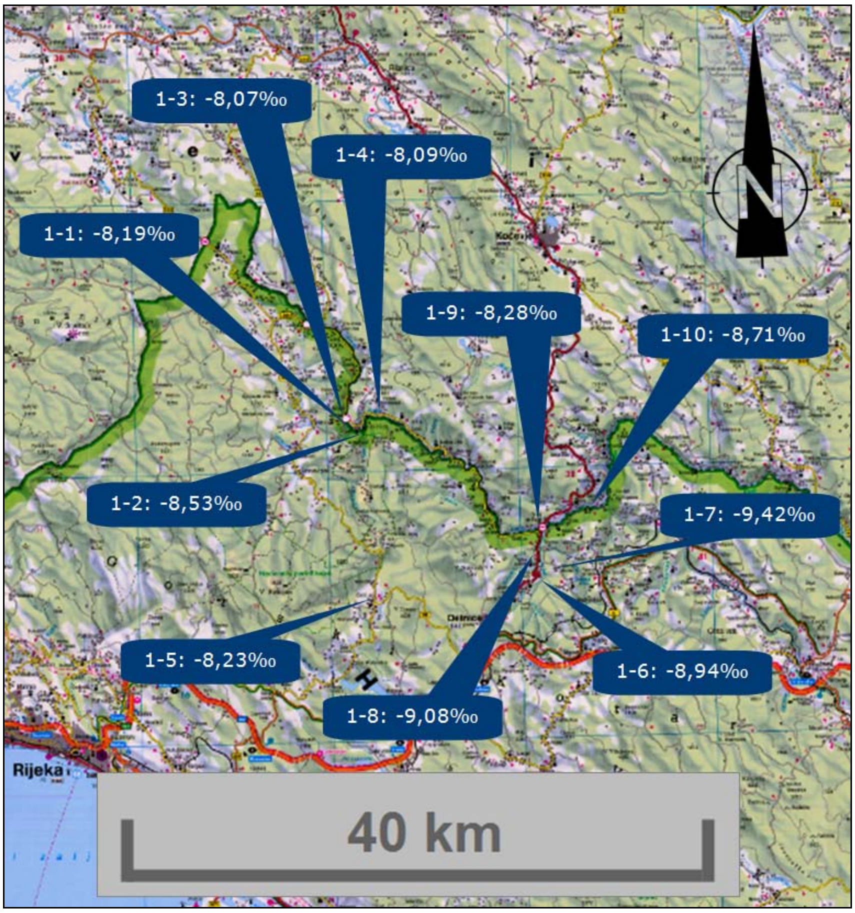

Figure 5. River water sampling locations and δ^{18}O values of lower Čabranka River and upper Kupa River near Brod na Kupi (modified from freytag & berndt, Croatia North 1:200.000).

Upper Kupa River from Brod na Kupi to Karlovac

After the mixture of Čabranka River with karst water from Kupica Spring and Kupa Spring its relatively high δ^{18}O values of -8,09‰ (sample 1-4) decrease along the distance of about 20 kilometres. After its confluence with Kupica River, the δ^{18}O value of Kupa River reaches -8,71‰ (sample ID: 1-10; Figure 6). Along its relatively long flow of about 130 kilometres down to Karlovac the isotopic composition of Kupa River does not change significantly. δ^{18}O values of -9,08‰ at 1-12 and -9,13‰ at sampling station 4-3, north of the confluence of Kupa River with Dobra River, lie within measurement accuracy. The inflow of Dobra River and Korana River, both rivers are characterized by δ^{18}O values lower than -10,0‰, leads to a decrease to -9,31‰ in Kupa River water east of Karlovac (sample 2-15).

