Hydrogeological relations in the northern part of the Croatian Dinaric karst with a recent erosion base

Boljat, Ivana

University of Zagreb

Faculty of Mining, Geology and Petroleum Engineering

Ivana Boljat

HYDROGEOLOGICAL RELATIONS IN THE NORTHERN PART OF THE CROATIAN DINARIC KARST WITH A RECENT EROSION BASE

DOCTORAL DISSERTATION

Zagreb, 2024

University of Zagreb

Faculty of Mining, Geology and Petroleum Engineering

Ivana Boljat

HYDROGEOLOGICAL RELATIONS IN THE NORTHERN PART OF THE CROATIAN DINARIC KARST WITH A RECENT EROSION BASE

DOCTORAL DISSERTATION

Supervisors:

Prof. Željko Duić, PhD

Josip Terzić, PhD

Zagreb, 2024

Rudarsko-geološko-naftni fakultet

Ivana Boljat

HIDROGEOLOŠKI ODNOSI U SJEVERNOM DIJELU HRVATSKOGA DINARIDSKOG KRŠA S RECENTNOM BAZOM OKRŠAVANJA

DOKTORSKI RAD

Mentori:

Dr. sc. Željko Duić, redoviti profesor

Dr. sc. Josip Terzić, znanstveni savjetnik u trajnom zvanju

Zagreb, 2024

Supervisors:

Prof. Željko Duić, PhD

University of Zagreb Faculty of Mining, Geology and Petroleum Engineering

Department of Geology and Geological Engineering

Josip Terzić, PhD

Croatian Geological Survey

Department of Hydrogeology and Engineering Geology

ACKNOWLEDGMENTS

Zahvaljujem…

….mentoru dr.sc. Josipu Terziću, na predloženoj temi, uspostavi istraživanja, neizmjernoj podršci, stručnom vodstvu, prenesenom znanju i povjerenju tijekom cijele suradnje

…mentoru dr.sc. Željku Duiću, na prihvaćanju mentorstva, usmjeravanju, podršci, i brojnim konstruktivnim savjetima tijekom izrade ovog rada

…članovima povjerenstva dr.sc. Jeleni Parlov, dr.sc. Kristijanu Posavcu i dr.sc. Jasmini Lukač Reberski na ekspeditivnom čitanju, korisnim savjetima i korekcijama rada

…dr.sc Renatu Buljanu i dr.sc. Tončiju Grgasoviću na velikoj pomoć pri upoznavanju područja istraživanja, terenima i ustupljenoj literaturi

…Ani Selak na brojnim terenima i dragocjenoj pomoći tijekom izrade disertacije, dr.sc. Maji Briški i dr.sc. Tamari Marković na provedenim laboratorijskim analizama, Tomislavu Novoselu, Nedjeljku Staniću, Hrvoju Buriću i Josipu Kolariću na terenskim istraživanjima, dr.sc. Andreju Stroju na konstruktivnim diskusijama, kolegama Ivanu Kosoviću, Matku Patekaru, Kosti Urumović, Staši Borović i Marcu Poli na moralnoj podršci

…svim kolegama koji su na bilo koji način pomogli pri izradi ovog rada

…Zavodu za hidrogeologiju i inženjersku geologiju na financijskoj i materijalnoj podršci

…kolegama s projekta CAMARO-D, posebno dr.sc. Barbari Čenčur Curk na prikupljanju i standardizaciji podataka

…djelatnicima Hrvatske elektroprivrede, prvenstveno gospodinu Milanu Sabljaku na velikom povjerenju, financijskoj potpori i ustupljenim podacima bez kojeg ne bi bila moguća izrada ovog rada

… Državnom hidrometeorološkom zavodu na ustupljenim podacima

…kolegici i prijateljici Jasmini na velikoj podršci, beskonačnom vremenu i brojnim savjetima tijekom istraživanja i izrade rada

…svojim najdražima Andreu i Marti, mami, tati, sestri, Darrenu, Mariji i Eliju na velikom strpljenju, pomoći, vremenskom odricanju, razumijevanju i ogromnoj podršci

ABSTRACT

A wide variety of reliefs and transition zone between deep and shallow karst distinguishes northern Dinaric Croatian karst, characterised by abundant and valuable water resources, and belongs to the Black Sea basin. A good understanding of hydrogeological properties, dynamics, intrinsic groundwater vulnerability, and anthropogenic impacts is crucial for the sustainable management and protection of such immense and heterogeneous karst systems. In this Ph.D. thesis, karst catchments are characterised through the determination of hydrochemical water properties, analysis of recharge processes, time series and hydrograms, and the identification and assessment of potential anthropogenic impacts on groundwater.

Spatial analyses of the water quality indices for surface water and groundwater were carried out in a GIS environment, and a detailed assessment of man-made hazards was conducted based on recommendations of COST Action 620. The produced maps offer insights into the qualitative status of water resources at a regional scale by indicating areas of potential negative impacts of land use, highlighting both point and diffuse sources of pollution. Higher values of the water quality indices for surface water and groundwater are observed in lowland areas, karst plateaus and poljes, where the impacts of anthropogenic activities such as agriculture and quarries take place on karstified permeable carbonate rocks. Hazard assessment showed how transport infrastructure induces a low hazard level. Based on the findings, hydrogeological researches were conducted in the narrowet research area, including the catchment areas of the Dobra, Mrežnica and Slunjčica Rivers.The main results and conclusions from the conducted hydrogeological, hydrochemical, and isotopic research are as follows: (I) the aquifers across Kapela Mt. mainly drain limestones; (II) water–rock interaction and carbonate weathering are significant contributors to water geochemistry; (III) there is a human impact on the Gojak and Tounjčica spring waters; (IV) the mean residence time of water in the observed aquifer is up to 1.5 years; (V) the new local meteoric water line (LMWL) was calculated for Kapela Mt. based on a three-year dataset (June 2018 – May 2021); (VI) in the north Dinaric karst, the predominant origin of precipitation is from the Mediterranean air mass; (VII) Velebit Mountain strongly influences the precipitation isotopic composition in the study area; (VIII) the deep karst zone is less developed than the shallow karst zone; (IX) groundwater exchange is significantly faster in shallow karst; (X) groundwater divides in the Kapela Mountain are zonal; (XI) the homogenisation of groundwater occurs during periods of high water levels; (XII) fast water exchange transpires without concurrent groundwater temperature homogenisation; and (XIII) the boundary between deep and fluviokarst in Croatia was defined.

This comprehensive regional-scale study is the first of its kind in this area. Although a regional study of the Kupa River catchment was conducted by Bojanić in 1972, it was limited by the instruments and methods available at that time. Previous research, made for the construction of hydrotechnical and water supply objects, was of local character and conducted only under specific hydrological conditions. For instance, around 20 tracer tests were carried out in the investigated area, but most of these date back to 1980 and should be critically reassessed and, if possible, conducted again under different hydrological conditions using more advanced *in situ* equipment and higher-resolution laboratory instruments.

PROŠIRENI SAŽETAK

Najsjeverniji dio dinaridskog krša u Republici Hrvatskoj pripada Crnomorskom slijevu, i do sada nije bio predmet detaljnih regionalnih hidrogeoloških istraživanja. Prostire se preko masiva Kapele na jugozapadu pa sve do Karlovca na sjeveroistoku i kondicira se sa slijevom rijeke Kupe. Hidrogeološki odnosi rezultat su kompresijske tektonike (**Tari, 2002**) i prirodno su vrlo zamršeni. Riječ je o prijelaznoj zoni dubokog krša u takozvani plitki krš ili fluviokrš.

Područje dubokog krša predstavlja planinski prostor Kapele i Gorskog kotara koji je zastupljen pretežito tektonski razlomljenim vapnencima i dolomitima s velikom pukotinskom poroznošću. Razvoj krških formi u mezozojskoj stijenskoj masi rezultira rijetkim, povremenim površinskim tokovima. Zbog velikog volumena okršenih kanala i pukotina, okršena stijenska masa može uskladištiti značajne količine vode, te ima veliki potencijal akumulirane vode u podzemlju. Izvori su povremeni, ili s velikim oscilacijama u izdašnosti, tipični krški. Nailaskom na dolomitnu barijeru vode izviru na površinu i formiraju vodene tokove duž krških polja, koji poniru u zoni plitkog krša te ponovo izviru nakon 5 do 15 km na stotinjak metara nižoj krškoj zaravni, kao niz izdašnih krških izvora. U zoni plitkog krša ili fluviokrša baza okršavanja relativno je poznata i vezana je uz erozijske baze kordunskih rijeka – Kupu, Koranu, Mrežnicu i Dobru. Sredinom prošlog stoljeća granica prijelaza dubokog u plitki krš deskriptivno je opisana (**Bahun, 1968**), a obilježena je velikim krškim izvorima kordunskih rijeka. U ovom je radu, na temelju detaljne analize prethodno izvedenih hidrogeoloških istraživanja (prvenstveno trasiranja), te provedenih statističkih analiza, utvrđeno da se vodonosnici planinskog masiva i vodonosnici podno krških polja bitno razlikuju. Stoga je zona razdvajanja između plitkog i dubokog krša pomaknuta na zapad, neposredno podno masiva Kapele (**Boljat et al., 2024a**). Promatrano područje najokršeniji je dio dinaridskog krša na prostoru RH prema gustoći ponikvi (**Pahernik 2012**).Trijaske vodonepropusne klastične stijene znatno su manje zastupljene, ali njihova raspodjela ima važan utjecaj na prostorni raspored vodnih pojava. U zasebnu kategoriju ulaze naslage kvartarne starosti, koje ispunjavaju krška polja i ponikve, nastale erozijskim procesima karbonatnih i klastičnih stijena. Propusnost ovih naslaga ovisna je o litološkom sastavu, debljini, tektonskoj poremećenosti, a njihova hidrogeološka funkcija ovisi i o hipsometrijskom i strukturnom položaju.

Hidrogeološki odnosi u promatranom krškom sustavu u velikoj su mjeri izmijenjeni ljudskim intervencijama, uglavnom vezanim uz hidroenergetiku. Jezera, brane, kanali i tuneli već desetljećima utječu na inicijalne hidrogeološke odnose te se danas mogu smatrati nultim stanjem ovog terena. Ukratko, 1959. godine na širem području Ogulina izgrađena je i puštena u pogon HE Gojak. Za svoj rad koristi vode Ogulinske Dobre i Zagorske Mrežnice. Nizvodno od izvora Zagorske Mrežnice izgrađena je brana visine 9 m, kojom je formirano jezero Sabljaci. Iz jezera voda se hidrotehničkim tunelom voda provodi u slijev Ogulinske Dobre do akumulacije Bukovnik i dalje do HE Gojak. Tim zahvatom se bitno smanjuje prihranjivanje rijeke Mrežnice preko njene glavne pritoke Tounjčice i preusmjerava u slijev rijeke Dobre. 2010. godine nizvodno od HE Gojak, izgrađena je vršna HE Lešće čija brana radi 12 km dug uspor na rijeci Dobri. Potencijal proizvodnje električne energije pokušat će se dodatno povećati retencijom u Drežničkom polju kojom se planira produžiti zadržavanje vode u slijevu Sabljaka, izgradnja je započela 2021. godine.

Ciljevi istraživanja bili su (i) hidrokemijskim i izotopnim metodama okarakterizirati područje istraživanja, odrediti srednje vrijeme zadržavanja i nadmorske visine područja prihranjivanja izvora, (ii) utvrditi nulto stanje dinamike sustava kao temelj za praćenje utjecaja novih hidrotehničkih zahvata unutar područja istraživanja, (iii) unaprijediti metodologije za istraživanje regionalnih krških sustava, s naglaskom na definiranje zone prelaska dubokog u plitki krš ili fluviokrš, (iv) izrada konceptualnog modela grupiranja izvora u zajedničke slijevne površine prema dinamičkim i hidrokemijskim značajkama. U skladu s navedenim su postavljene sljedeće hipoteze: (i) korištenje prostora i hidrogeološke značajke vodonosnika izravno utječu na kakvoću podzemnih voda u kršu, (ii) izvori istraživanog područja mogu se grupirati prema dinamičkim i hidrokemijskim značajkama u zajedničke podsljevove, (iii) prosječno zadržavanje podzemnih voda u vodonosnicima istraživanog područja dinaridskog krša je manje od dvije godine, i (iv) iz razlike sadržaja stabilnih izotopa kisika i vodika u oborinama mogu se izdvojiti utjecaji mediteranskih i kontinentalnih oborina koje napajaju izvorske vode istraživanog područja.

Prije uspostave hidrogeoloških istraživanja u okviru ovog rada, za cijelo područje slijeva rijeke Kupe, uključujući i područje u Republici Sloveniji, prikupljeni su i obrađeni svi dostupni literaturni i prostorni podatci, podloge, analize te točkasti i linijski podaci koji imaju ili mogu imati utjecaj na vodonosnik. Na temelju rezultata analiza prikupljenih podataka (1) uspostavljeno je hidrogeološko istraživanje u središnjem dijelu područja i (2) izrađena je regionalna karta ranjivosti i hazarda za krško područje slijeva rijeke Kupe u Republici Hrvatskoj i Sloveniji (**Selak et al., 2020**).

Karta ranjivosti temelji se na izračunu Indeksa kvalitete podzemne vode (WQIgw) prema metodi uspostavljenoj u projektu CC-WARE (**Čenčur Curk et al., 2014**) i karta hazarda prema COST620 metodi (**Zwahler, 2004**). WQIgw dobiven je izračunom hidrogeoloških parametara, parametara načina korištenja pokrova i koeficijenta efektive infiltracije, dok je karta hazarda bazirana na identifikaciji mjesta mogućih opasnosti s procjenom utjecaja i rizika.

Područje istraživanja u kojem je uspostavljeno hidrogeološko istraživanje obuhvaća sljevove rijeka Dobre, Mrežnice i Slunjčice. Sjevernu granicu područja istraživanja definira razvodnica neposrednog slijeva rijeka Kupe i Dobre, zapadna se podudara s razvodnicom Jadranskog i Crnomorskog slijeva, južna se proteže od Plitvičkih jezera do Slunja, dok istočnu definiraju izvori rijeka Donje Dobre, Mrežnice i Slunjčice, odnosno prijelazna zona dubokog krša u plitki krš ili fluviokrš.

S ciljem definiranja krškog hidrogeološkog sustava područja koje se istražuje, uspostavljen je trogodišnji hidrološki i hidrokemijski monitoring, koji uključuje i monitoring stabilnih izotopa vode. U tu svrhu, postavljen je sakupljač oborina te na 7 lokacija automatski mjerači razina, elektolitičke vodljivosti i temperature. Također, prikupljeni su meteorološki i hidrološki podaci Državnog hidrometerološkog zavoda Republike Hrvatske i Hrvatske elektroprivrede te podatci o kakvoći voda koja se koristi u vodoopskrbi. U sklopu ove disertacije obrađeni su podatci prikupljeni na 8 izvora.

Krški dio slijeva rijeke Kupe klasificiran je u 5 klasa prema indeksu kvalitete podzemne vode. Zbog rijetke naseljenosti i slabe ljudske aktivnosti oko 95% površine nema negativni utjecaj na podzemnu vodu. Na području istraživanja nisu zabilježeni hazardi visoke opasnosti. Identificirani su hazardi srednje opasnosti u koje su uvrštena naselja bez kanalizacije, prometne trase, industrija, odlagališta otpada, te nisko rizični s poljoprivredom kao glavnim hazardom. Statistički gledano upotreba prostora sjevenog dinaridskog krša u vrlo malom postotku utječe na kvalitetu podzemne vode, no utvrđeno je da je područje izrazito okršeno i da se potencijalni onečišćivači vrlo brzo mogu infiltrirati u podzemlje i pojaviti na izvorima u roku od tri četiri dana na izvorima podno Kapele, odnosno od par sati do maksimalno dva i pol dana na izvorima podno Ogulinskog polja, ovisno o hidrološkim uvijetima.

Sjeverni dinaridski krš u Hrvatskoj razlikuje se od ostatka dinaridskog krša po dubini okršavanja i dubini cirkulacije podzemne vode kroz vodonosnik. U području istraživanja izdvojene su dvije zone koje se razlikuju prema navedenom kriteriju, zona dubokog krša u kojem su krški sustavi razvijeni do dubine od nekoliko stotina metara i zona plitkog krša ili fluviokrša u kojem je okršavanje maksimalno razvijeno do dubine od 200 metara, odnosno do erozijske baze kordunskih rijeka. Analize kroskorelacija, recesijskih krivulja i rezultati trasiranja ustvrdili su 10 puta brži protok vode u zoni plitkog krša nego u zoni dubokog krša odnosno u vodonosnicima razvijenim u planinskom masivu Kapele. U sklopu disertacije kritički su sagledana povijesna trasiranja i objašnjeni su kontradiktorni rezultati. Izrađen je konceptualni model područja istraživanja u vrijeme niskih i visokih voda i objašnjeno je različito kretanje podzemne vode ovisno o hidrološkim uvijetima u slijevu.

Hidrokemijskim analizama utvrđen je razvoj krških vodonosnika dominantno u vapnencu s manjim udjelom dolomita bez kontakta s drugim vrstama stijena. Izvori pitke vode imaju izrazito kvalitetnu vodu sa zanemarivim ljudskim pritiskom. Ljudski pritisak zabilježen je na izvorima u zoni plitkog krša, odnosno nizvodno od krških polja.

Konstruirana je nova meteorska linija vode za planinu Kapela na temelju trogodišnjeg seta podataka prikupljenih u mjecečnim intervalima u periodu od lipnja 2018 godine do svibnja 2021 godine. Na temelju prostorne raspodjele stabilnih izotopa kisika i vodika u izvorskim vodama konstatiran je značajan kontinentalan efekt oborinskih voda na jugu područja. Razvijeni reljef planinskog masiva Velebita utječe na osiromašenje oborine težim izotopima kisika i vodika koja dolazi s prostora Mediterana. Izračunato je prosječno zadržavanje vode do godine i pol u planinskom masivu Kapele, odnosno do godine dana u vodonosnicima nizvodno od krških polja.

KEYWORDS:

karst hydrogeology

time series analysis

hydrochemistry

stable isotopes

retention time

groundwater endangerment,

deep-to-shallow karst transition zone

Kapela Mountain

Ogulin polje

KLJUČNE RIJEČI:

krška hidrogeologija

vremenske serije

hidrokemija

stabilni izotopi

vrijeme zadržavanja

ugroženost podzemne vode

zona razdvajanja dubokog i plitkog krša

masiv Kapela

Ogulinsko polje

CONTENT

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

1.1 General background

Due to its horseshoe shape, Croatia has an extremely long national border, leading to numerous cross-border aquifers. The abundant aquifers in Croatia's northern Dinaric karst region are uniquely unaffected by neighbouring countries, contributing to their high groundwater quality. Hence, the aquifers across Kapela Mtn. and the Gacka River catchment area have been declared a first-degree strategic drinking water reserve (Water Management Strategy 2008, Croatian Parliament).