Dobra River

The lowest δ^{18}O value (-11,01‰) of the about 100 km long Dobra River was found in its upper part northeast of Skrad (sample location 1-11), and -10,22‰ south of Vrbovsko (sample ID: 3-7), where the recharge area in eastern Gorski Kotar rises up to an elevation of 960 m (Ostri vrh), and 1000 m at Crna kosa, respectively. The δ^{18}O values of Dobra River then increase downstream to Ogulin with differing (mixture) values ranging between -9,93‰ to -9,68‰ (samples 3-8, 3-9 and 4-9). The water sample from the northern end of the artificial Sabljak Lake (4-10) with -9,58‰ indicates no significant evaporation effect. After the subsurface flow of Dobra River northeast of Ogulin, some 40 kilometres down to Kupa River (samples 4-11 to 4-2), the $\delta^{18}O$ values of Dobra River range between -9,76‰ and -9,94‰ (Figure 6).

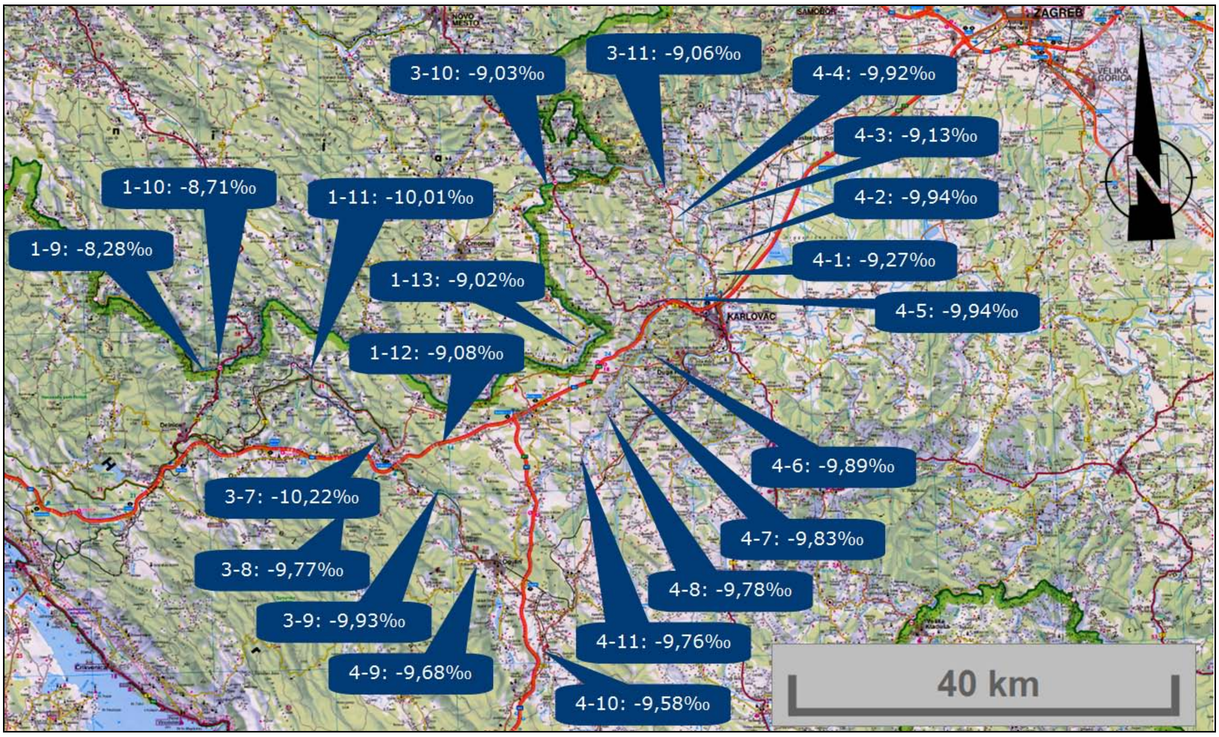

Figure 6. River water sampling locations and $\delta^{18}O$ values of upper Kupa River from Brod na Kupi to Karlovac, and sampling stations along Dobra River (modified from freytag & berndt, Croatia North 1:200.000).

Figure 7 gives a general map of the sampling area in the lower part of the Kupa Basin. In order not to overburden the figures with data of stable isotopes, two maps at original scale 1:200.000 were drawn, one for isotopic values of Kupa catchment north of Karlovac, also comprising Korana River, Mrežnica River and Utinja-Golinja catchment (Figure 8), and another for $\delta^{18}O$ values of river water sampled along Kupa River from Karlovac down to Sisak (Figure 9).

The Žumberak/Samobor catchment and discharge from depression Draganićka šuma to Kupa River

Many small rivers discharge the Žumberak/Samobor catchment, and flow into the depression of Draganićka šuma. Artificial channels only discharge this depression tributing Kupa River to the south. The recharge areas of these smaller rivers, such as Konšćica (sample ID: 5-1), upper Volavčica (5-2), and Kupčina (5-3) lie in the southern hills of Žumberačka- and Samoborska gora (Figure 8). The altitude of this mountain range west of Samobor varies between 200 and 300 metres, with its maximum elevation at 879 m. These river waters are characterized by relatively low $\delta^{18}O$ values ranging between -9,43‰ and -9,93‰. Waters from channels discharging the depression of Draganićka šuma were not measured, but the $\delta^{18}O$ value of -8,51‰ represents a mixture of Brebernica River water and Kupa-Kupa channel water (sample 2-13), and indicates a lower recharge area compared to the river waters discharging Žumberačka- and Samoborska gora.

Mrežnica River

Mrežnica River is about 60 kilometres long and tributes Korana River south of Karlovac. The $\delta^{18}O$ values of lower Mrežnica River (sample locations 4-12, 4-13 and 4-15; Figure 8) range between

-10,37‰ and -10,24‰ (which is within the measurement accuracy). Mrežnica River discharges a highly karstified hilly area north of Mala Kapela, the altitudes of which do not exceed 600-900 metres.

Figure 7. Overview of catchments presented in Figure 8 (upper Kupa River, Korana River, Mrežnica River, Utinja-Golinja catchment) and in Figure 9 (lower Kupa River) (modified from ESRI, ArcGIS, National Geographic Map).

Korana River

The about 130 kilometres long Korana River, with its very big and karstified catchment, tributes Kupa River south of Karlovac. The relatively very low $\delta^{18}O$ values of the Korana catchment, namely -10,45‰ to -10,10‰, are representative for smaller tributary rivers (station: 0-1 to 0-5; Figure 8), such as Radonja River and Trupinjska River, which discharge the mountain range bordering Bosna i Herzegovina rising up to altitudes of 400 meters only. The southernmost catchment west of Plitvice lakes rises up to 1279 m (Seliški vrh), however.

Lower Kupa River from Karlovac to Sisak

At a distance of about 140 kilometres Kupa River meanders from Karlovac (112 m a.s.l) down to Petrinja (104 m a.s.l.) through the hilly region of Vukomeričke Gorice, and the Utinja-Glina-catchment, the altitudes of which do not exceed 200-400 metres. Larger rivers mainly tribute Kupa River from the south, namely Dobra-, Mrežnica-, Glina- and Petrinjčica River. Due to the inflow of rivers discharging mountain ranges at different altitudes, the $\delta^{18}O$ values of Kupa River water at that distance (sample locations 2-14, 2-12, 2-11, 2-10, 2-1, 2-5; Figure 9) vary differently ranging from -9,58‰ to -9,32‰ downstream. The higher $\delta^{18}O$ values of Kupa River water between station 2-12 (-9,55‰) and 2-11 (-9,58‰), southeast of the Draganićka šuma depression, result from a bigger amount of inflow from a (northern) recharge area at lower altitudes, for which the Brebernica River is taken as an example (compare to sampling location 2-13).