The aquifers across and downstream of Kapela Mtn. are primarily impacted by anthropogenic activities such as the exploitation of hydropower. For decades, accumulations, ditches, tunnels, and dams have altered the initial intrinsic hydrogeological relations, and nowadays, these modifications are considered the baseline condition of the area (**Bonacci and Andrić, 2010; Buljan et al, 2019**). In 1959, the hydropower plant HPP Gojak was built in the vicinity of Ogulin, and it utilises the waters of two rivers, Ogulin Dobra and Zagorska Mrežnica. The hydropower plant and accompanying constructions caused significant changes in hydrogeological and hydrological settings. The HPP Lešće, on Dobra River near Lešće settlement, was put into operation in 2010. The hydropower potential will be additionally exploited as the construction of retention at Drežnica polje started in 2021 (**Buljan et al., 2019**).

Furthermore, the ongoing revitalisation of a ski resort, hotel settlement, and sports-recreation centre of the Croatian Olympic Centre Bjelolasica could cause additional pressure on the strategically crucial hydrogeological system and the water quality. The main water management challenge in the northern karst region of Croatia involves addressing the water supply issues faced by the municipalities Plitvička Jezera and Rakovica. Currently, this area relies on surface water intake from the lakes, a practice which is unsustainable for the dynamics of natural system and drinking water quality. Plans are underway to construct a water intake at Lička Jesenica watercourse. However, a final solution has not yet been reached due to discrepancies between experts and policymakers.

Previous hydrogeological research addressed conditions prior to the hydropower interventions. Consequently, there is limited understanding of the new hydrogeological relationships crucial for effectively managing vulnerable karst water resources. The defined boundaries of the catchment areas exhibit discrepancies across different directives (e.g. sanitary water protection zones, boundaries of water bodies, and river catchment areas), with some having been established using unreliable methods.

Recent hydrogeological research has been conducted only locally, while hydrogeological techniques have never characterised the transition zone between deep and shallow karst. In addition to human interventions, recent climate change greatly affects groundwater dynamics. In the last decade, the duration and amount of snow cover, which was the main source of aquifer recharge, has significantly decreased. The amount of precipitation remained in the general average; however, frequent extreme events lead to substantial yields over a short period, resulting in predominantly surface runoff and/or rapid groundwater flow through the aquifer without effective accumulation.

1.2 Study area

The primary focus of the first scientific paper in this doctoral dissertation is the karst region of the Kupa River catchment area, spanning Croatia and Slovenia. Based on the findings, areas of higher risk and the least explored regions were identified, specifically within the central part of the basin that includes the catchments of the Dobra, Mrežnica, and Slunjčica Rivers. Hydrogeological monitoring has been conducted in this area as the basis for the other two papers, which characterised the area using dynamic and hydrochemical methods (Figure 1).

The northern Dinaric karst is part of a complex transboundary catchment of the Kupa River, which drains an area of ~10,605 km^2 (**Francisković-Bilinski et al., 2012**). According to the spatial data provided by the Croatian Waters and Slovenian Waters, the size of the Kupa river's catchment within Croatia's territory amounts to 8,483.15 km^2, while the catchment takes up around 486.20 km^2 of Slovenian territory (Figure 1). Approximately half of this area is covered by karst terrain, which stretches through three countries: Croatia (~79%), Slovenia (~18%), and Bosnia and Herzegovina (~2%). Determining the exact extent of the karst terrain is challenging due to the poorly defined northeastern boundary between the Dinarides and the Pannonian basin. This boundary has been previously delineated differently by several authors, including **Bura** (1958), **Roglić** (1969), **Herak** (1972), and **Bogunović** and **Bensa** (2005). In this thesis, a rough NE boundary was used for data processing. This border is situated downstream of the investigated area and has no impact on the objectives of the doctoral thesis. Furthermore, it does not serve as a presumed boundary in any manner.

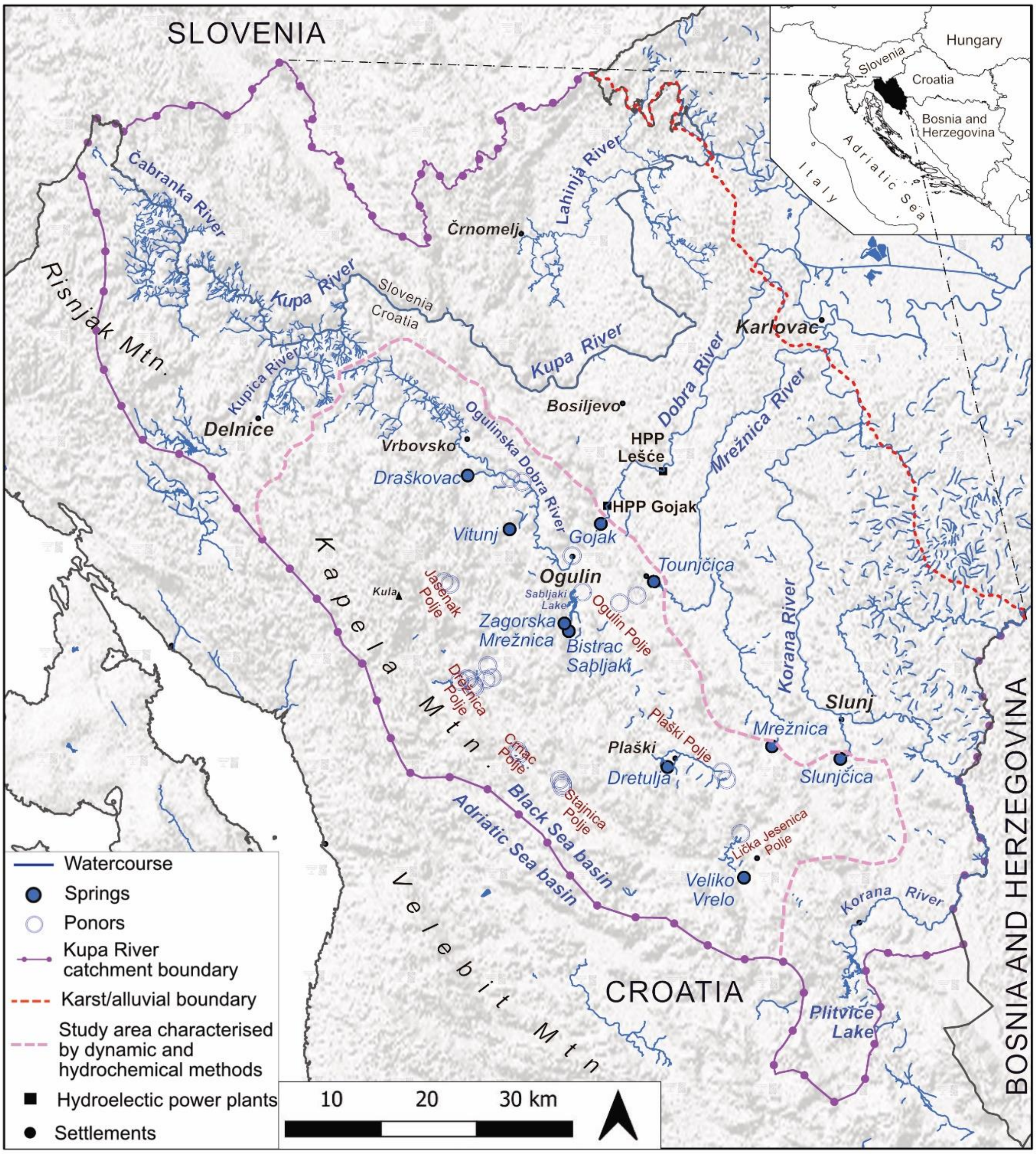


Figure 1. The karst part of the Kupa River catchment area

The northern boundary of the Kupa River catchment area is located in the Republic of Slovenia. Tracer tests define the boundary with the Sava River basin (**Habič et al., 1990**; **Habič and Kogovšek, 1992**), and the western boundary between the Adriatic Sea and the Danube River basins (**Bojanić, 1972**). A state border with Bosnia and Herzegovina defines the southern boundary of the study area.

The Kupa River originates from several springs in the Risnjak National Park, located in the Gorski Kotar region of Croatia. It flows southeastward, forming approximately 100 km of the state border between Slovenia and Croatia before fully entering Croatian territory in Kamanje and after 297.2 km long watercourse merging with the Sava River in Sisak on the alluvial plain outside the study area. The karstic part of the Kupa River catchment area has several sub-catchment areas formed by its main tributaries (Table 1). The Čabranka River originates in Slovenia and forms 17.5 km of the border between Slovenia and Croatia before joining the Kupa River near Brod na Kupi. The Lahinja River and the Dobličica River are located in Slovenia and flow through the Bela Krajina region, contributing to the Kupa near Jurovo. In Croatia, the sinking rivers Dobra and Mrežnica drain the Kapela mountain. The rivers springing at the foot of massif, forming watercourses in the Ogulinsko polje, sink eastward into the highlands and, together with the Korana River, flow into the Kupa in Karlovac. In the southern part of the study area, the Korana River forms a watercourse as a continuation of the Plitvice Lakes. In addition, the Korana River drains the south area of Kapela Mtn. through the sinking river Lička Jesenica, which reaches its right tributary, Slunjčica. In the middle of the watercourse, Korana receives the left tributaries, which drain a non-karstic area of the Petrova gora outside the study area, where the Radonja River is noteworthy.

Table 1. The areas of river sub-catchments within the karstic part of the Kupa River catchment

<table>
<tr><th>River</th><th>Watercourse length (km)</th><th>Catchment area (km²)</th><th>Catchment area of karst part of Kupa catchment area (%)</th><th>Reference/source</th></tr>
<tr><td>Kupa (immediate watershed to Lahinja)</td><td>30</td><td>1,740</td><td>30%</td><td rowspan="3">Croatian waters, 2021</td></tr>
<tr><td>Čabranka</td><td>17.4</td><td>134</td><td>2%</td></tr>
<tr><td>Lahinja</td><td>33.4</td><td>273</td><td>5%</td></tr>
<tr><td>Dobra</td><td>53 + 52</td><td>1,354</td><td>24%</td><td>Pavlić, 2016</td></tr>
<tr><td>Mrežnica</td><td>71.4</td><td>980</td><td>17%</td><td>Croatian waters, 2021</td></tr>
<tr><td>Korana</td><td>142</td><td>1,227**</td><td>21%</td><td>Croatian waters, 2021</td></tr>
<tr><td>Plitvička jezera*</td><td>-</td><td>151</td><td>3%</td><td>Meaški, 2011</td></tr>
<tr><td>Slunjčica*</td><td>6.5</td><td>273</td><td>5%</td><td>Pavlić, 2016</td></tr>
<tr><td>Radonja*</td><td>31</td><td>232</td><td>4%</td><td>Buljan et al., 2020</td></tr>
<tr><td>Karst part of Kupa</td><td>297.4</td><td>5,608</td><td>100%</td><td>Croatian waters, 2021</td></tr>
</table>

* belongs to the catchment area of Korana River; ** Croatian part of the catchment area

Karst part of the Kupa catchment spans from the mountainous areas of Gorski Kotar to the Karlovac Basin. The altitude of the catchment area ranges from the highest peak Kula of 1534 m a.s.l., located at Bjelolasica – Kapela Mtn. in the west to about 100 m a.s.l. of Kalovac Basin in the northeast. The average altitude of the catchment area is about 520 m a.s.l., while the slope (gradient) reaches up to 75°. Relief is a main factor that determines this area's climate and significantly impacts temperature reduction. According to the geographical distribution of Köppen climate types in Croatia, for the standard period 1961-1990, most of the study area belongs to climate type Cfb, characterised by a temperate humid climate with warm summers (mean air temperature of the warmest month is below 22 ˚C) **(Zaninović et al., 2008)**.

In contrast, some mountainous areas, such as those around Bjelolasica, experience climate type Df, which is classified as a humid boreal climate. According to the Thornthwaite index values, a perhumid climate is prevalent in the highland part of Croatia. The average rainfall in the karst part of the Kupa catchment is 1255 mm, with a runoff coefficient of 55%. Maximum annual precipitation was registered in the upstream section of the catchment in Lividraga (929 m a.s.l – 3,721 mm), while the minimum was measured in Karlovac (104 m a.s.l – 867 mm). The mean annual temperature for the whole catchment area is around 10°C. The temperature in the karst part of the catchment varies between mountainous regions in the west and lowland areas towards the east and northeast. During winter, mountainous areas are around 23°C colder than lowland areas. Gorski Kotar has colder springs than autumns, mainly due to the vicinity of the Adriatic Sea and mountainous terrain, while these differences are negligible in continental downstream parts of the catchment. The warmest months are July and August, while the coldest one is January.

The karst part of the Kupa catchment area is predominantly covered by natural land, with around 77% forest and 9.3% agricultural land with significant areas of natural vegetation **(CLC, 2018)**, notably contributing to evapotranspiration. The potential evapotranspiration, calculated for Ogulin station over the period 1971-2000, averages 701 mm according to the Croatian Meteorological and Hydrological Service web service **(DHMZ, 2020)**.

According to the last Census of Population, Households and Dwellings 2021, most of the study area is characterised by a population density of 20-40 citizens per km^2. The whole area exhibits an uneven spatial distribution of the population, reflecting spatial and economic development. Given that the depopulation process is strongly present and the population is mainly concentrated in larger settlements and cities, numerous smaller villages are completely abandoned and neglected.

The Kupa River catchment area comprises the contact of two main tectonostratigraphic units within the Dinarides orogenic system: the Outer Dinarides, which primarily consist of thick carbonate succession deposited on the Adriatic Carbonate Platform, and Internal Dinarides, characterised by deep water succession deposited on the passive margin of the Adria

Microplate (**Schmid et al., 2008**). Main structures and faults generally have the typical Dinaric strike (NW-SE), and in some cases, N-S strike due to neo-tectonic activity (**Prelogović et al., 1995**). The karst relief is predominantly influenced by compression tectonics during the formation of Dinarides (Alpine orogenesis).

The region encompasses geological formations spanning from the Palaeozoic to Quaternary epochs, with a prevalence of deposits from the Mesozoic era. The oldest rocks in the study area are of Palaeozoic age (Permian and Carboniferous), represented primarily in the northern part of the area, in Gorski Kotar, and partly in Slovenia to Kočevska Reka and east of the Kači Potok. Lithological composition is clay schists, sandstones, quartz conglomerates, shales, siltstones, and occasionally limestones and dolomites. The impermeability of these rock masses has resulted in surface runoff and the formation of a dense network of surface watercourses, such as the upper course of the Kupa, Čabranka, and Ogulinska Dobra rivers.

The study area consists mainly of karstified Mesozoic carbonate rocks of Jurassic and Cretaceous age. The mountainous area of Kapela Mountain is the first recharge area formed by substantially fractured limestones and dolomites of high secondary porosity. Due to numerous karstic forms, the area is characterised by rare and ephemeral surface watercourses. Highly karstified rocks enable the accumulation of groundwater in significant amounts. The Triassic dolomites form a hydrogeological barrier, direct the groundwater, and cause abundant springing along karst poljas at the foot of the mountain, as Ogulin, Plaški, Begovac, Lička Jasenica poljes (**Bahun, 1968**; **Kovačević, 2005; Buljan et al., 2019**). In the area characterised by highly permeable limestones, surface water sinks into the underground and subsequently reappears at the surface after travelling a distance of 5 to 15 km to the karst plateau, which is around 100 m lower in elevation.

Impermeable rocks are represented by Triassic clastites, which appear locally in the study area but have a significant hydrogeological function by enabling water retention in hydrotechnical lakes in Ogulin polje. The unconsolidated Quaternary deposits, originating from the erosion of carbonate and clastic rocks, overlay the karst poljes, river valleys, and thinly cover the carbonate deposits throughout the entire study area.

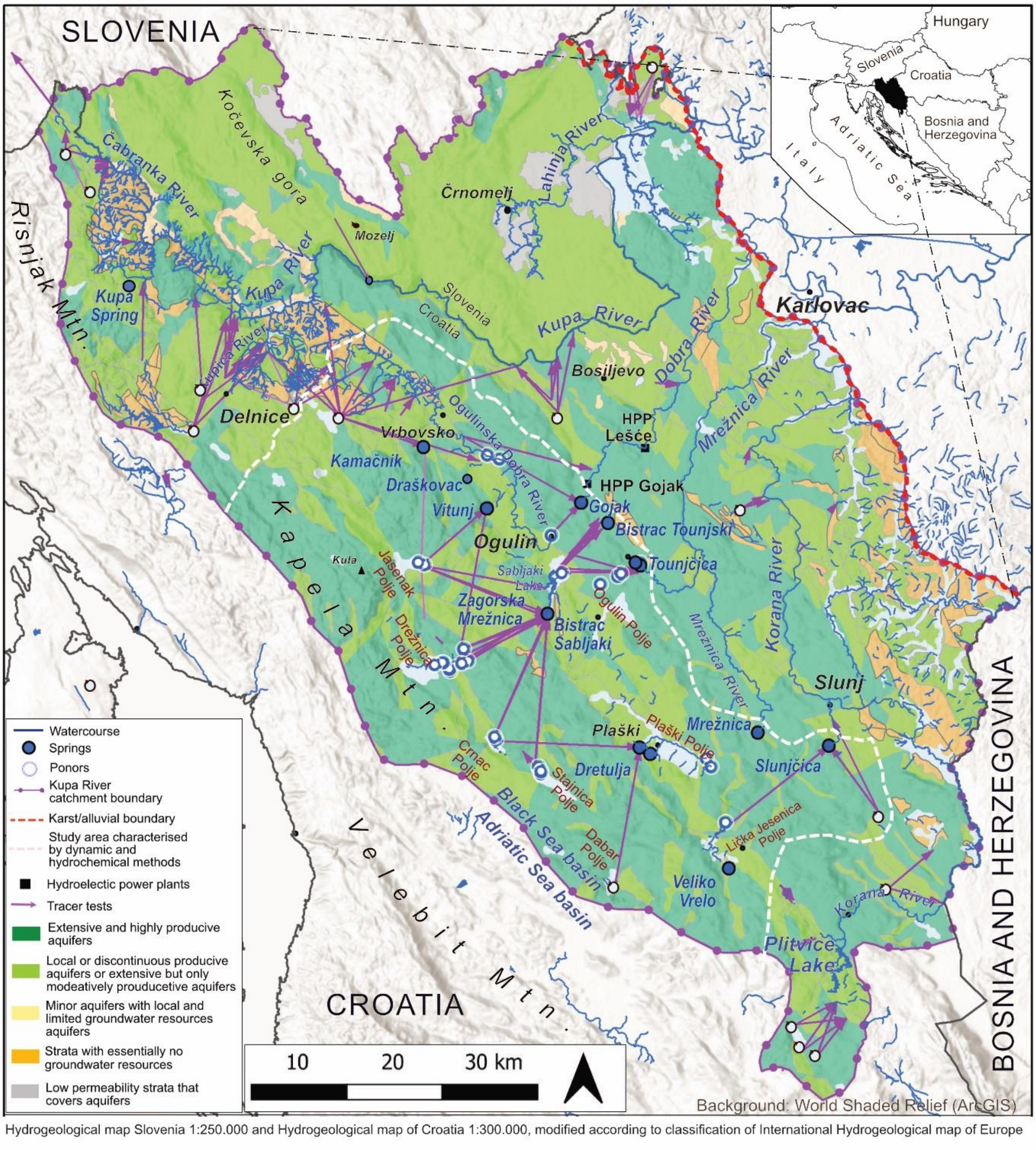


Figure 2. Hydrogeological map of the north Dinaric karst in Croatia and Slovenia

The central part of the Kupa River catchment area has the most important aquifers in the area, as they supply not only the significant karst springs used for drinking water supply but also rivers utilised for hydroelectric power production. Therefore, the sub-catchments of Dobra, Mrežnica, and Slunjčica rivers were selected for applied hydrogeological research presented within this doctoral research (**Boljat et al., 2024a; Boljat et al., 2024b**).