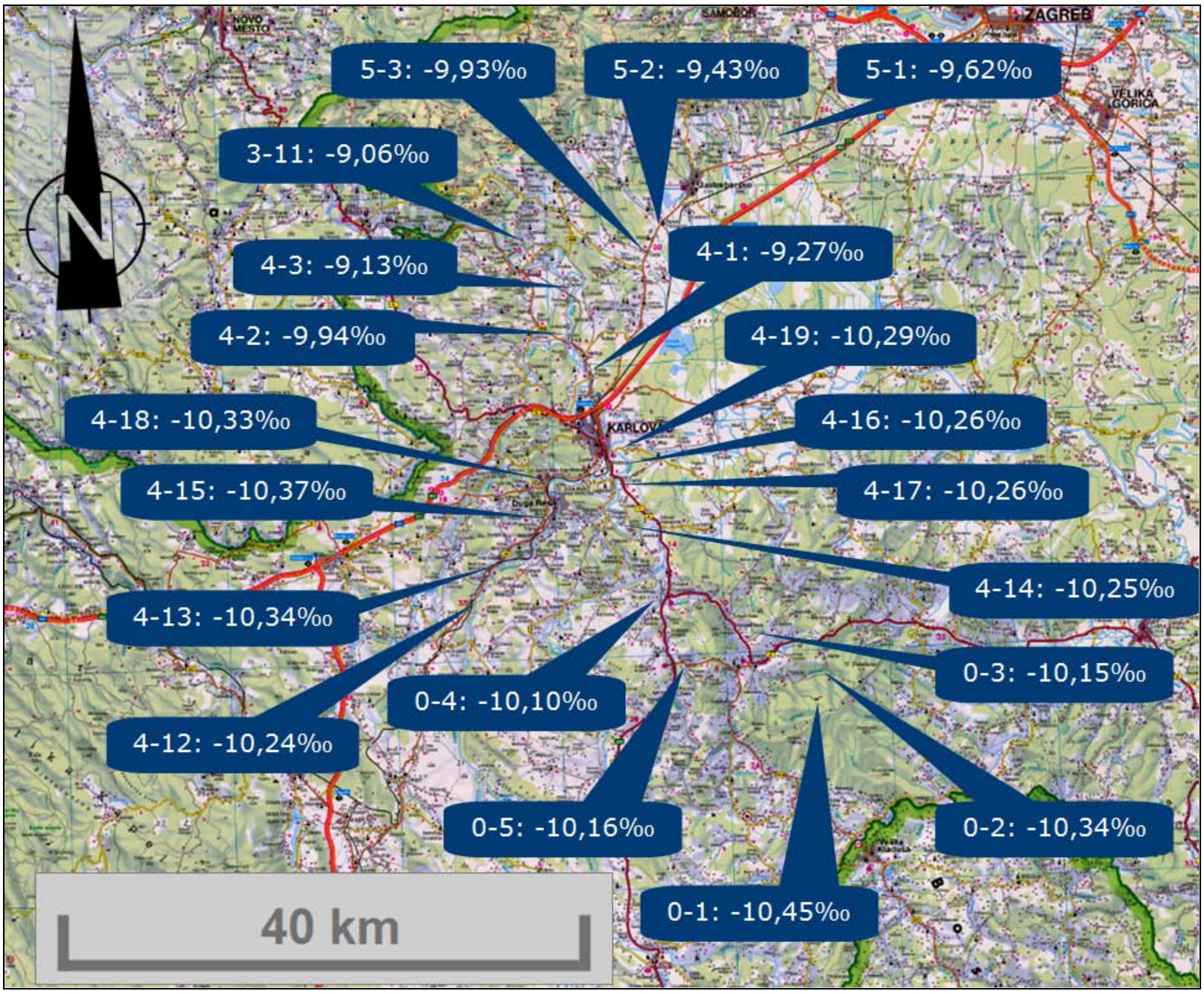

Figure 8. River water sampling stations and $\delta^{18}O$ values north of Karlovac, of Korana River, Mrežnica River, and of Utinja-Golinja catchment (modified from freytag & berndt, Croatia North 1:200.000).

Utinja-Golinja catchment

From the relatively big catchment between Utinja River in the west and Golinja River in the east, the water from Golinja River sampled close to Donje Taborište (sample 2-9) with -9,30‰ is representative for the hilly catchment of an elevation up to 220 m, whereas the water from Utinja River sampled close to its confluence with Kupa River (sample 2-16) with -9,60‰ is representative for the hilly catchment of an elevation up to 380 m (Figure 9).

Petrinjčica River

The Petrinjčica Valley is north-south oriented with a catchment situated in the 400 up to 700 m high mountain range of Zrinski Gora. The $\delta^{18}O$ value of -9,72‰ of the river water sampled close to the confluence with Kupa River at Petrinja (ID: 2-6) indicates a relatively higher recharge area (Figure 9).

West of the confluence of Kupa with Sava River (Figure 9) the $\delta^{18}O$ values of Kupa River range between -9,46‰ (sample 2-2) and -9,72‰ (sample 2-4). This variation probably represents different mixtures of river water with relatively higher $\delta^{18}O$ values (-9,46‰) west of Petrinja compared to the inflow of tributary rivers from the south with lower values of Petrinjčica River south of Petrinja (-9,72‰) the waters of which probably were mixed downstream.

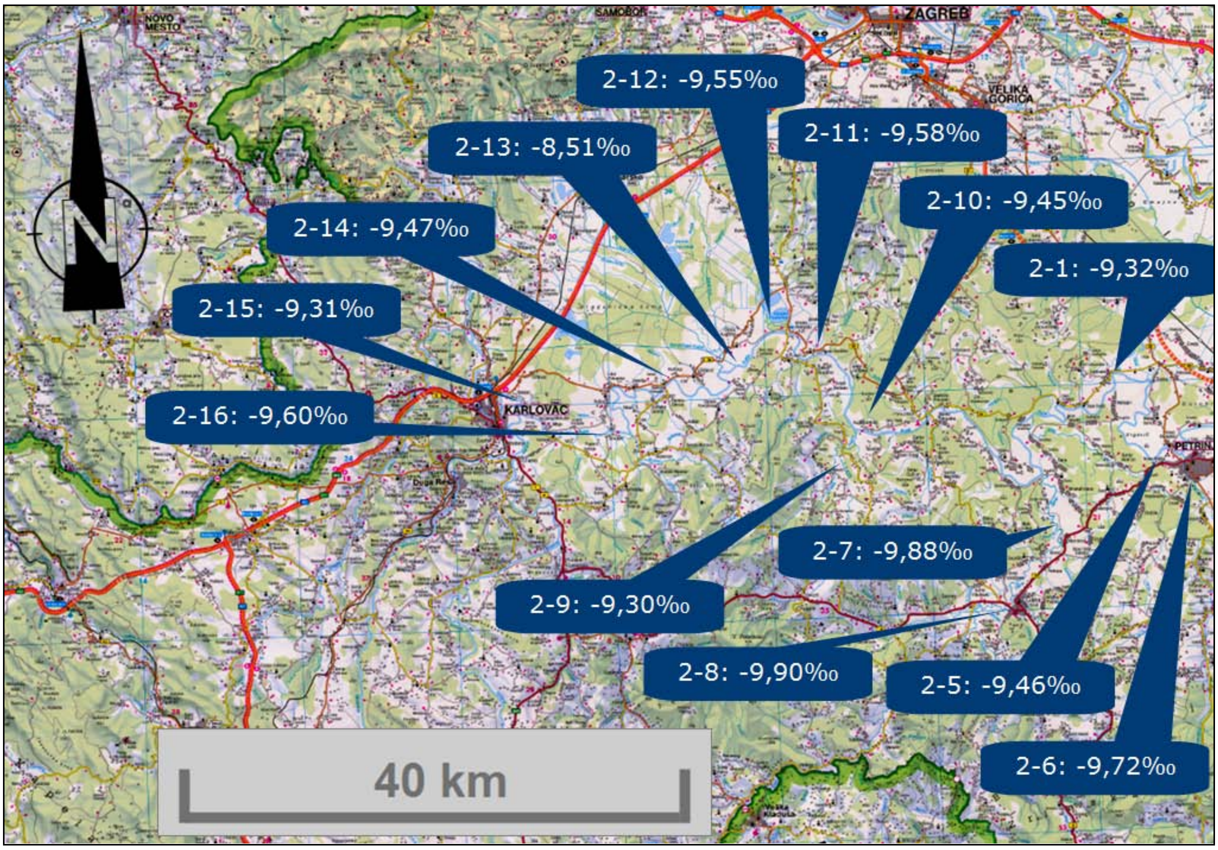

Figure 9. River water sampling stations and $\delta^{18}O$ values of lower Kupa River from Karlovac to Sisak (modified from freytag & berndt, Croatia North 1:200.000).

In Figure 10 the sub-basins of the Kupa River are delineated according to their orographic and hydrogeologic catchment respectively. The drainage pattern clearly reveals that the entire western catchment of Kupa River is characterized by karstified hills, where subsurface run off prevails. Therefore we only roughly can draw the borders between the upper catchments of Dobra-, Mrežnica - and Korana River. The upper catchment of Kupa River borders Čabranka-, Dobra- and Žumberak-Samobor catchment.

5 Discussion and recommendation