The area extending from Kapela Mtn. to the Karlovac Basin exhibits two distinct karst types: (1) deep, classical karst with karstification extending over several hundred meters in depth, and

(2) shallow or fluviokarst with a karstification depth below 200 m. These two karst types are separated by a hydrogeological barrier located at the foot of the mountain massif. As a result of an extremely high degree of karstification, the rock mass is comprised of a complex network of channels and cracks, making the delineation of springs and rivers catchment areas very challenging. The geological structures often impede the deep vertical movement of groundwater, resulting in the predominantly horizontal development of karst channels.

1.3 Previous investigation

In the early 20th century, **Dragutin Gorjanović-Kramberger (1912, 1914)** was the first to investigate the hydrogeology of the northern Dinaric karst, which he presented in two publications. In 1912, he documented the presence of the shallow karst near Generalski Stol and studied the hydrogeological phenomena near Lešće. In 1914, he analysed the previous Ogulinska Dobra watercourse and assumed the time of the Đula sinkhole formation. **Poljak** (**1922, 1925**) established the initial hydrogeological relations of the Ogulin-Plaški valley and comprehensively described the Begovac ephemeral lake and Ogulin polje. **Poljak (1948)** and **Herak (1953, 1954, 1956)** conducted several studies to establish hydrogeological relationships as a foundation for planning the use of hydroenergy in this region. **Bahun** (**1968, 1970**) consolidated and classified existing hydrogeological knowledge and provided a conceptual understanding of hydrogeological relationships in the karst region spanning from Kapela Mtn. to Kordun, which classifies the studied region into two recharging zones and two springing zones. In a regional study of the Kupa River basin, **Bojanić** (**1972**) investigated the hydrogeological function and characteristics of rocks, estimated the yield of water resources, and used tracing tests to identify the catchment areas of the main rivers.

Additionally, the study aimed to determine the boundary between Adriatic and Black Sea watersheds. **Jurak** (**1983**) examined the disparities in the water flow from karstic and non-karstic terrains in the catchment areas of Mrežnica, Korana, and Glina Rivers. Based on existing data, **Kovačević (2005)** divided the Karlovac County region into hydrogeological regions. Her master's thesis provides a comprehensive regional overview of geology, structural geology, tectonic and hydrogeological phenomena. **Pavičić et al**. (**2008**) conducted hydrogeological research to establish protection zones and assess the water-supply potential of Lička Jesenica springs. The data was processed and published by **Terzić et al.** (**2012**). **Biondić R. et al. (2003, 2014)** established the sanitary water protection zones for springs in Vrbovsko and Ogulin cities. Based on the geological research (**Prelogović et al., 2005**), the conceptual model of groundwater dynamics in the catchment area of Zagorska Mrežnica spring was made to determine the possibility of an artificial enlargement of the natural retention of Drežničko polje (**Buljan et al., 2013, 2019**). The catchment area of Slunjčica Spring was determined with tracer test **(Ivičić, 2003)**.

The archives of scientific and economic institutions, such as the Croatian Geological Survey, Croatian Elektroprivreda, Elektroprojekt, Croatian Waters, Faculty of Mining, Geology and Petroleum Engineering, Vodoprivreda Karlovac, and Geotehnika, contain numerous valuable studies and reports on geological, hydrogeological, hydrological, and geomorphological topics. However, a significant portion of the documentation is incomplete or partially lost. The well-known experts who significantly influenced hydrogeological research for the construction of HPP Gojak were **Bojanić and Ivičić (1981), Ivičić et al. (1987, 1990, 2001) and Magdalenić (1956, 1957)**, and subsequently **Ivičić et al. (1985, 1988, 1989), Viljevac and Ivičić (1990)** for HPP Lešće.

1.4 Interdisciplinary approach

The establishment of regional hydrogeological relationships commenced with an examination of prior studies and the compilation of accessible data. This research had four phases: (I) the identification of land-use pressures on the groundwater using spatial analysis, (II) the determination of structural characteristics and recharge areas of main springs based on groundwater dynamics and previous trace tests, and (III) providing insights into origin, pathways, and residence time of groundwater within the subsurface made of a complex underground network of conduits and fissures, and (IV) the determination of anthropogenic impacts on karst aquifers by employing hydrochemical and stable isotope investigations.

The initial phase involved analysing existing spatial data in the karstic part of the transboundary catchment area of the Kupa River. A Geographical Information System (GIS) database was utilised to organise and analyse spatial data, encompassing raster and vector data that may impact the groundwater. For the karstic part of the Kupa River catchment area, the following raster and vector data were critically considered: (I) hydrogeological and geological maps, (II) pedological substrates, (III) climatological data (spatial distribution of annual precipitation and temperature), (IV) springs, ponors, water supply and water protection facilities, watercourses, (V) flood hazard maps, (VI) land use maps (CLC 2000-2018), (VII) groundwater vulnerability maps of Slovenia and Croatia, (VIII) register of point and line pollutants and estimated anthropological impact, and (IX) an analysis of the relief (inclination, dips).

To identify areas with potential land use impacts on water resources quality, man-induced hazards were assessed according to the Water quality index (WQI) mapping. This approach is based on the methodology proposed in the CC-WARE project (**Čenčur Curk et al., 2014**) and a detailed hazard assessment and mapping of point, linear, and diffuse pollution sources, utilising the methodology outlined in COST Action 620 (**Zwahlen, 2004**).

Based on spatial data analysis, the hydrogeological investigation focused on the central part of the study area, specifically the catchments of Dobra, Mrežnica, and Slunjčica rivers. The investigation identified areas with significant anthropogenic influence on the functioning of hydrogeological system caused by hydropower technical interventions, which directly impact river regimes and important springs used for drinking water supply. Furthermore, the catchment area of the Plitvice Lakes in the south (**Babinka, 2007, 2008**; **Biondić et al., 2006, 2010**; **Čanjevac et al., 2023**; **Hunjak et al., 2013**; **Meaški et al., 2016**) and the immediate catchment of the Kupa River in the north (**Biondić et al., 2021**; **Pavlić & Parlov, 2019; Frančišković-Bilinski et al., 2012**) have been hydrogeologically explored and consequently excluded from further hydrogeological research.

Groundwater dynamic

Understanding hydrogeological dynamics is crucial for the management and protection of water resources. The methodology for determining infiltration, percolation, groundwater flow direction, retention, and accumulation is challenging in highly karstified aquifers like the one in question. Based on encapsulating the system's global response, the main objectives in northern Dinaric Croatia were to (1) define the hydrological characteristics of the transition zone from deep to shallow karst, (2) develop a conceptual hydrogeological model to address the discrepancies in tracer test results within the Kapela Mountain, and (3) characterise new hydrogeological relations concerning human interventions in the area as a zero-state.

To achieve these aims, from January 2018 to December 2022, hourly discharge and water temperature data were systematically collected at six gauging stations. Four springs, situated at the foot of the Kapela Mountain, reflected the mountain massif's dynamic (Vitunj, Draškovac, Zagorska Mrežnica, and Bistrac Sabljaki), and two springs downstream, the Ogulin polje characterised the transition zone between deep and shallow karst (Tounjčica and Gojak). The springs Draškovac, Vitunj and Gojak belong to the catchment area of the Dobra River, while the Bistrac Sabljaki, Zagorska Mrežnica, and Tounjčica springs belong to the Mrežnica River catchment area (Figure 4). The Croatian Electric Power Company (HEP) provided discharge and water temperature data of springs water, and HOBO Water Level Data Loggers (Oneset Computer Corporation, Bourne, MA, USA) were deployed in February 2020 in the Tounjčica and Zagorska Mrežnica springs to minimise atmospheric influences and accurately measure the water temperature, and as data controls for water levels measurement.

Hourly precipitation data from three meteorological stations within the study area were collected by the Croatian Meteorological and Hydrological Service (DHMZ): Jasenak station in Kapela (629 m a.s.l.), Ogulin station (328 m a.s.l.) and Gorinci station (203 m a.s.l.). Daily precipitation data were obtained from meteorological stations at Dabar polje (573 m a.s.l.) and Plaški station (395 m a.s.l.).

The catchment areas of monitored springs were characterised and cross-compared with time series analyses based on a five-year dataset: (1) Flow Duration Curve (FDC) analysis, which provides a graphical representation of the percentage of time specific discharge rates are equalled or exceeded, thereby offering insights into the variability and reliability of water flow over time; (2) Recession Curve Analysis (RCA), which involves studying the declining limb of a hydrograph following peak discharge to infer aquifer properties, such as storage and permeability, and to understand the aquifer's depletion rate; and (3) Autocorrelation Function (ACF) analysis, which measures the correlation degree between values of a time series at different time lags, helping to determine the memory effect and temporal structure of the spring's discharge. In addition, Cross-Correlation Function (CCF) analysis and water temperature dynamics were utilised to elucidate the karst system's response to precipitation events and to examine the interconnectedness between different springs, providing a comprehensive understanding of the hydrological behaviour and interdependence within the karst network. The ACF and CCF were performed using the XLSTAT (Lumivero, Denver, CO, USA) in the Excel 2021 program (Microsoft, Redmond, WA, USA), and the RCA and FDC were performed using the the MRCTools v3.1 "matching-strip" tool program (**Posavec et al., 2006, 2010, 2017**), which operates on an Excel Visual Basic for Applications (VBAs) algorithm. The results of implemented methodologies were compared and interpreted with the tracer tests carried out across the study area, resulting in the conceptual model of the hydrogeological system under different hydrological conditions.

Environmental tracers

To assess the anthropogenic impacts on karst aquifers, as well as additionally investigate hydrological and hydrogeological processes within a complex underground network of conduits and fissures, monthly observations of physicochemical and chemical parameters in spring waters were established, including stable isotopes, at eight springs located at two springing zone levels. The first springing zone encompasses four springs characterising the deep karst aquifer, and the second four springs in the shallow karst area that are in direct hydraulic connection to them. At the foot of the Kapela Mtn., the Vitunj Spring contributes to Ogulin Dobra River, which resurfaces at the Gojak spring, the same as the spring Zagorska Mrežnica which feeds the catchment area of the Tounjčica River, the left tributary of the Mrežnica River. The Dretulja Spring forms a sinking river, which emerges through the Mrežnica Spring, and the Veliko Vrelo Spring is a starting point of the sinking Lička Jesenica River, which is hydraulically connected with the Slunjčica Spring.

Hydrogeological facies were assessed using the Piper diagram (**Piper, 1944**). Pearson's correlation coefficient (r) was used to quantify the degree of linear correlation between observed parameters and evaluate geochemical processes. The Mg^{2+}/Ca^{2+} molar ratio was utilised to reconstruct the history of water-rock interaction and determine the lithology of the aquifer. Stable isotopes of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) were employed to trace water's origin, movement, history, recharging altitude, and retention time within the aquifer system.

The physicochemical and chemical parameters were measured through 33 monitoring campaigns conducted between September 2018 and May 2021. Stable isotopes were observed in spring waters and precipitation during 40 campaigns from February 2018 to May 2021.

The physicochemical parameters (water temperature, pH, specific electrolytic conductivity (SEC), and oxygen concentration) were measured *in situ* employing a WTW (Multi 3630 IDS SET G) multi-parameter probe. The HCO_3^- ion concentration or alkalinity was measured in the field through volumetric titration using 1.6N H_2SO_4 to pH 4.5, employing a HACH digital titrator. The groundwater and precipitation samples were analysed in the hydrochemical laboratory of the Department of Hydrogeology and Engineering Geology of the Croatian Geological Survey. The concentrations of the major anions (Cl^-, NO_3^-, and SO_4^{2-}) and cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) were measured using ion chromatography (Thermo Scientific Dionex ICS-6000 HPIC System). Stable isotopes of oxygen and hydrogen were analysed with a Picarro L2130-i Isotope and Gas Concentration Analyzer (Picarro, Santa Clara, CA, USA), and the Secondary Water Isotopes Standard Kit (Picarro) was used to calibrate the results. Precipitation was collected using oil-free Palmex® rain collectors (Palmex d.o.o., Zagreb, Croatia) that effectively prevent evaporative isotopic enrichment (**Michelsen et al., 2018**). The sampler was positioned at the observation station of Croatian Roads (HAC) (45°05'3422 N, 15°12'42" E) on Kapela Mtn., at 888 m a.s.l.

All applied methods within this work are explained in detail in the following chapters containing original scientific papers.

1.5 Objectives and hypotheses of research

The main objectives of this research are:

1. Characterise the study area with hydrochemical and isotopic research. Define groundwater retention times, age, and recharge area elevation.
2. Identify the null state of system dynamics as the basis for monitoring new hydrotechnical interventions in the study area.
3. Improve the methodology for investigating regional karst systems with an emphasis on defining of the transition zone between deep karst and shallow or fluviokarst, which significantly differs from other Dinaric karst areas.
4. Outline the conceptual grouping model of springs sharing catchment areas according to dynamics and hydrochemical properties.

Hypothesis:

1. Land use and hydrogeological properties of catchment directly influence the quality of karst groundwater.
2. Springs occurring in the study area can be grouped according to dynamics and hydrochemical properties in common sub-catchments.
3. The mean groundwater retention time in Dinaric karst is less than two years.
4. Differences in content stabile isotope enable us to distinguish the Mediterranean and continental precipitation influence on spring water in the study area.

1.6 Dissertation structure

The presented dissertation follows a cumulative structure comprising three scientific papers. It is divided into six chapters: (1) Introduction (with corresponding Subchapters 1.1 General Background, 1.2 Research Area, 1.3 Previous Research, 1.4 Multidisciplinary Approach, 1.5 Objectives and Hypotheses, and 1.6 Structure of the Dissertation), (2) Original Research Papers (three subchapters, each presenting one research paper), (3) Discussion, (4) Conclusion, and (5) References. The dissertation also contains an Abstract, an Extended Abstract in Croatian, keywords in English and Croatian, and the author's biography with a list of published papers.

2. ORIGINAL SCIENTIFIC PAPERS

Paper 1 (P1):

Impact of Land Use on Karst Water Resources—A Case Study of the Kupa (Kolpa) Transboundary River Catchment

By

Selak, Ana; Boljat, Ivana; Lukač Reberski, Jasmina; Terzić, Josip, Čenčur Curk, Barbara

water

MDPI

Article

Impact of Land Use on Karst Water Resources—A Case Study of the Kupa (Kolpa) Transboundary River Catchment

Ana Selak [1,*], Ivana Boljat [1], Jasmina Lukač Reberski [1], Josip Terzić [1] and Barbara Čenčur Curk [2]

1 Croatian Geological Survey, 10000 Zagreb, Croatia; iboljat@hgi-cgs.hr (I.B.); jlukac@hgi-cgs.hr (J.L.R.); jterzic@hgi-cgs.hr (J.T.)

2 Faculty of Natural Sciences and Engineering, University of Ljubljana, 1000 Ljubljana, Slovenia; barbara.cencur@ntf.uni-lj.si

* Correspondence: aselak@hgi-cgs.hr

Received: 2 October 2020; Accepted: 15 November 2020; Published: 18 November 2020

Abstract: This paper presents a qualitative approach for assessing land-use pressures on the water resources of a transboundary Dinaric karst catchment of the Kupa River in Southeast Europe. Spatial analyses of the water quality indices for surface water and groundwater were carried out in a GIS environment, as well as a detailed assessment of man-made hazards based on recommendations of COST Action 620. The produced maps provide an insight into the qualitative status of water resources at a regional scale by indicating areas of potential negative impacts of land use through the identification of point and diffuse sources of pollution. Higher values of the water quality indices for surface water and groundwater are observed in lowland areas, karst plateaus and poljes, where the impacts of anthropogenic activities such as agriculture and quarries take place on karstified permeable carbonate rocks. Hazard assessment showed how transport infrastructure induces a low hazard level. Settlement areas without proper sewerage systems impose moderate hazard levels, while direct wastewater discharges into groundwater and waste illegally disposed in karst swallow holes and caves located near settlements were classified as having high hazard levels. The applied methods proved to be suitable even in challenging karst environments where the complex properties and structure make the exploration and monitoring of groundwater resources difficult and scarce.

Keywords: water quality index; hazard assessment; COST Action 620; water resources; land use; Kupa (Kolpa) River catchment; karst hydrogeology; CAMARO-D project

1. Introduction

Increasingly frequent weather extremes coupled with unsustainable land-use practices and exacerbated by spatially heterogeneous water resources allocation due to complex hydrogeological conditions, pose various challenges in terms of water quantity and quality. Driven by various socio-economic factors and affected by climate change, land-use changes have a negative impact on water resources, especially on vulnerable karst groundwater sources used for water supply [1,2]. Consequently, sustainable development that implies a synergy between economic and spatial growth, water resource management and protection objectives, while adapting to climate change, is of strategic importance for transboundary catchments like the Kupa (in Slovenian Kolpa) River basin [3]. To adequately manage and protect this part of the Danube River basin, decision-makers need to address ongoing water protection and flood risk issues not only at the local and national levels but also at the transnational level. The transnational efforts mentioned above were undertaken in the Interreg Danube Transnational Program CAMARO-D project, in which the partner institutions worked on advanced management routines for the impacts of land use on the water regime in the Danube River basin. As primary project results, the partnership elaborated "Guidance for the Danube Region on Sustainable Land-Use Planning" (GUIDR), followed by a "Transnational Catchment Based Concept for Land-Use Planning" (LUDP). Together, these documents serve as a basis for the appropriate coordination and harmonization of different function-oriented sustainable land-use management activities [4].

Faced with more frequent severe seasonal flooding, the population of the Kupa (Kolpa) River basin is still employing some of the inadequate land-use practices. These include urbanization, development, and agriculture in the flood plain; excessive use of pesticides; inappropriate or non-existent manure storage; inadequate use of heavy agricultural/forestry machinery and equipment; illegal waste dumpsites in karst swallow holes and caves; direct urban drainage into watercourses; and missing or inadequate sewerage systems due to dispersed settlements [5]. In addition, built hydro-technical objects significantly changed the hydrological system and water regime [6,7], which made the protection of water resources and flood mitigation even more challenging. Various legislative acts and protection instruments are proclaimed on multiple levels, to protect water resources through either a system of spatial planning or environmental protection [8–11]. However, their implementation alone is not sufficient to achieve good quantitative and qualitative water status. It is also necessary to raise awareness and promote the participation of all relevant decision-makers, practitioners, and the general public at the local, regional, and national levels. Thus, the CAMARO-D project focused on initiating site-specific innovative solutions in the form of best management practices based on the results of previously implemented pilot action activities such as hydrogeological field investigations, climate change modeling, and GIS-based hazard assessment and mapping.

The main objective of this paper is to present the results of the hazard assessment and, together with the mapping of the water quality index, to identify the karst areas in need of action, to contribute to the water resources protection, and to promote sustainable land-use management practices at the level of Kupa River basin. The water quality indices assessment carried out in this study was based on the methodology proposed by Čenčur Curk et al. [12] in the CC-WARE project, which was focused on the assessment of the vulnerability of water resources under climate change in Southeast Europe. This methodology has been applied in recent studies on a regional scale [13,14]. Furthermore, for the assessment of the hazards present within the Kupa River catchment the recommendations of COST Action 620 project "Vulnerability and risk mapping for the protection of carbonate (karst) aquifers" [15] were followed. The conceptual "European approach" developed with COST Action 620, which can be tailored to areas with different scales and various hydrogeological conditions, has proved to be one of the indispensable methods for producing vulnerability, hazard, and risk maps of karst aquifers [16–19].

2. Study Area

Located in the SE of Europe (Figure 1), Kupa (Kolpa) River catchment drains an area of approximately about 10,605 km^2 and covers three neighboring countries: Croatia (79.32%), Slovenia (18.32%), and Bosnia and Herzegovina (2.36%) [20]. However, in this paper, Croatian (only karstic area –4505.02 km^2) and Slovenian parts (1102.98 km^2) of the catchment area are considered (5608 km^2 in total). Most of the border between Slovenia and Croatia is not seen in Figure 1, as the border is the river Kupa (Kolpa) itself.

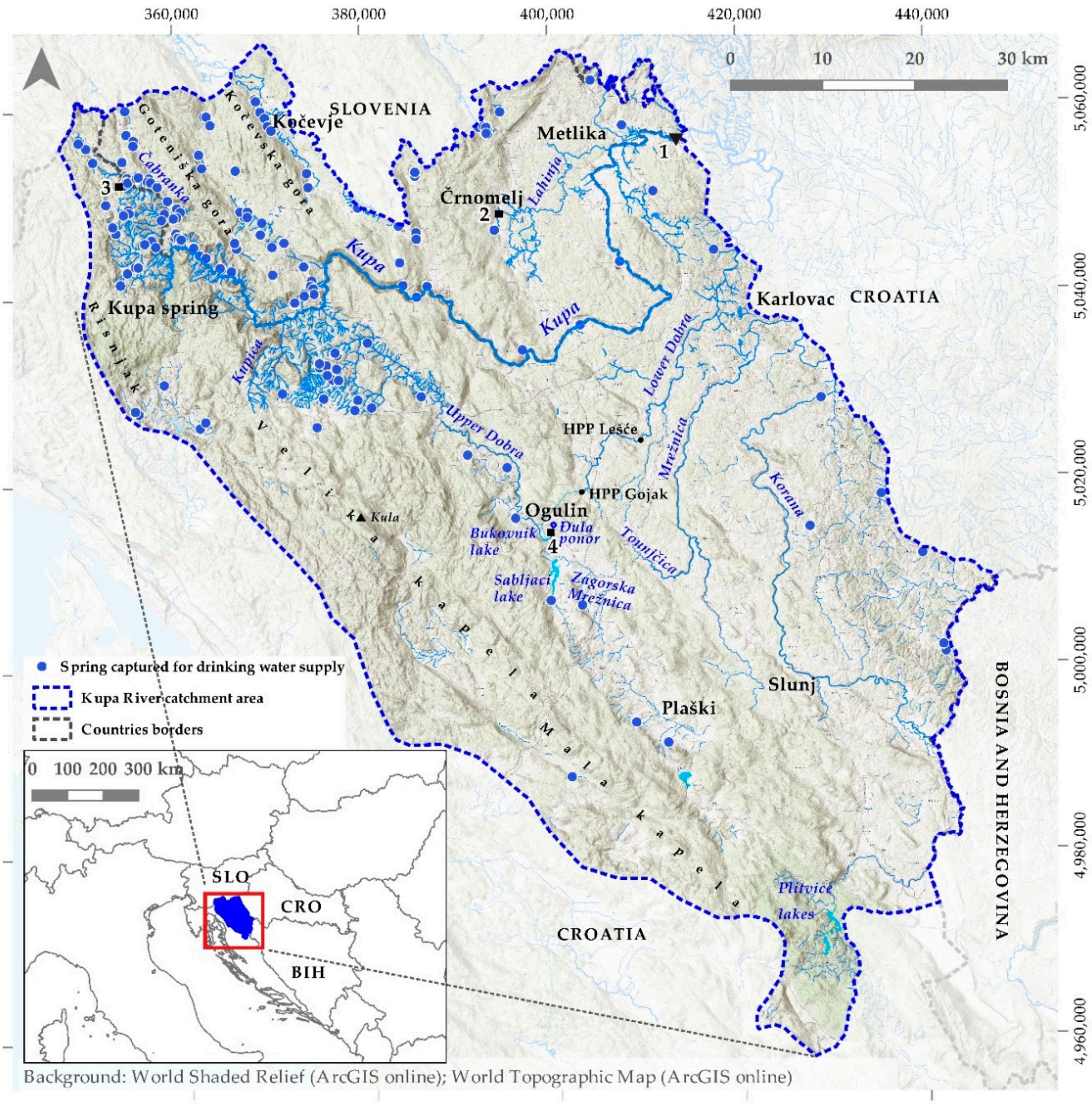


Figure 1. Location of the study area ((1) hydrological station Kamanje; meteorological stations: (2) Črnomelj, (3) Parg, (4) Ogulin).

The river Kupa (Kolpa) (294.4 km long) is part of the Danube River basin. Due to the hydrogeological complexity of its karstic part, the exact catchment boundaries are difficult to determine. The SW catchment boundary, which represents the contact between the Adriatic Sea and the Danube River basins [3,6,21], and the N boundary in Slovenia are clearly defined with tracing experiments [22,23]. The NE boundary, which corresponds to the contact between the Dinarides and the Pannonian basin, was previously defined by several authors, namely Bura [24], Roglić [25], Herak [26], and Bogunović and Bensa [27]. The catchment boundary with Bosnia and Herzegovina is defined with the state border, as this part of the catchment area has not yet been sufficiently explored.

The distinctive spatial diversity of the catchment's natural features is due to the mountainous forest karst areas of the Dinarides in SW, followed by the fluviokarst and further into the NE lowlands and the cultivated Karlovac alluvial plain (outside the study area). The altitude of the area ranges from about 100 m a.s.l. in the north to 1534 m a.s.l. of Kula the highest peak in the researched area located at Bjelolasica–Velika Kapela Mountain. The average altitude of the catchment area is about 520 m a.s.l., while the slope (gradient) reaches up to 75°. In general, the catchment's morphology (e.g., mountain ranges and karst poljes) coincides with the so-called "Dinaric" northwest-southeast strike of the main geological structures.

The heterogeneous relief is one of the main factors that define the climate of the study area, which shows Mediterranean influence in the south, while in the northern parts a continental influence is present. According to the geographical distribution of Köppen's climate types, the study area belongs mainly to a temperate humid climate with warm summers (type Cfb). In contrast, in the high mountain areas of both Croatia and Slovenia, the climate is humid boreal (type Df) [28,29]. A mean monthly air temperature is the highest in July and August and ranges from 16.9 °C (data period 1950–2018) for Parg (the station with the highest altitude of 863 m a.s.l.) [30] to 21.2 °C (data period 1981–2010) for the station Dobliče near Črnomelj (157 m a.s.l.) [31]. The minimum mean air temperature is measured for January and ranges from −1.5 °C for Parg to 0.3 for the station Ogulin (328 m a.s.l.) [30].

The abundant precipitation periods in autumn, winter, and spring generate most of the runoff in the upstream catchment area, while long summer periods are generally dry [32]. In the Slovenian part of the catchment area, the mean annual precipitation ranges from 1839 mm/year in the NW to 1089 mm/year in the NE [29]. Similarly, the mean annual precipitation in Croatia ranges from 1843 mm/year in the mountainous region of Gorski kotar to 1558 mm/year in Ogulin (central part of the study area) and 1101 mm/year in the lowland NE area [33].

As a result of spatially dynamic geomorphological settings (from mountainous to lowland areas) and contact of two climate types across the study area, the typology of discharge regimes of rivers is diverse. In highly karstified mountain massifs with plentiful karst phenomena, the surface hydrographic network is poorly developed, as the water infiltrates either dispersedly through numerous fissures or via sinkholes into the underground. The water is drained towards the abundant springs zone of Kupa River and its main tributaries of the upstream part: Čabranka, Lahinja, and Kupica. All these rivers (Kupa up to Kamanje station) are characterized by a Dinaric pluvial-nival regime, which implies two distinct annual discharge peaks, the first in spring and the second in autumn. The minimum discharges are observed in August, January, and February [34]. The Kupa begins its flow with an abundant Vauclusian spring at an altitude of 321 m a.s.l in the Risnjak National Park located in the Gorski kotar region, Croatia. The river then forms an approximately 100 km long state border between the Republic of Croatia and the Republic of Slovenia before it reaches Kamanje. Further downstream and outside the study area, the Kupa River enters an extensive alluvial plain and reaches Sava River at the altitude of 97 m a.s.l.

In the central part of the catchment area, the main tributaries of the Kupa are Dobra, Mrežnica, and Korana (Figure 1), which in their canyon-like flow intersect the fluviokarst area with a distinct morphology. The dual nature of the Dobra River is evident in its torrential flow of Upper Dobra with the Dinaric pluvial-nival regime and the canyon flow of the Lower Dobra with Mediterranean pluvial-nival regime (maximum discharge in December and April, minimum in July or August and February or March). The water of Upper Dobra sank in the Đula ponor near Ogulin until 1957, when the course was diverted with overflow dam to the accumulation lake Bukovnik and hydroelectric power plant (HPP) Gojak. Only during periods of heavy precipitation, the riverbed between the dam and the ponor fills up with water, occasionally flooding the Ogulin area. The Upper Dobra River then flows underground and reappears after HPP Gojak as Lower Dobra, which flows for 52 km before it reaches the Kupa River [35]. Another hydroelectric power plant that also uses the water of the Lower Dobra is the HPP Lešće, located SE of HPP Gojak. The spring of Zagorska Mrežnica occurs with several other smaller springs and was dammed to form the artificial hydro-technical lake Sabljaci, while its water is transported through the tunnel towards Bukovnik Lake and the HPP Gojak. Moreover, during the rainy season, a significant volume of water flows over the dam, forming the flow of Zagorska Mrežnica River that sinks several kilometers downstream and flows underground into the adjacent catchments of the Tounjčica and Dobra rivers [6]. The Mrežnica River has Peripannonian pluvial-nival regime with the first discharge maximum in March or April and the second in December, while a minimum is observed in August and February [36]. Before the confluence with the Kupa, the Mrežnica

River joins with the Korana River. The latter emerges at Plitvice lakes located in the south of the observed area. Like the Lower Dobra, Korana River (upstream of Slunj) also has a Mediterranean pluvial-nival regime.

A concise overview of the complex geological and hydrogeological characteristics of the study area was based on the survey of the Geological Map of the Republic of Croatia 1:300,000 [37]; the Basic Geological Map of the Republic of Slovenia 1:250,000 [38]; the Hydrogeological Map of the Republic of Slovenia 1:250,000 [39], and the Hydrogeological Map of the Republic of Croatia 1:300,000 [40]. On this basis, the joint Croatian and Slovenian hydrogeological map was produced (Figure 2) in the QGIS software and compared with the International Hydrogeological Map of Europe 1:1,500,000—IHME1500 [41]. This required a modification of the Hydrogeological Map of the Republic of Croatia 1:300,000 according to the categories of IHME1500.

The studied part of the Kupa River catchment area comprises the contact of two main tectonostratigraphic units of the Dinarides orogenic system: "Outer Dinaridic Platform," i.e., Karst Dinarides, and Internal Dinaridic Platform, i.e., "Pre-Karst and Bosnian Flysch Unit of Internal Dinarides" [42,43]. Outer Dinarides consist mainly of thick carbonate succession deposited on the Adriatic Carbonate Platform [42]. Inner Dinarides, which extend between Outer Dinarides and the Pannonian basin, are characterized by deep water succession deposited on the passive margin of the Adria Microplate [43]. The catchment consists mainly of karstified soluble Mesozoic carbonate rocks of Jurassic and Cretaceous age, which are strongly tectonically compressed [37]. Depending on the occurrence of highly permeable limestone components or less permeable dolomites, the Mesozoic rocks are categorized either as "extensive and highly productive aquifers" or as "local or discontinuous productive aquifers or extensive but only moderately productive aquifers" (Figure 2) [41]. These are the most important aquifers in the area, as they supply not only the significant karst springs that are used for drinking water supply but also rivers utilized for the production of hydroelectric power. In the Slovenian part of the Kupa River catchment area, Jurassic dolomites, limestones, and breccia prevail. Cretaceous limestones and dolomites occur in wide areas of the Croatian part of the catchment area, while in the Slovenian part, they outcrop along with non-clastic siliceous sedimentary rocks, Cretaceous flysch, and other basin sediments in some areas. Triassic dolomites, Seisian and Campilian deposits, and rare pyroclastic deposits constitute some of the mountainous areas and mainly surround Paleozoic deposits. Paleozoic (Carboniferous and Permian) predominantly clastic rocks, rarely limestones and dolomites, are the oldest rocks in the catchment area. In contrast to Mesozoic rocks, Paleozoic rocks are found in smaller parts of the catchment area. Paleozoic rocks are characterized as insignificant aquifers (IAH categories "minor aquifers with local and limited groundwater sources" and "strata with essentially no groundwater resources" (Figure 2) [41] due to their general low permeability) and therefore enable surface runoff and developed river network such as rivers Čabranka, Kupa, and Upper Dobra. Tertiary deposits are represented by Paleocene and Eocene carbonate flysch and clastites and Miocene Dinaric deposits. Quaternary unconsolidated sediments are present in river valleys and lakes. They are mainly classified as "local or discontinuous productive aquifers or extensive but moderately productive porous aquifers" while in Slovenia, some of the Pliocene to Holocene terrestrial deposits are classified as "low permeability strata that cover either porous of fissured aquifers" (Figure 2).

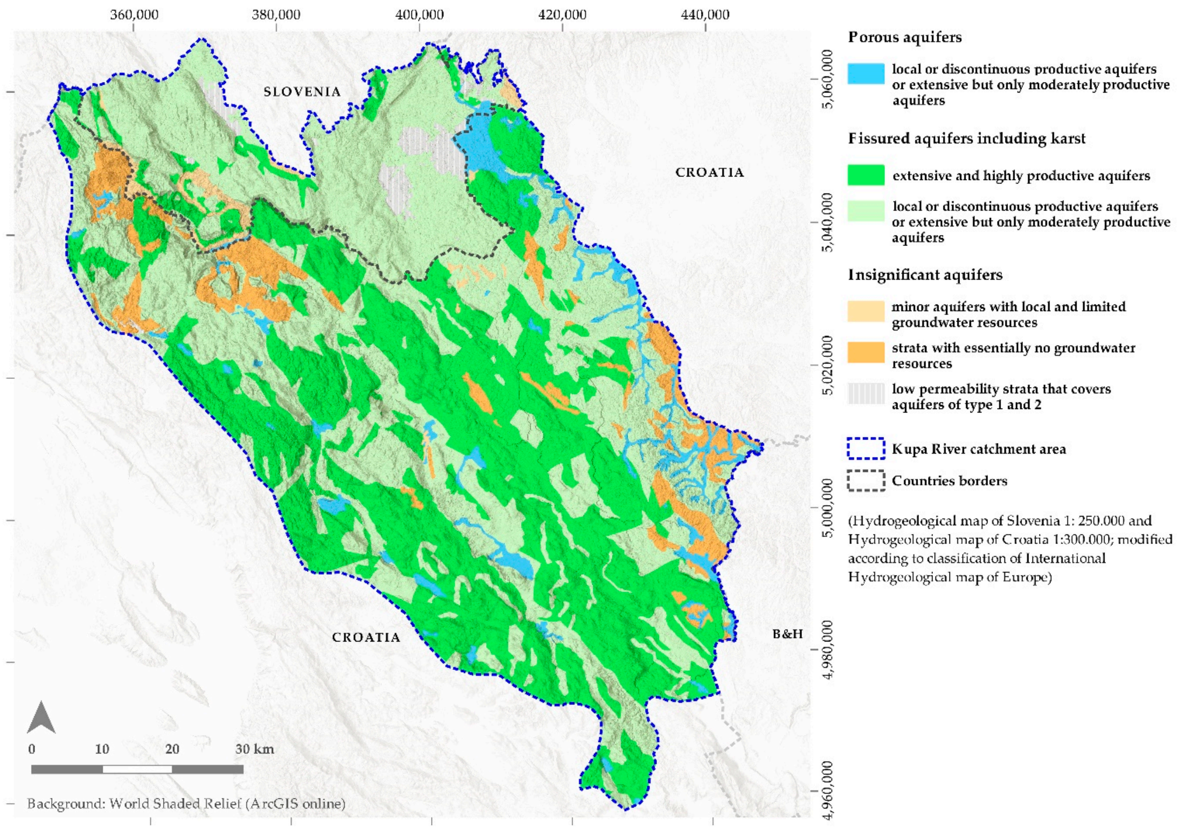


Figure 2. Hydrogeological map of the Kupa River catchment [39,40], according to the classes of the International Hydrogeological Map of Europe 1:1,500,000 [41].

As in fractured and karstified terrains, the water resources in the Kupa River catchment area are particularly vulnerable to pollution due to the intrinsic karst properties. Generally thin or non-existent overlaying soil layers, low retention capacity, a relatively rapid exchange between surface and groundwater bodies, concentrated infiltration through numerous swallow holes, and potentially far-reaching and relatively fast groundwater flow along preferential paths of karst conduits and channels, could lead to rapid and long-distance spreading of man-made pollution. Given the relatively low hypsometric position of the riverbeds and the low hydraulic gradient, the Kupa, Korana, Dobra, and Mrežnica rivers are the erosional basis for groundwater and represent the groundwater table. In other parts of the terrain, the depth to the groundwater varies depending on the hydrogeological properties of the rocks. The permeability of the Upper Jurassic to Eocene limestone and limestone with dolomite intercalations ranges from 10^{-4} to 10^{-6} m/s. Poorly permeable rocks (dolomites, dolomitized limestones from the Upper Triassic to Lower Cretaceous) have the permeability ranging from 10^{-6} to 10^{-8} m/s. Flysch complex from the Lower Triassic to Eocene has permeability $<10^{-8}$ m/s as mentioned by Buljan et al. [6] based on [44]. The groundwater level in Jurassic and Cretaceous limestone corresponds to the nearest surface flows. Groundwater can be characterized by a flow generally oriented south and southeast, as the rivers flow.