We interpret isotope ratios considering the geologic conditions, relief, and the effects of both more maritime and more continental influence on the isotopic composition of precipitation water in the Kupa Basin. Despite the fact that the recharge areas for Dobra River, Mrežnica River and Korana River in the Velika Kapela do not exceed 900 metres in elevation, their $\delta^{18}O$ values are lower (below -10,0‰) than those of Kupa- and Kupica catchment, the elevation of which exceeds 1600 metres in the Gorski Kotar ($\delta^{18}O$ values ranging from -9,0‰ to -8,5‰). Considering the altitude effect of oxygen isotope fractionation, the very low isotopic values should represent the highest recharge areas (of up to 2000 m), which is not the case for Dobra-, Mrežnica-, and Korana River catchment. The reasons for low $\delta^{18}O$ values of rivers tributing lower Kupa River south of Karlovac are probably continental effects, either gradual rainout from the clouds on the way from the coast over the mountain ranges or the influence of continental air masses as has been generally recorded at the Zagreb meteorological station (see Vreča et al., 2006, fig. 4), resulting in a shift to lower values. Southwest of Petrinja smaller rivers tribute Kupa River from the south, such as Utinja River (sampling site: 2-16), Maja River (2-8), and Petrinjčica River (2-6), which discharge the mountain range Zrinska gora, the altitudes of which range between 450 and 590 metres. The $\delta^{18}O$ values of river waters in these smaller sub-basins range between -9,90‰ (2-8) and -9,30‰ (2-9). Considering the lower vertical gradient of stable isotopes in the catchment east of Karlovac, these drainage basins probably are influenced by more continental precipitation.

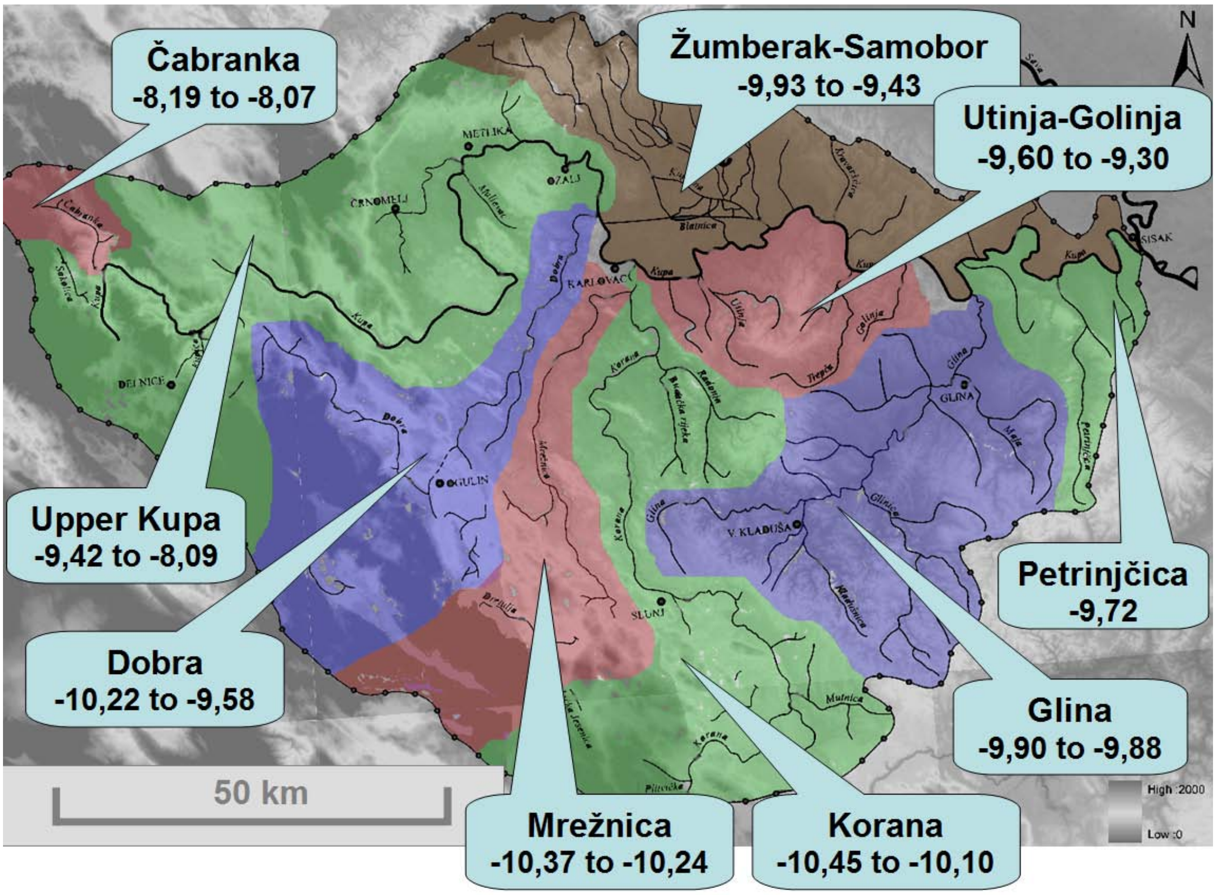

Figure 10. Distribution of isotope values δ^{18}O in river waters of the sub-basins of Kupa catchment (modified from Frančišković-Bilinski et al., 2005; digital elevation model courtesy of NASA: asterweb.jpl/nasa.gov).

To sum up, we interpret the oxygen isotopic composition of the high part of the catchment of the upper Kupa River, comprising Čabranka River and its smaller tributaries down to Karlovac with higher δ^{18}O-values of river waters, as predominantly influenced by maritime precipitation from the Kvarner Bay. The catchment of lower Kupa River and its tributaries, from Karlovac down to Sisak, and also the southern catchment of Dobra- and Korana River predominantly are influenced by precipitation out of more continental (humid) air masses. This more continental influence does not necessarily imply precipitation out of drier air masses from the continental side but may also be the result of rainout influences on the isotopic composition of primary maritime air moisture. The high values of the deuterium-excess of Kupa River waters (d = 11‰ to 17‰) are similar to those reported by Vreča et al. (2006, tab. 2) for the station Zavižan – Mt. Velebit (d = 12‰ to 17‰) and disagree with those of the station Zagreb-Grič (d = 7‰ to 10‰). We therefore conclude that precipitation from the Adriatic side predominantly charges both karst water and river water of the Kupa catchment.

For a more sound interpretation of oxygen isotope ratios of river waters in the Kupa Basin the knowledge of the seasonal variations of the isotopic composition of precipitation water in the recharge area, as well as of river waters at various sampling sites downstream is necessary. To obtain a better knowledge on the seasonal variation we therefore recommend setting up a monitoring network comprising precipitation stations, spring waters and river waters in the Kupa drainage basin.

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