The abundance of high-quality spring water (with minimum discharges, generally ranging from 0.1 m^3/s to up to 2 m^3/s [40]) and the transboundary nature of the Kupa River basin make its water resources strategically important [3], which evokes the need for international management and protection. Furthermore, the population in the study area is very dispersed in numerous small settlements, so all aquifers are very important. For the majority of surface and groundwater abstraction points (out of total 168 abstraction points for drinking water, 66 are located in Croatia and 102 in Slovenia) (Figure 1), drinking water protection zones are declared, covering an area of about 2010 km^2 or 36% of the total catchment area.

3. Materials and Methods

To identify areas with potential impacts of land use on water resources quality in the Kupa River catchment area, first insight into the climatic, hydrological, geological, and hydrogeological settings is given in the description of the study area. This was followed by an assessment of the man-induced hazards according to the Water quality index (WQI) mapping (diffuse and partly point sources) based on the methodology proposed in the CC-WARE project [12] and a detailed hazard assessment and mapping (point, linear, and diffuse pollution sources) based on the methodology proposed in COST Action 620 [15]. The handling and graphical data processing on a spatial scale were carried out using the Geographic Information System (QGIS Version 2.18.21).

3.1. The Water Quality Index

A probability that pollutants, originating from different land-use activities, will reach water resources is represented by the water quality index. The maps for the surface water and groundwater quality index have been produced using the modified methodology proposed by Čenčur Curk et al. [12].

The impact of land use on water quality is expressed in terms of land-use load coefficients (LUSLI), which are estimated for each individual land use (CLC level 3). LUSLI presents potential surface water pollution. It is assumed that LUSLI is proportional to the nutrient (phosphorus and nitrogen) export coefficients [45] assigned to each Corine Land Cover (CLC) 2018 dataset of land-use categories [46] (Table 1). The normalization of values (by scaling between 0 and 1) enabled the classification into five different classes from very low to very high water quality index for surface waters (*WQIsw*).

Table 1. Land use load coefficient (LUSLI) applied for Corine land cover 2018 categories in the Kupa River catchment area.

Corine Land Cover			
CLC 2018 Code	**CLC Description**	**Land Use Load Coefficient (LUSLI)**	***WQIsw* (Normalized LUSLI)**
112	Discontinuous urban fabric	5.5	0.458
121	Industrial or commercial units	5	0.417
122	Road and rail networks and associated land	7.5	0.625
131	Mineral extraction sites	9	0.750
133	Construction sites	7	0.583
142	Sport and leisure facilities	4	0.333
211	Non-irrigated arable land	12	1.0
221	Vineyards	6	0.5
222	Fruit trees and berry plantations	5	0.417
231	Pastures	3.5	0.292
242	Complex cultivation patterns	8.3	0.692
243	Land principally occupied by agriculture, with significant areas of natural vegetation	5.5	0.458
311	Broad-leaved forest	3.6	0.3
312	Coniferous forest	2.5	0.208
313	Mixed forest	2.8	0.233
321	Natural grasslands	2.5	0.208
322	Moors and heathland	2.7	0.225
324	Transitional woodland-shrub	2.6	0.217
511	Watercourses	3	0.25
512	Water bodies	3	0.25

The sensitivity of groundwater to pollution depends primarily on the type of aquifer or, more precisely on the effective infiltration coefficient (Table 2), which represents the portion of rainfall that infiltrates into groundwater and carries pollution load into groundwater. The water quality index for groundwater is thus a function of the pollution load, expressed as *WQIsw*, and the effective infiltration coefficient (*EIC*). The latter was determined as a function of the aquifer type (hydrogeological map; Figure 2), with an *EIC* (Table 2) assigned to each aquifer type [12]. Multiplying the water quality index for surface waters (*WQIsw*) by the effective infiltration coefficient (*EIC*) and normalizing it from 0 to 1 gives the indicator for groundwater quality—Water quality index for groundwater (*WQIgw*). The *WQIgw* map consists of five equally distributed classes.

$$WQIgw = WQIsw \cdot EIC \quad (1)$$

Table 2. Effective infiltration factor (*EIC*) (modified from Čenčur Curk et al. [12]).

Aquifer Type	Effective Infiltration Coefficient (*EIC*)
Aquifer in which flow is mainly intergranular	
extensive and highly productive aquifers	0.6
local or discontinuous productive aquifers or extensive but only moderately productive aquifers	0.3
Confined extensive aquifer	0.2
Fissured aquifers, including karst aquifers	
extensive and highly productive aquifers	0.8
local or discontinuous productive aquifers or extensive but only moderately productive aquifers	0.4
Strata (granular or fissured rocks) forming insignificant aquifers with local and limited groundwater resources or strata with essentially no groundwater resources	
minor aquifers with local and limited groundwater resources	0.1
strata with essentially no groundwater resources	0.05
low permeability strata that cover porous and intergranular aquifers	0.05

3.2. Hazard Assessment (COST620)

The hazard assessment and mapping for the karstic part of the Kupa River catchment area was based on the recommendations of the COST Action 620 project "Vulnerability and risk mapping for the protection of carbonate (karst) aquifers" [15]. Altogether, the evaluation comprised three steps: identification of potentially hazardous activity, and the characterization and quantification of the hazards. The input data were collected from the Slovenian Environment Agency (WFS server of Environmental Atlas), The Surveying and Mapping Authority of the Republic of Slovenia, the Croatian Environmental Pollution Register, and the Croatian Environmental Information System (WFS server). Depending on the type of land use, the data of the hazard inventory were then systematically distributed to the following categories: point sources, which include industrial activities, disposal of wastewater from treatment facilities (discharge into surface and groundwater), and waste disposal (landfills as well as illegal dump sites); linear sources as traffic corridors and settlements as polygonal diffuse sources (sewerage system, cesspits). Information on existing wastewater and sewerage systems was obtained from the published spatial plans of municipalities and compared with data of entities responsible for wastewater treatment and disposal.

The hazard index *HI* is calculated as follows [15]:

$$HI = H \cdot Q_n \cdot R_f \quad (2)$$

where H is the weighting coefficient, Q_n is the ranking factor (0.8–1.2), and R_f the reduction factor (0–1.0). Weighting allows comparing different hazard categories by allocating values ranging from 0 to 100. The ranking factor enables differentiation within the same type of hazard category. For instance, the ranking factor of 0.8 was applied to closed landfills, 1.0 to active landfills, and 1.2 to active landfills undergoing remediation. As far as agricultural production is concerned, a ranking factor of 0.8 was applied to all agricultural land with significant natural vegetation, while vineyards, orchards, and berry plantations were rated at 1.0. The ranking factor of 1.2 was assigned to non-irrigated arable land and complex cultivation patterns, as areas with more intensive production activities. The reduction factor as an empirical number enables the estimation of contamination event probability. Thereby, for each linear and point hazard sources, impact zones were determined with the corresponding reduction factor R_f (Table 3). It follows that R_f of 0 means that there is no possibility of water resources contamination; R_f of 0.5 represents the reduction of negative impact likelihood by 50%, while R_f of 1.0 means that there are no reasons to reduce the possibility of contamination.

Table 3. Hazards impact zones, categorized according to the data type.

Data Type	Hazard	Impact Zone	Reduction Factor (R_f)
Point	Industry effluents	0–50 m 50–100 m	1.0 0.5
	Wastewater treatment plants effluents	0–50 m 50–100 m	1.0 0.5
	Landfills	0–50 m 50–100 m	1.0 0.5
	Illegal waste sites	0–50 m 50–100 m	1.0 0.5
Linear	Railway	0–5 m 5–25 m	1.0 0.5
	Road	0–5 m	1.0

The final graphical interpretation of the hazard data shows the potential degree of harmfulness for hazards of anthropogenic origin, the locations of point sources of contamination, the extent of the impact zones for linear sources, and polygonal diffuse sources. Table 4 shows the hazard indices, classes, and levels with corresponding colors representing the degree of harmfulness. Each hazard map layer of vector data was accompanied by tables with stored attribute information that encompasses the type of harmful activity; values for H, Q_n, R_f, and HI; and hazard classes. Depending on the availability of the collected data, information on quantities and types of potentially harmful compounds emitted or stored is also included, with the coordinates defining the precise location of the point sources.

Table 4. Hazard index and hazard index classes.

Hazard Index	Hazard Index Class	Hazard Level	Colour
0–24	1	No or very low	
>24–48	2	Low	
>48–72	3	Moderate	
>72–96	4	High	
>96–120	5	Very high	

Where certain types of hazard overlap, those with the highest value were selected to represent the harmfulness of the hazard in specific locations.

4. Results

4.1. Water Quality Index

4.1.1. Surface Water Quality Index (*WQIsw*)

Normalized *WQIsw* values were applied to CLC categories, which were identified within the Kupa River catchment area. The CLC map of the Kupa River catchment area (Figure 3) shows how broad-leaved forests (~34.8%) and mixed forests (~24%) occupy most of the catchment area, which includes highland and mountainous areas and surrounding settlements with adjacent agricultural land. Agricultural land is generally characterized by significant areas of natural vegetation (~9.3%), which interchanges with transitional woodland-shrubs (~8.8%) and coniferous forests (~8.1%). Complex cultivation patterns (~6.7%) are mainly present in several karst plateaus, hilly areas, and smaller karst poljes. Areas used as pastures are mainly found in the Slovenian part and the eastern to south-eastern parts of the catchment area in Croatia, which together make up ~3.7% of the total catchment area.

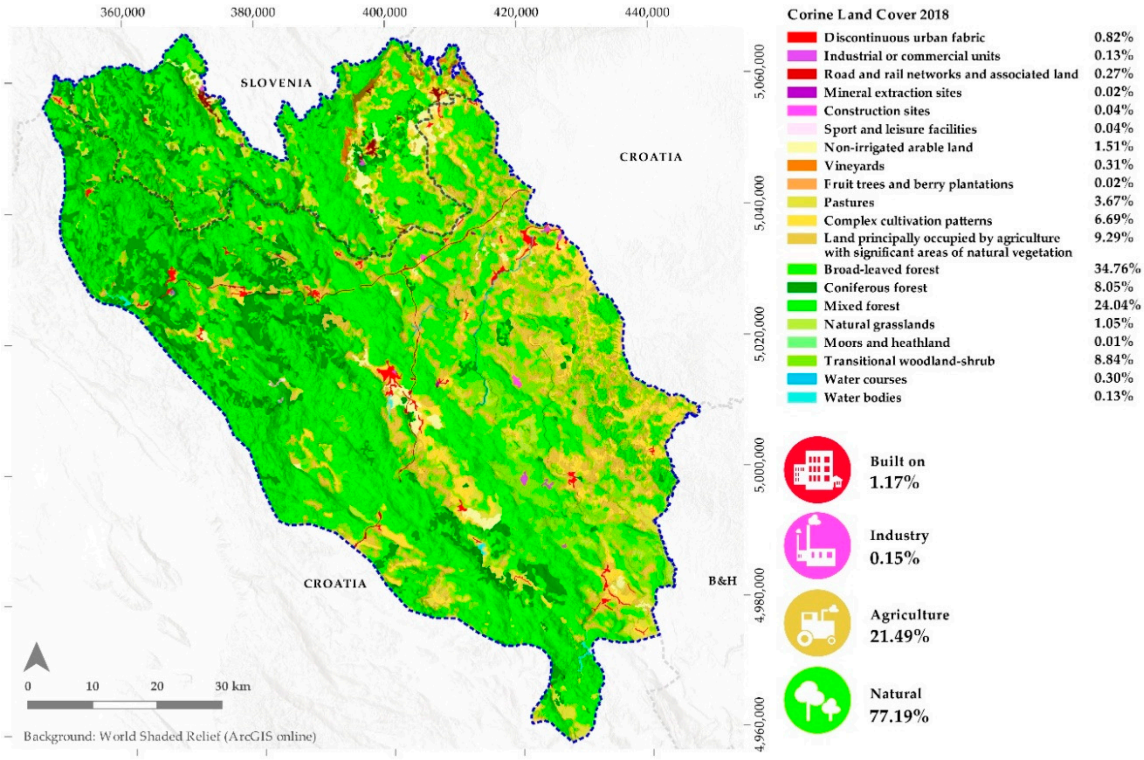


Figure 3. Land-use map of the studied area (input data source: Corine land cover, 2018).

The map showing the Surface water quality index (*WQIsw*) is presented in Figure 4 and shows five equally distributed classes from very low (min. value 0.21) to very high (max. value 1.0) *WQIsw* values. Higher values of *WQIsw* are assigned in lowland areas, karst plateaus and poljes, where anthropogenic activities and their impacts are significant. Accordingly, very high *WQIsw* values refer to non-irrigated arable land, while high *WQIsw* values consider complex cultivation patterns and mineral extraction sites. Medium *WQIsw* values were determined for construction sites, roads, railway networks, and their associated areas. Conversely, natural and semi-natural areas where human impact is negligible have lower *WQIsw* values. About 11% of the total Kupa River catchment area has low *WQIsw* values, while very low *WQIsw* values cover over ~81% of the study area. Agricultural land with significant natural vegetation shows low *WQIsw* values, while very low values were allocated to mountainous forest areas and pastures. Urban areas and settlements have low *WQIsw* values.

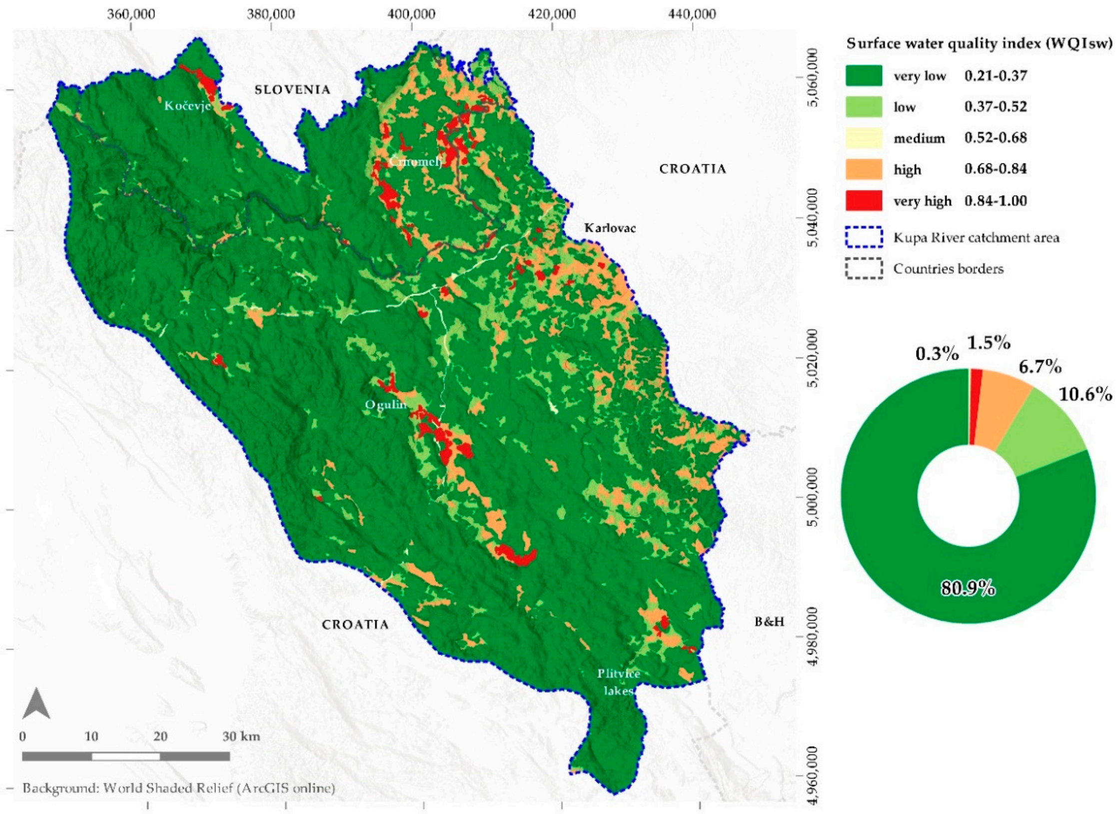


Figure 4. Surface water quality index (*WQIsw*) for the Kupa River catchment area with the percentage of the respective class.

4.1.2. Groundwater Quality Index (*WQIgw*)

The water quality index for groundwater is a function of the pollution load, expressed as *WQIsw*, and the effective infiltration coefficient (*EIC*). *EIC* was determined as a function of the aquifer type (Figure 2), with an *EIC* (Table 2) assigned to each aquifer type. The map showing the spatial distribution of effective infiltration coefficient (*EIC*) values for the Kupa River catchment is shown in Figure 5. It should be noted that there are no "extensive and highly productive aquifers" and "confined extensive aquifers" in the study area. However, an additional aquifer type "low permeability strata that cover porous and fissured aquifers" is introduced, for which the *EIC* factor of 0.05 is assigned.

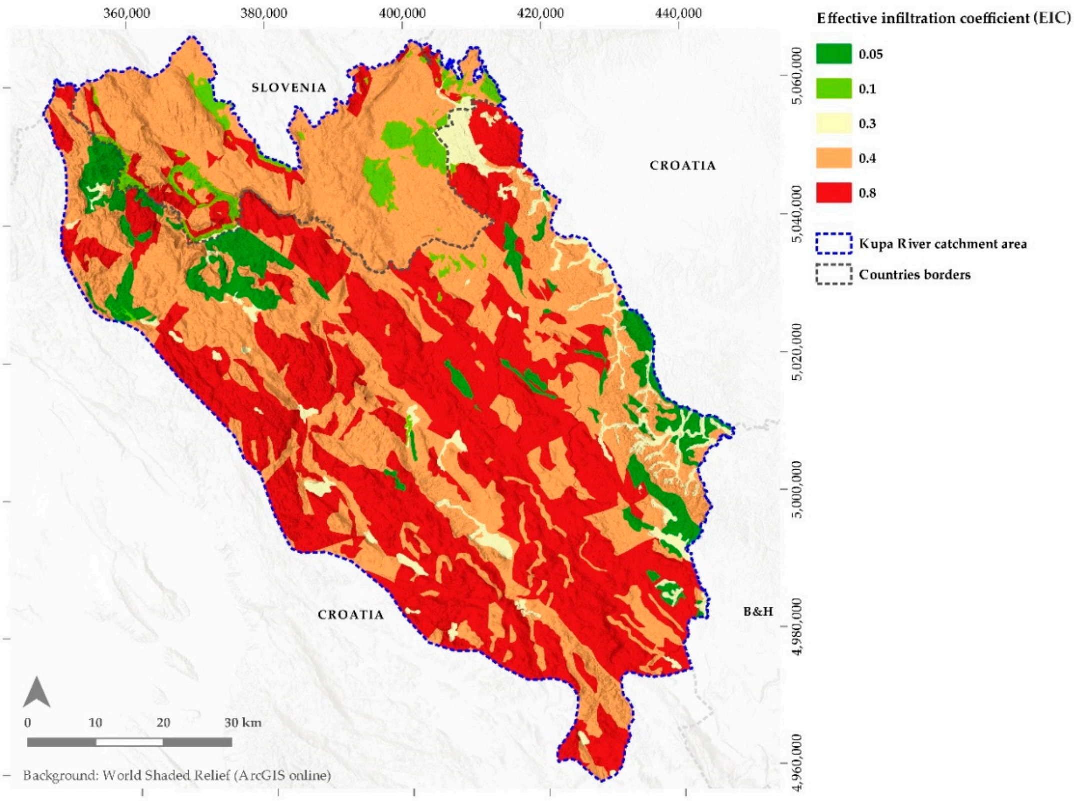


Figure 5. Effective infiltration coefficient (*EIC*).

The effective infiltration coefficient reflects the hydrogeological characteristics of the Kupa River catchment area. Hence, higher *EIC* values indicate a higher groundwater quality vulnerability, whereas low groundwater vulnerability is indicated by low *EIC* values. As the majority of the study area (~70%) consists of fractured and karstified carbonate rocks with highly and moderately productive aquifers, their intrinsic vulnerability is very high (red colors for carbonate rocks with aquifers of high to very high permeability) and high (orange colors for carbonate rocks with aquifers of medium permeability). In contrast, clay and marl deposits are insignificant aquifers with low permeability and are characterized by low vulnerability.

Obtained groundwater quality index (*WQIgw*) values (non-normalized) range from 0.01 to 0.8. Figure 6 shows five equally distributed classes of normalized values from very low (min. value 0.01) to very high (max. value 1.0) *WQIgw* values. Very high and high values of *WQIgw* are found in the vicinity of settlements where agricultural activities take place on land consisting mainly of carbonate rocks with good permeability. This also applies to traffic networks laid over karstified carbonate rocks. Medium *WQIgw* values were assigned to built-up areas such as settlements, industrial and commercial areas, and construction sites. Medium *WQIgw* values also refer to agricultural land with significant natural vegetation areas that extend over carbonate rocks with good permeability and to vineyards and non-irrigated arable land on carbonate rocks with medium to low permeability. Low and very low *WQIgw* values were assigned to the largest part (~52%) of the Kupa River catchment area. These are forest areas on carbonate rocks with medium (low *WQIgw*) to low permeability (very low *WQIgw*) or areas without aquifers and anthropogenic activities occurring in areas consisting of intergranular Quaternary deposits.

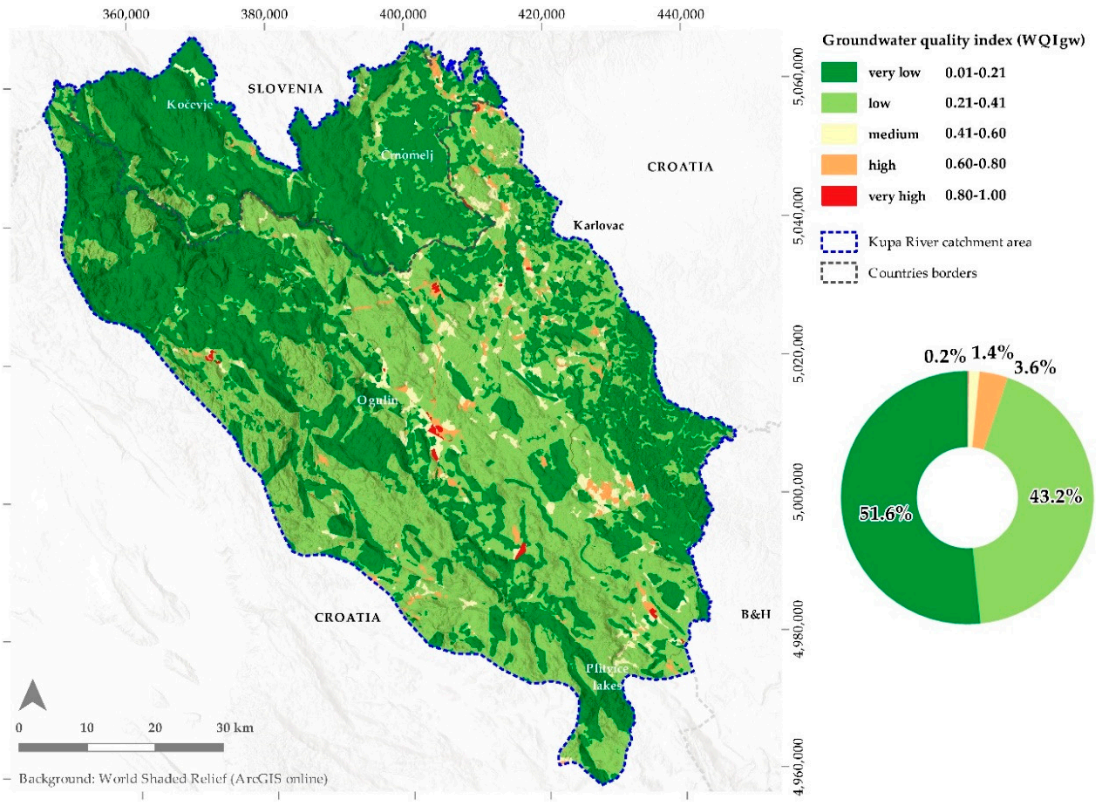


Figure 6. Groundwater quality index (*WQIgw*) for the Kupa River catchment, with the percentage of the respective class.

4.2. Hazard Map

Weighting values (ranging from 10 to 85) were assigned to each hazard type identified within the Kupa River catchment area, as shown in Table 5. The illegal waste dump sites category was introduced.

Table 5. Weighting values for hazards identified within the Kupa River catchment area (adapted from [15]).

No.	Hazard Type	Weighting Value
1	Infrastructural development	
	Urbanization (leaking sewer pipes and sewer systems)	35
	Urbanization without sewer systems	70
	Septic tank, cesspool, latrine	45
1.2	Municipal waste	
	Sanitary landfill	50
	Illegal waste dumpsites	85
1.3	Fuels	
	Gasoline station	60
1.4	Transport and traffic	
	Road, unsecured	40
	Railway line	30
	Runway	35
	Car parking/repair area	35
2	Industrial activities	

Table 5. *Cont.*

No.	Hazard Type	Weighting Value
2.1	Mining (in operation and abandoned)	70
	Mine, other non-metallic	
2.2	Excavation sites	
	Excavation and embankment for development	10
	Quarry	25
2.4	Industrial plants	
	Iron and steelworks	40
	Metal processing and finishing industry	50
	Paper and pulp manufacture	40
	Leather tannery	70
	Food industry	45
2.5	Power plants	
	Gasworks	60
2.6	Industrial storage	
	Stockpiles of raw materials and chemicals	60
2.7	Diverting and treatment for wastewater	
	Wastewater injection well	85
	Discharges of treatment plants	40
3	Livestock and Agriculture	
3.1	Livestock	
	Factory farm	30
	Pastures	25
3.2	Agriculture	
	Arable land	30
	Vineyards and orchards	30

Two hazard maps have been produced, which represent collected data. The topographical map was omitted to improve the visibility of the hazard symbols and the overall map readability; instead, a shaded relief was used (greyscale areas in the maps with no hazards). The unclassified hazard map shows all identified hazard types within the study area (Figure 7). The classified hazard map of the Kupa River catchment area describes the potential impacts of various hazard sources (Figure 8), based on a detailed assessment that followed the recommendation of COST Action 620. The Hazard Index classification ranges between 10 and 85. There are no hazards classified at a very high level within the study area. High hazard levels have been identified for direct wastewater treatment outflows into karst and waste illegally disposed in karst swallow holes and caves located generally in the vicinity of settlements. Moderate hazard levels have been identified for active landfills with remediation process and wastewater effluents from various industrial activities discharged into the watercourses. Agricultural activities in the form of arable land, vineyards, and orchards have been classified as inducing low hazard levels. Similarly, pastures situated mainly in karst mountain areas or near arable land and settlements were characterized by a very low hazard level. The road network, which mainly lacks proper stormwater runoff, was classified as a low hazard level in the 5 m impact zone and a very low hazard level in the 5–25 m zone. Likewise, the railway network in the 5 m impact zone was assigned with a low hazard level. Due to many settlement areas without a sewerage system, a moderate hazard level was assessed, while the low hazard levels were determined for those with potentially leaking sewer network.

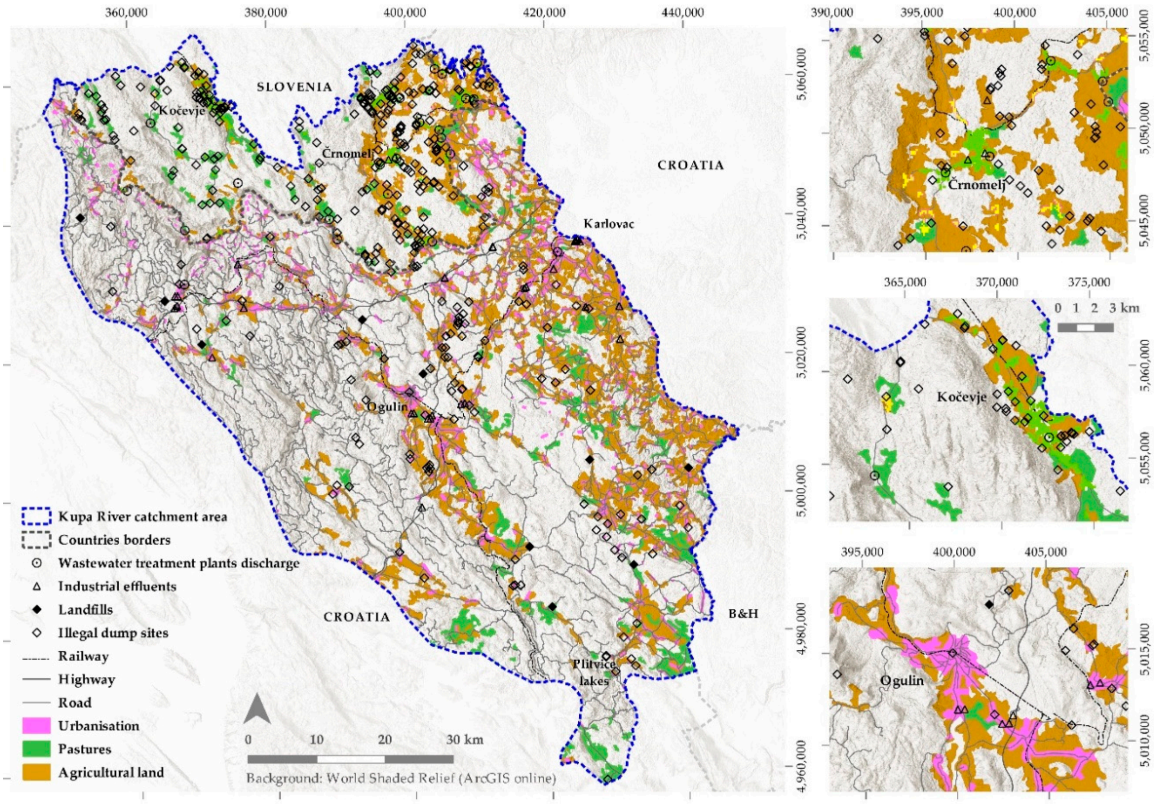


Figure 7. Unclassified hazard map of the Kupa (Kolpa) River catchment area.

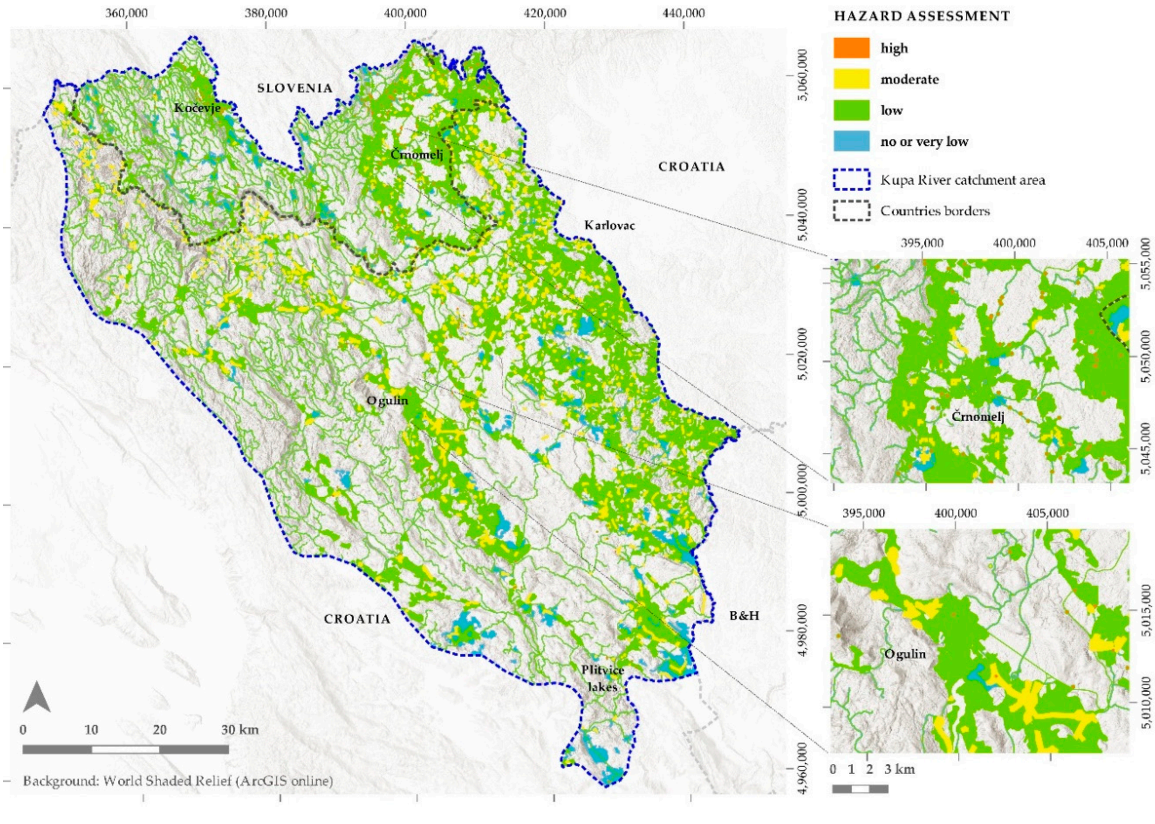


Figure 8. Classified hazard map of the Kupa (Kolpa) River catchment area, showing hazard levels.

5. Discussion

Water resources of sufficient quantity and good quality can support spatial and economic development through various ecosystem services, taking into account the health of the population and ecosystems. Thus, if the potential and actual impacts of land-use activities are not taken into account and existing or newly developed land-use and water management tools are not used, an opportunity is missed to contribute efficiently to the protection and sustainable water resources management. From the perspective of protecting water resources and their ecosystem services (drinking water), it is important to obtain actual data on areas associated with activities that pose a threat (hazard) to surface water or groundwater. In particular, the hazard maps provide a comprehensive overview of point and diffuse sources of pollution and their spatial distribution within the catchment area. Accordingly, they can serve as valuable input data for future spatial planning, the designation of protected areas (especially measures as prohibitions and restrictions), and the allocation of water monitoring stations in recognized hot-spots, which is particularly important in areas of vulnerable karst water resources.

Groundwater quality index (*WQIgw*) maps are merely visualizations of water pollution hazards, and their accuracy depends to a large extent on the correctly prepared input data of the Corine land cover and its resolution. These maps do not indicate exact locations of the negative impacts but rather a zonal spatial distribution. Consequently, *WQIgw* maps based on CLC and hydrogeological map are applicable for regional-scale studies and not for detailed scale, which is required for delineation of drinking water protection zones, where precise locations of activities causing adverse effects are required. However, they can be used as a schematic outline or as a first step towards more detailed hazard maps. It should be noted that the *WQIgw* index and hazard maps represent the potential for groundwater pollution. The realization of this potential can be seen in the measured water quality. For this reason, a more detailed hazard assessment needs to be carried out and examined with data from qualitative status monitoring.

Comparing the water quality index and hazard maps, it is evident that arable land has a very high index (pollution load), while the hazard map shows low hazard. Large areas with a low and very low groundwater quality index are mainly forest areas, which are not classified as a hazard in the hazard map (no color in the hazard map).

The findings of the carried out hazard assessment are in line with previous studies in the Kupa (Kolpa) River catchment area. A similar hazard assessment and mapping study was previously carried out by Biondić [16] on a much smaller spatial extent of the upper part of the Kupa River catchment, also based on the recommendations of COST Action 620. He assessed moderate hazard levels for settlements without adequate wastewater collection and discharge systems, landfills, quarrying, and industrial activities, while the transport infrastructure was classified as having a low hazard level. In his study Biondić [16] identified no hazards that could induce "very low," "high," and "very high" hazard levels, as opposed to this research where high hazard levels have been associated with illegal waste disposal sites and direct discharges of wastewater. Furthermore, Meaški [18] prepared a hazard map for the Plitvice Lakes National Park, the southernmost part of the Kupa River catchment area. The impact zones of point, linear, and polygonal hazard sources were defined similarly, with the classified hazard level categories largely corresponding to those identified in the presented work. The difference lies in the classification of agricultural land, for which Meaški assessed very low hazard levels and inner impact zones of roads as imposing a moderate hazard level. This results from applying different Q_n factors, which Meaški [18] estimated, taking into account the purpose of the hazard assessment and mapping scale, as it encompassed the national park area with very valuable water resources and natural assets. Contrary to previously mentioned research, this paper gives for the first time a comprehensive hazard assessment for the whole karstic part of the Kupa River catchment area, taking into account its transboundary character and part of the catchment located in the neighboring country Slovenia. In addition, for the first time, water quality index mapping was done for the Kupa River catchment on a transboundary scale.

Furthermore, existing groundwater vulnerability maps of Slovenia [47] and Croatia [48] indicate predominant categories of extremely and highly vulnerable groundwater resources, which were determined for highly karstified areas with numerous ponors, where direct contact of surface contamination with groundwater is possible. When correlating these areas with the water quality indices and hazard maps of this study, it is clear how most settlements and agricultural land are located in areas of moderate to high groundwater vulnerability.

The methodology of hazard assessment according to COST Action 620 includes the mapping of hazards that are represented in point, linear, and polygonal forms. This proved to be a certain challenge from the point of view of mapping scale, as point sources on maps at the regional scale can be lost within linear and polygonal hazards. However, regional hazard maps require much more generalized input data; therefore, it is common practice to represent industrial plants and landfills as points on such a spatial scale. In contrast, more detailed scales, as they can be used in spatial planning within drinking water protection zones, include polygonal hazard forms, i.e., buffer zones with graded effects. It can be concluded that the methodology used in the presented study has proven to be applicable for such a regional study for aquifers on a transboundary scale, even in challenging karst environments where the complex properties and structure make the exploration and monitoring of groundwater resources laborious and often scarce. However, a more detailed scale for better localization of potential hazards should be preferred for the decision-making on appropriate protection measures in vulnerable parts of the Kupa River catchment. This is particularly true for urban (settlements) and industrial areas with a wide range of different types of hazard, the cumulative effect of which should be taken into account and studied in more detail.

It is important to note that the hazards in the study area are not continuously present during a year. Their temporal resolution was not considered in this study, but it can be assumed that the occurrence and duration of agricultural hazards (such as fertilization, tillage, grazing) depend on the season. It must also be considered how the hazard maps can change substantially over time depending on spatial development and land-use change, which can occur quite rapidly in developing urban areas. Particularly in Croatia, a large number of wastewater collection and treatment projects are currently being planned for settlements without existing networks and facilities. In order to be able to locate all recent hazards in a particular area, it is necessary to constantly update the maps with new data.

Moreover, there is a risk that hazard assessments are often subjective, because of the expert's knowledge base and experience background, as the parameters (e.g., weighting factors in the methodology of COST Action 620, land-use load, and effective infiltration coefficients in the CC-WARE methodology) and evaluation of hazards are based on a qualitative assessment of parameters as expert judgment.

It is important to note that not all existing hazards have been mapped, as only those activities that are mandatory to be reported and have an appropriate environmental permit are collected from national inventories. Unfortunately, there is a lack of environmentally aware public behavior with regards to waste disposal, manure storage, application of pesticides, and so forth. For instance, the inventory of illegal waste disposal sites in Croatian karst swallow holes and caves is constantly updated by various speleological societies through a voluntary initiative for waste cleanup.

Thus, an integrated management approach is required to efficiently preserve the water resources of the Kupa River catchment, which are already exposed to various anthropogenic pressures (as shown by the water quality indices and hazard mapping) and additionally threatened by climate change. As water resources cross administrative boundaries, a legal framework [10,11,49] is established at the transnational level to protect and ensure their long-term sustainable use. However, as highlighted in the GUIDR (Guidance for the Danube region for sustainable land use planning) [4] developed by the CAMARO-D project, land-use planning should provide a basis for the sustainable management of water resources and related social and economic systems, by coordinating competing demands based on adequate planning mechanisms. It should be noted that not only the sectoral synergy is essential, but that an important factor in efficient and sustainable management is also the engagement of all relevant stakeholders in the decision-making process and the raising of public awareness by providing information on hazards related to harmful land-use practices. This applies in particular to vulnerable karst areas, where the inhabitants should understand the multiple benefits of maintaining and improving the status of the water environment as crucial to achieving the objectives of sustainable management. The outcomes of the combined approach to water quality indices and hazard assessment applied to karst water resources in the present study can be easily understood by non-experts, thus facilitating their dissemination outside the scientific community.

6. Conclusions

The present study aimed at investigating methods to assess potential impacts of land-use on vulnerable karst water resources in the wide transboundary catchment area of the Kupa River. This was achieved by using spatial analyses in GIS software for water quality index mapping for surface and groundwater resources, followed by detailed mapping of man-made hazards. The final results depicted on the water quality index map show predominant zones with "very low" and "low" water quality indices for surface and groundwater resources. However, higher values are observed in lowland areas, karst plateaus, and poljes where the impacts of anthropogenic activities such as agricultural production and quarrying take place on permeable karstified carbonate rocks. Overall, the assessment and mapping of the water quality index proved to be a straightforward method applicable for a generalized representation of the interrelations between land use and water resources of karst aquifers on a regional scale.

Despite the complex data preparation, the hazard assessment proved to be successful and delivered satisfactory results, which are in line with the results of the water quality indices assessment and the findings of previous studies carried out on a detailed scale for parts of the Kupa River catchment. The hazard map pinpoints the areas with potentially harmful impacts on water resources caused by various point and diffuse sources of pollution. Illegal waste dumps in the areas of karst swallow holes and caves, and direct wastewater discharges into the karst underground have been identified as potentially problematic areas and classified as high hazard levels. Moreover, numerous scattered settlements without adequate sewerage systems represent a moderate hazard level, while low hazard levels were determined for the surrounding agricultural activities and transport infrastructure that cross the entire catchment area.

Both methods examined in the present study can be used as the first screening tool for the qualitative status of water resources at a regional scale. This is particularly true for transboundary catchments, as the maps highlight the areas where certain action steps might be required to meet the water quality requirements established by the existing legislation. In combination with existing regional vulnerability maps, the resulting water quality index and hazard maps can serve as a basis for future adaptation strategies in the context of water protection, water management, and climate change, so that further deterioration of water resources quality can be prevented. Hazard inventories and graphical interpretations could be useful to different sectors, from local actors such as water managers, spatial planners, and nature conservationists to wider decision-making and legislative bodies, whose cooperation is a key factor for the sustainable management of the Kupa River catchment's water resources.

In order to build on the results presented in this study, future research should consider a more detailed assessment and mapping of areas where a higher hazard density has been identified, as well as areas with highly vulnerable karst water resources, drinking water protection zones, or nature reserves. Moreover, downscaling to areas of special interest will allow a more thorough correlation between the potential hazards collected from several data inventories and the on-site situation. A step forward could also be the development of a Kupa River catchment risk map based on existing vulnerability and hazard maps, which has been elaborated in the presented study.

Author Contributions: Conceptualization, B.Č.C. and A.S.; data preparation, A.S. and B.Č.C.; writing—original draft preparation, A.S.; writing—review and editing, B.Č.C., J.L.R., J.T., and I.B.; visualization, A.S.; supervision, J.L.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research's activities have been undertaken within the framework of CAMARO-D (Cooperating towards Advanced Management Routines for land use impacts on the water regime in the Danube River basin) project co-funded by the European Union funds European Regional Development Fund and Instrument for Pre-Accession Assistance. Croatian Geological Survey funded the APC.

Acknowledgments: The authors would like to express their gratitude to Prvoslav Marjanović for his guidance through the water quality index assessment.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Taylor, R.G.; Scanlon, B.; Döll, P.; Rodell, M.; Van Beek, R.; Wada, Y.; Longuevergne, L.; Leblanc, M.; Famiglietti, J.S.; Edmunds, M.; et al. Ground Water and Climate Change. *Nat. Clim. Chang.* **2013**, *3*, 322–329. [CrossRef]
2. Lukač Reberski, J.; Rubinić, J.; Terzić, J.; Radišić, M. Climate Change Impacts on Groundwater Resources in the Coastal Karstic Adriatic Area: A Case Study from the Dinaric Karst. *Nat. Resour. Res.* **2020**, *29*, 1975–1988. [CrossRef]
3. Biondić, B.; Biondić, R.; Kapelj, S. Karst Groundwater Protection in the Kupa River Catchment Area and Sustainable Development. *Environ. Geol.* **2006**, *49*, 828–839. [CrossRef]
4. Marjanović, P.; Pejović, D.; Marjanović, M. GUIDR—Guidance for the Danube Region for Sustainable Land Use Planning. 2019. Available online: http://www.interreg-danube.eu/uploads/media/approved_project_output/0001/37/5b8d5a835624b6a9538ab8bc7e4f92cc625eb3c8.pdf (accessed on 10 August 2020).
5. Federal Ministry of Agriculture Regions and Tourism; Agricultural Research and Education Centre Raumberg-Gumpenstein; Municipality of the City of Vienna Department 31—Vienna Water; University of Ljubljana; Public Water Utility JP VOKA SNAGA; Croatian Geological Survey; Forest Research Institute Baden-Württemberg. Transnational Cluster-Specific Characteristics Cluster 1 "Land Use and Vegetation Cover—Protection of Groundwater Resources". 2019. Available online: www.interreg-danube.eu/approved-projects/camaro-d/outputs?page=1 (accessed on 15 August 2020).
6. Buljan, R.; Pavlić, K.; Terzić, J.; Perković, D. A Conceptual Model of Groundwater Dynamics in the Catchment Area of the Zagorska Mrežnica Spring, the Karst Massif of Kapela Mountain. *Water* **2019**, *11*, 1983. [CrossRef]
7. Pavlić, K.; Jakobović, D. High Flows from Gornja Dobra Basin. *Rud. Geol. Naft. Zb.* **2018**, *33*, 45–52. [CrossRef]
8. International Commission for the Protection of the Danube River. The Danube River Basin District Management Plan. 2015. Available online: www.icpdr.org/main/activities-projects/river-basin-management-plan-update-2015 (accessed on 5 September 2020).
9. International Commission for the Protection of the Danube River. *Convention on Cooperation for the Protection and Sustainable Use of the Danube River*; International Commission for the Protection of the Danube River: Vienna, Austria, 1994; p. 21.
10. The Croatian Government. *Plan Upravljanja Vodnim Područjima 2016–2021. (River Basin Management Plan 2016–2021)*; The Croatian Government: Zagreb, Croatia, 2016.
11. The Slovenian Government. *Načrt Upravljanja Voda na Vodnem Območju Donave za Obdobje 2016–2021 (Danube River Basin Management Plan 2016–2021)*; The Slovenian Government: Ljubljana, Slovenia, 2016.
12. Čenčur Curk, B.; Cheval, S.; Vrhovnik, P.; Verbovšek, T.; Herrnegger, M.; Nachtnebel, H.; Marjanović, P.; Siegel, H.; Gerhardt, E.; Hochbichler, E.; et al. *CC-WARE—Mitigating Vulnerability of Water Resources under Climate Change. WP3—Vulnerability of Water Resources in SEE*; Report Version 5; 2014. Available online: https://www.researchgate.net/publication/301889158_CC-WARE_Mitigating_Vulnerability_of_Water_Resources_under_Climate_Change_WP3_-_Vulnerability_of_Water_Resources_in_SEE (accessed on 29 January 2020).
13. Nistor, M.-M. Groundwater Vulnerability in the Piedmont Region under Climate Change. *Atmosphere* **2020**, *11*, 779. [CrossRef]

14. Stevanović, Z.; Marinović, V. A Methodology for Assessing the Pressures on Transboundary Groundwater Quantity and Quality-Experiences from the Dinaric Karst. *Geol. Croat.* **2020**, *73*, 1–12. [CrossRef]
15. *COST Action 620 Vulnerability and Risk Mapping for the Protection of Carbonate (Karst) Aquifers*; Final Report; Zwahlen, F. (Ed.) European Commission, Directorate-General for Research: Luxembourg, 2004.
16. Biondić, R. Zaštita Voda Gornjeg Dijela Sliva Kupe (Water Protection of the Upper Part of the River Kupa Catchment Area). Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, Croatia, 2005.
17. Kovačič, G.; Ravbar, N. The Protection of Karst Waters. *Acta Carsologica* **2007**, *36*, 254. [CrossRef]
18. Meaški, H. Model Zaštite Krških Vodnih Resursa na Primjeru Nacionalnog parka "Plitvička Jezera" (Model of the Karst Water Resources Protection on the Example of the Plitvice Lakes National Park). Ph.D. Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, Croatia, 2011.
19. Loborec, J.; Kapelj, S.; Novak, H. Analysis of Groundwater Pollution Hazard in Karst: A Case Study of Jadro and Žrnovnica Catchment Area. *Građevinar* **2015**, *67*, 1093–1103. [CrossRef]
20. Frančišković-Bilinski, S.; Bhattacharya, A.K.; Bilinski, H.; Bhaskar, D.B.; Mitra, A.; Sarkar, S.K. Fluvial Geomorphology of the Kupa River Drainage Basin, Croatia: A Perspective of Its Application in River Management and Pollution Studies. *Z. Fur Geomorphol.* **2012**, *56*, 93–119. [CrossRef]
21. Meaški, H.; Biondić, B.; Biondić, R. Delineation of the Plitvice Lakes Karst Catchment Area, Croatia. In *Karst without Boundaries*; Stevanović, Z., Krešić, N., Kukurić, N., Eds.; CRC Press/Balkema: Boca Raton, FL, USA, 2016; pp. 269–284.
22. Habič, P.; Kogovšek, J.; Bricelj, M.; Zupan, M. Izviri Dobličice in njihovo širše kraško zaledje. *Acta Carsologica* **1990**, *19*, 5–100.
23. Habič, P.; Kogovšek, J. Sledenje voda v kraškem zaledju Krupe v JV Sloveniji. *Acta Carsologica* **1992**, *21*, 35–76.
24. Bura, D. *Statistika Krša Jugoslavije (Statistical Analysis of Jugoslavian Karst)*; Savezno savjetovanje o kršu: Split, Croatia, 1958; pp. 67–98.
25. Roglić, J. Geografski aspekt Dinarskog krša (Geographical aspect of Dinaric karst). In *Krš Jugoslavije 1*; Petrik, M., Ed.; JAZU: Zagreb, Croatia, 1969; pp. 19–39.
26. Herak, M. Karst of Yugoslavia. In *Karst: Important Karst Regions of the Northern Hemisphere*; Herak, M., Stringfield, V.T., Eds.; Elsevier: Amsterdam, The Netherlands, 1972; pp. 25–83.
27. Bogunović, M.; Bensa, A. Tla krša-temeljni čimbenik biljne proizvodnje (Karst Soils-Fundamental Factor of Agriculture Production). In *Hrvatski Krš i Gospodarski Razvoj*; Biondić, B., Božičević, J., Eds.; Centar za Krš: Gospić/Zagreb, Croatia, 2005; pp. 41–50.
28. Šegota, T.; Filipčić, A. Köppen's Classification of Climates and the Problem of Corresponding Croatian Terminology. *Geoadria* **2003**, *8*, 17–37. [CrossRef]
29. Kozjek, K.; Dolinar, M.; Skok, G. Objective Climate Classification of Slovenia. *Int. J. Climatol.* **2017**, *37*, 848–860. [CrossRef]
30. Croatian Hydrological and Meteorological Service. Mean Monthly Temperature for Stations Parg and Ogulin. Available online: https://meteo.hr/klima.php?section=klima_podaci&param=k1 (accessed on 2 November 2020).
31. Slovenian Environment Agency (ARSO). Mean Monthly Temperature for Station Dobliče. Available online: http://www.meteo.si/uploads/probase/www/climate/table/sl/by_location/doblice/climate-normals_81-10_Doblice.pdf (accessed on 2 November 2020).
32. Biondić, B.; Biondić, R.; Kapelj, S. Protection of the Kast Aquifers in the River Kupa Catchment Area and Sustainable Development. *Environ. Geol.* **2003**, *50*, 33–36.
33. Pavlić, K.; Kovač, Z.; Jurlina, T. Analiza Trendova Srednjih i Maksimalnih Protoka u Ovisnosti o Klimatskim Promjenama—Primjer Na Krškim Slivovima Hrvatsk. *Geofizika* **2017**, *34*, 157–174. [CrossRef]
34. Frantar, P.; Hrvatin, M. Pretočni Režimi v Sloveniji Med Letoma 1971 in 2000. *Geogr. Vestn.* **2005**, *77*, 115–127.
35. Bonacci, O.; Andrić, I. Impact of an Inter-Basin Water Transfer and Reservoir Operation on a Karst Open Streamflow Hydrological Regime: An Example from the Dinaric Karst (Croatia). *Hydrol. Process.* **2010**, *24*, 3852–3863. [CrossRef]
36. Čanjevac, I. Tipologija Protočnih Režima Rijeka u Hrvatskoj. *Hrvat. Geogr. Glas.* **2013**, *75*, 23–42. [CrossRef]
37. Croatian Geological Survey. *The Geological Map of the Republic of Croatia at 1:300,000 Scale*; Croatian Geological Survey: Zagreb, Croatia, 2009.

38. Bauser, S. *Basic Geological Map of the Republic of Slovenia at Scale 1:250,000*; Geological Survey of Slovenia: Ljubljana, Slovenia, 2010.
39. *Hydrogeological Map of the Republic of Slovenia 1:250,000—IAH*; Geological Survey of Slovenia: Ljubljana, Slovenia, 2004.
40. Biondić, B.; Biondić, R.; Brkić, Ž. *Basic Hydrogeological Map of Croatia 1:300,000*; Croatian Geological Survey: Zagreb, Croatia, 2003.
41. BGR (Bundesanstalt für Geowissenschaften und Rohstoffe). International Hydrogeological Map of Europe 1:1 500 000. 2015. Available online: https://www.bgr.bund.de/EN/Themen/Wasser/Projekte/laufend/Beratung/Ihme1500/ihme1500_projektbeschr_en.html (accessed on 26 November 2019).
42. Vlahović, I.; Tišljar, J.; Velić, I.; Matičec, D. Evolution of the Adriatic Carbonate Platform: Palaeogeography, Main Events and Depositional Dynamics. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2005**, *220*, 333–360. [CrossRef]
43. Schmid, S.; Bernoulli, D.; Fügenschuh, B.; Matenco, L.; Schefer, S.; Schuster, R.; Tischler, M.; Ustaszewski, K. The Alpine-Carpathian-Dinaridic Orogenic System: Correlation and Evolution of Tectonic Units. *Swiss J. Geosci.* **2008**, *101*, 139–183. [CrossRef]
44. Terzić, J. Hydrogeology of Adriatic Karst Islands. Ph.D. Thesis, University of Zagreb, Zagreb, Croatia, 2006.
45. Wochna, A.; Lange, K.; Urbanski, J. The influence of land cover change during sixty years on non point source phosphorus loads to Gulf of Gdansk. *J. Coast. Res.* **2011**, *64*, 1820–1824.
46. European Environment Agency & Copernicus Land Service. Corine Land Cover 2018. Available online: https://land.copernicus.eu/pan-european/corine-land-cover/clc2018 (accessed on 26 November 2019).
47. Prestor, J.; Janža, M. *Assessment of the Infiltration (Kennessy Method) and Groundwater Vulnerability of Slovenia*; Geological Survey of Slovenia: Ljubljana, Slovenia, 2006.
48. Biondić, R.; Biondić, B.; Rubinić, J.; Meaški, H.; Kapelj, S.; Tepeš, P. *Ocjena Stanja i Rizika Cjelina Podzemnih Voda na Krškom Području u Republici Hrvatskoj—Završno Izvješće (Assessment of status and Risk of Groundwater Bodies in the Karst Area of Croatia—Final Report)*; Faculty of Geotechnical Engineering, University of Zagreb: Varaždin, Croatia, 2009. (unpublished). Available online: https://www.voda.hr/sites/default/files/dokumenti/ocjena_stanja_i_rizika_podzemnih_voda_na_krskom_podrucju_u_rh_varazdin_2009.pdf (accessed on 5 November 2020).
49. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community Action in the Field of Water Policy. *Off. J. Bruss.* **2000**, *327*, 1–73.

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Paper 2 (P2):

Conceptual Model Based on Groundwater Dynamics in the Northern Croatian Dinaric Region at the Transition from the Deep Karst and Fluviokarst

By

Boljat, Ivana; Terzić, Josip; Duić, Željko; Lukač Reberski, Jasmina; Selak, Ana

water

Article

Conceptual Model Based on Groundwater Dynamics in the Northern Croatian Dinaric Region at the Transition from the Deep Karst and Fluviokarst

Ivana Boljat [1], Josip Terzić [1], Željko Duić [2,*], Jasmina Lukač Reberski [1] and Ana Selak [1]

[1] Department of Hydrogeology and Engineering Geology, Croatian Geological Survey, Milana Sachsa 2, 10000 Zagreb, Croatia; iboljat@hgi-cgs.hr (I.B.); jterzic@hgi-cgs.hr (J.T.); jlukac@hgi-cgs.hr (J.L.R.); aselak@hgi-cgs.hr (A.S.)

[2] Department of Geology and Geological Engineering, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia

* Correspondence: zeljko.duic@rgn.unizg.hr; Tel.: +385-1-5535757

Abstract: The Dinaric karst in the north differs from the rest of the karst in Croatia in terms of karstification depth. The infiltrating precipitation drains in cascades from deeply karstified mountainous areas to the shallow or fluviokarst, forming the tributaries of the Kupa River. Time series analyses were conducted on a 5-year dataset to elucidate the hydrogeological conceptual model of the area and clarify disparate findings from tracer tests under varying hydrological conditions. The flow duration curve, autocorrelation functions, and recession curves were used to evaluate the spring discharge variability, the karstification degree, and the karst aquifer's size. The crosscorrelation function and temperature dynamics were employed to assess the spring's response to recharge and the hydrogeological system behavior. Comparative analysis with previous studies was conducted to contextualize the obtained results. The research outcomes delineated several key findings: (i) the deep karst zone is less developed than the shallow karst zone; (ii) groundwater exchange is significantly faster in shallow karst; (iii) groundwater divides in the Kapela Mountain are zonal; (iv) the homogenization of groundwater occurs during periods of high water levels; (v) fast water exchange transpires without concurrent groundwater temperature homogenization; and (vi) a definition of the boundary between deep and fluviokarst in Croatia.

Keywords: karst hydrogeology; time series analysis; groundwater dynamic; Dinaric karst; Kupa catchment; Mrežnica; Dobra

Citation: Boljat, I.; Terzić, J.; Duić, Ž.; Lukač Reberski, J.; Selak, A. Conceptual Model Based on Groundwater Dynamics in the Northern Croatian Dinaric Region at the Transition from the Deep Karst and Fluviokarst. *Water* **2024**, *16*, 1630. https://doi.org/10.3390/w16111630

Academic Editor: Cesar Andrade

Received: 16 May 2024
Revised: 31 May 2024
Accepted: 1 June 2024
Published: 6 June 2024

1. Introduction

Karst aquifers are widely acknowledged as the most anisotropic and heterogeneous groundwater systems, with limits in research possibilities [1]. The high permeability of karst rocks facilitates rapid infiltration of precipitation and swift drainage of water through well-developed conduit systems, referred to as fast-flow. Conversely, slower drainage is attributed to the laminar flow within a matrix or fissures, fractures, and small conduits, known as base-flow [2–4]. Hydraulic conditions within the aquifer govern the pathway of the water flow, which tends to gravitate towards areas of lower pressure, directly depending on aquifer saturation. The interconnected karst network culminates in a discharge at an exsurgence, or a karst spring. The hydrograph of karst springs typically exhibits distinct, sudden peaks caused by discharge fluctuations, with short-term delayed reactions to rainfall and a gradual decline during dry periods [4,5]. Hydrodynamical characterization of an extensive karst system with similar behaviors to karst springs is challenging. Conventional hydrogeological surveys, such as tracing and borehole tests, supplemented by geophysical and speleological observations, provide only limited insights into the hydraulic properties and spatial configuration of underground networks, depending on the survey locations and hydrological conditions at the time of investigation [6,7].

Consequently, a good understanding of the hydrodynamics and functioning of karst aquifers is achieved through comprehensive analysis of karst spring hydrographs, which encapsulate the system's global response, including recharge, storage and throughflow [8]. Karst aquifers represent formations with conduits, fractures, and fissures embedded within relatively low-permeability rock with numerous outflows. In highly karstified environments, catchment boundaries often exhibit variable zonation, causing difficulty in quantifying and spatially delineating input into the system. Hence, time series statistical analyses are a valuable tool for elucidating the characteristics of specific systems and their interconnections.

Time series analyses of a springs discharge and water temperature, accompanied by classical hydrogeological prospection techniques from previous studies, have proven instrumental in comprehending the dynamics of complex karst systems, particularly in extensive karst mountains where numerous springs react differently depending on the precipitation distribution and aquifer saturation levels. Hydrograph recession curve analyses (RCA) have been used for over a century, undergoing constant methodological refinements [9–21], and serving to infer aquifer hydraulic or geometrical properties [3,21,22] and/or ascertain the karstification degree based on the flow type [6,23,24].

The flow duration curve (FDC) provides a graphical representation of the percentage of time within a given period when the discharge rate equals or exceeds a specific threshold. This method is employed to evaluate the range and fluctuation of spring discharge [25–27].

Autocorrelation functions (AFC) quantify the system's memory effect [7,28], while the crosscorrelation function (CCF) offers a comprehensive perspective of the relationship between two series, such as precipitation and spring discharge [29–31], allowing definition of the aquifer's response to recharge impulses and the interrelationship between discharge patterns [25,32,33].

However, approx. 50% of Croatia's territory lies within karstic areas, primarily in the Dinaric karst regions. The study area exhibits pronounced karstification attributed to tectonics, and is recognized as the most karstified part within the Dinaric karst region, according to the high sinkhole density [34]. However, due to the sparse population and low anthropogenic activities in the mountain catchment area, low to very low values of the groundwater quality index (WQIgw) are assigned to the most significant part of the study area [35], meaning good water quality.

The terrain has also been disturbed by numerous hydrotechnical constructions, including accumulations, dams, and tunnels. These man-made interventions, dating back almost a century, are considered as baseline conditions for the area. The construction of a hydropower plant caused significant changes in the hydrogeological and hydrological settings, while the hydropower potential will be additionally exploited as the construction of retention walls in the Drežnica polje started in 2022. Furthermore, the ongoing revitalization of a ski resort, hotel settlement, and sports-recreation center of the Croatian Olympic Centre Bjelolasica could cause additional pressure on the strategically crucial hydrogeological system and the water quality.

The hydrogeology of the study area has been described based on its tectonics and lithological composition [36]. Numerous groundwater tracing tests were carried out over 70 years ago to define the catchment boundaries, yet were greatly limited by available instruments and methods, reflecting only certain hydrological conditions.

This paper examines a 5-years dataset from six springs and five meteorological stations, utilizing analysis including RCA, FDC, ACF, and CCF, alongside temperature dynamics. The objectives are to (1) define the hydrological characteristics of the transition zone from deep to shallow karst in north Dinaric Croatia, (2) develop a conceptual hydrogeological model to address the discrepancies in tracing results within the Kapela Mountain (referred to as Kapela), and (3) characterize new hydrogeological relations concerning human interventions in the area as zero-state.

The groundwater dynamics of the deeply karstified area in Kapela was performed through time series analyses of four observed springs: Draškovac, Vitunj, Zagorska Mrežnica, and Bistrac Sabljaki. These springs feed short watercourses through the Ogulin polje and subsequently sink into a well-developed karst network up to 100 m deep, contributing groundwater downstream to numerous springs, from which the Gojak and Tounjčica springs are analyzed in this paper, and form the Kupa River tributaries. This paper is the first of its kind in this study area, employing statistical methods to characterize the regional hydrogeological relationships. In this research area, many open questions remain, and the watersheds are not clearly defined. For example, the Jasenak polje, according to official sanitary protection zones, belongs within the catchment area of the Mrežnica River, while according to official river watershed classifications, it falls within the catchment area of the Dobra River. A combined hydrological and hydrogeochemical approach was previously used in research on the neighboring catchments like the Gacka River springs [33,37,38], the mountainous section of the Kupa River in the north [39,40], and the Lička Jesenica catchment [41]. In this research area, Buljan et al. [42] studied the immediate watershed of the Zagorska Mrežnica spring, and Bonacci and Andrić [43] examined the effects of hydro-technical building and climate change on the Dobra River catchment.

The scientific novelty of this research lies in the comprehensive time series analysis, alongside temperature dynamics, to understand the hydrological characteristics and groundwater dynamics, and give new insights into the hydrogeological impacts of long-standing human interventions. This research addresses discrepancies in historical groundwater tracing results giving explanations for illogical tracing results and provides evidence that tracer tests are not unambiguous and depend on the conditions, primarily on the aquifers saturation in which they are performed, contributing to effective and sustainable management. Additionally, the applied methods and review of previous studies dynamically characterized the transition zone from a deep to shallow karst, which has been only described descriptively so far, and positions it more precisely geographically.

2. Materials and Methods

2.1. Setting

The study area is located in the northern part of the Dinaric karst region of Croatia (Figure 1) and is a central part of the karstic transboundary Kupa River catchment area. Its western boundary delineates the catchment divide between the Adriatic and Black Sea. The Ogulinska Dobra and Zagorska Mrežnica are sinking rivers that form a karst landscape, the Dobra Valley and the Ogulin polje. The Ogulinska Dobra River originates in clastic formations with numerous small springs in the north, transversing less permeable dolomite to dolomitic limestone over a 51.2 km long watercourse. The research area starts where Ogulinska Dobra waterflow receives significant water input from right tributaries, namely the Kamačnik, the Ribnjak stream, and the Vitunjčica River, which drains the highly tectonized limestone. About 4 km upstream of Ogulin city, the Bukovnik Reservoir collects water from the Ogulinska Dobra. Water from the reservoir is conveyed via a technical tunnel to the Gojak hydropower plant (HPP Gojak). Naturally, or when the reservoir is full, the Ogulinska Dobra River sinks into a 40 m deep ponor, located in Ogulin city. The ponor marks the start of an extensive cave system, Đula-Medvedica, a natural karst drainage system spanning 16 396 m through limestone, with a vertical range of 83 m. The underground flow reemerges at the Gojak spring, where the Dobra River starts its watercourse. The shortest aerial distance between the Đula ponor and the Gojak spring is approx. 4.6 km [43]. The HPP Gojak was built about 100 m downstream from the Gojak spring.

The major spring of the Ogulin polje, the Zagorska Mrežnica, along with the Bistrac Sabljaki and many smaller springs on the south edge, fill the artificial hydro-technical Sabljaki lake. This reservoir was built in 1954, alongside the natural course of the Zagorska Mrežnica River. Before the intervention and during high water levels, the river used to submerge into numerous sinkholes spanning the SW part of the polje. The groundwater connections within the Tounjčica catchments were identified through the first tracing experiment conducted in Croatia [44].

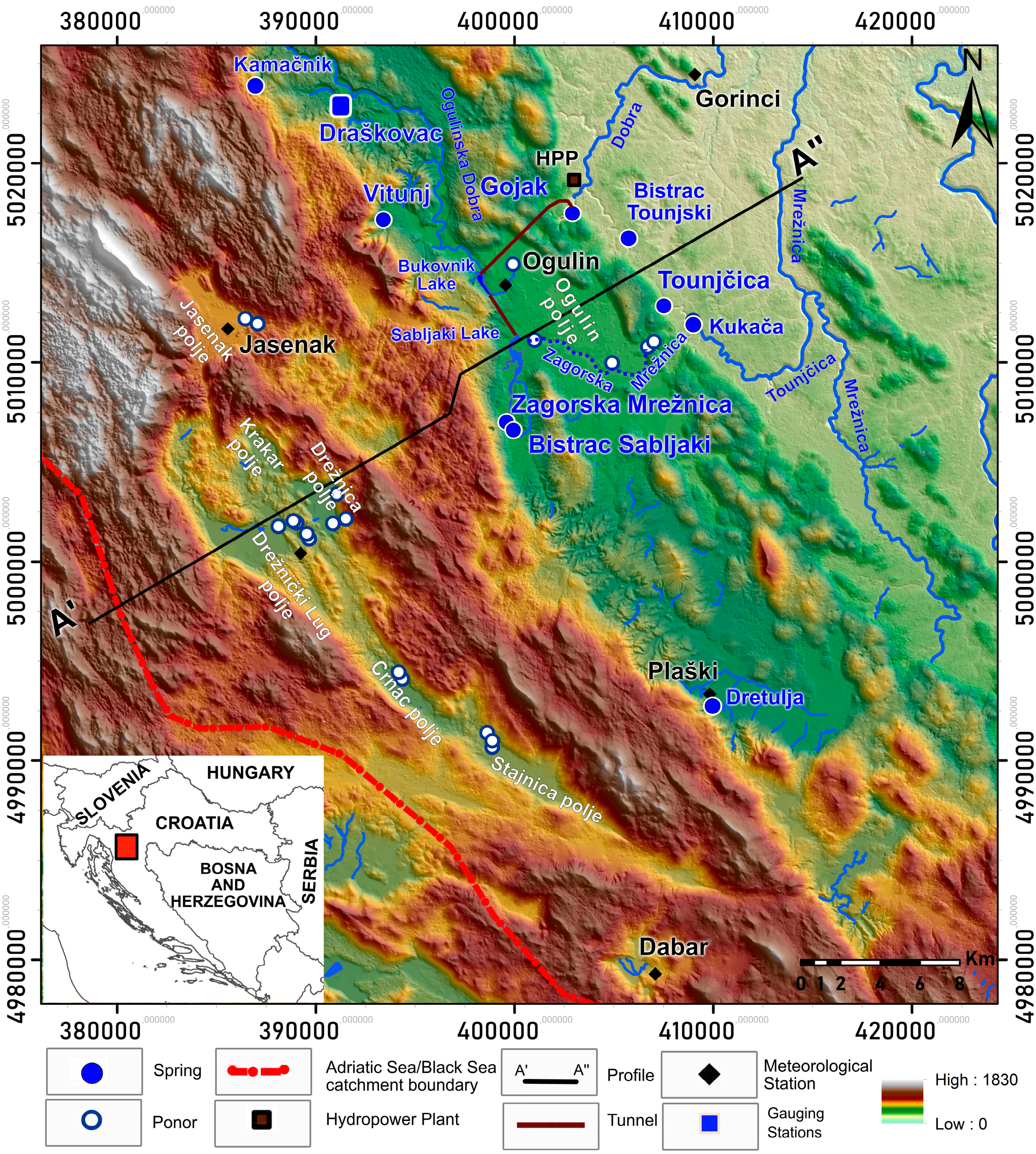


Figure 1. Location of the north Dinaric karst in Croatia (hillshade map modified according to Geoportal). Državna geodetska uprava. Available online: https://geoportal.dgu.hr/ (accessed on 19 December 2023).

Water is transferred via a tunnel from the Sabljaki Reservoir to the Bukovnik Reservoir and then to the HPP Gojak on the Dobra River. This inter-catchment process redirects water from the Mrežnica River to the Dobra River catchment area, thereby decreasing water levels in the Tounjčica River, with a substantial drop in the average annual discharge, which is now 9.8 m^3/s [43]. These authors noted that the construction of the HPP Gojak did not exert any discernible impact on the discharge of the Zagorska Mrežnica and Vitunj springs. However, the reduction of water loss at the gauging stations upstream in Ogulinska Dobra was explained with an increase in the groundwater level in the broader area of the Ogulin polje caused by the construction of the reservoirs.

In addition to its importance for hydroenergy, the Zagorska Mrežnica serves as the main source of drinking water for Ogulin city with a maximum capacity of 200 L/s (with an average of 74 L/s), which is far below the spring's potential capacity. In the wider area of the polje, the water supply is equipped with a few smaller captured springs up to a flow rate of <16 L/s. Across the Kapela, two water intakes meet the needs of the sparse population, in the Jasenak and Krakar polje, each with a flow rate of 5 L/s. According to the water law license, the cumulative maximum flow rate for the Ogulin water supply system is 18.302 m^3/day. The study area exhibits a continental and mountainous climate regime, predominantly influenced by the relief's horizontal and vertical division. The Kapela obstructs the humid air masses from the Mediterranean and Atlantic, resulting in the highest amount of precipitation in Croatia. The mean annual temperature of the mountainous belt remains below 6 °C. Annual precipitation levels are considerable and vary between 1750 and 2500 mm, contributing to substantial spring discharges at the mountain's foothills. Furthermore, the dynamics of aquifers is notably affected by the snow cover, which typically persists for approx. 60 days annually. The seasons are much more pronounced in the wider area of the Ogulin polje, with prolonged periods without precipitation. Summers are dry and warm, while the winters are wet and cold. The average annual temperature in the lower parts ranges from 10 to 11 °C with an average annual rainfall of 1250–1500 mm. The duration of snow cover in these areas averages around 40 days per year [45,46].

2.2. Hydrogeological Characteristics

The area under investigation represents a part of the Adriatic carbonate microplate formed by the sedimentation of carbonate rocks between the Triassic and Lower Cretaceous. This geological formation has been analyzed and interpreted in numerous publications [47–50]. Nevertheless, researchers remain focused on the complex geological, structural, and tectonic frameworks caused by ongoing compressional tectonics that began in the Paleogene era and resulted in a zone of steep faults, generally striking in a NW–SE direction [51]. A basic geological map at a scale of 1:100,000 was created for the entire research area and is divided into three sheets: Ogulin [52], Crikvenica [53] and Črnomelj [54]. The rocks within the research area were classified into three primary hydrogeological groups regarding their lithology and structural–geological relations:

High-permeability carbonates—represented predominantly by limestone and thinner beds or interbeds of dolomite or dolomitic limestone, formed by deposition between the Jurassic and the Cretaceous.

Low-permeability carbonates—lower degree of karstification, mainly composed of dolomite, dolomitized limestone, or dolomite/limestone exchange, with dissolution cavities infilled with secondary materials like silt, sand, and fragments, deposited from the Upper Triassic to Lower Cretaceous.

Quaternary deposits—encompass heterogeneous deposits, mostly mixtures of rock fragments and fine-grained material. The soil covers the carbonate base across the entire area, but their hydrogeological significance is only notable within morphological depressions such as karst poljes.

The lithology, thickness, and tectonics define the rock permeability, while their hydrogeological function depends on the hypsometric and structural positions. Groundwater flow is influenced by numerous, often regional, intersecting fractures, normal and inverse folds, reverse faults, and thrusts.

The part of the Croatian Dinaric karst investigated in this study differs from the rest of the Croatian karst due to the most recent erosional base. Unlike the majority of karst formations in the Dinarides, the erosional base in this area is relatively shallow and has not accumulated like most of the karst in the Dinarides. The karst of the Adriatic catchment area, located to the southwest of the study area, is distinguished by significant karstification depths exceeding 1500 m, particularly in southern regions with pronounced vertical karstification [55]. The study area can be divided into three distinct zones: (1) the Kapela, characterized by karstification depths of several hundred meters and cascading discharge, (2) the Ogulin polje serving as a hydrogeological barrier, and (3) a shallow karst or fluviokarst zone with karstification depths reaching a maximum of approx. 200 m. As a result of significant karstification across the study area, groundwater primarily flows orthogonal to the NW-SE oriented Dinaric formations.

Kapela is the first recharge area formed by substantially fractured Jurassic and Cretaceous rocks of high secondary porosity, provided by limestone with thinner beds of dolomites or dolomitic limestone. Abundant karstic forms in this area result in rare and ephemeral surface watercourses during dry periods. Highly karstified rocks facilitate substantial groundwater accumulation. The caves are primarily horizontal and shallow, not exceeding 100 m [56]. Typical for karst, the springs are periodic and have large discharge oscillations. During wet seasons, the flooded karst poljes feed the springs situated at the mountain's base. Groundwater connections under varying hydrological conditions have been elucidated through numerous tracing experiments (summarized in Section 3.2. Hidrogeological Conceptual Model of Karst System). Tracing results have revealed a direct connection between the Crnac, Drežnica and Stajnica poljes only with springs located at the southern side of the Sabljaki lake, including the Zagorska Mrežnica and Bistrac Sabljaki springs (Figure 2). In the northernmost Jasenak polje, tracing experiments were carried out twice under different hydrological conditions. In 1972, during high water levels, tracing established a groundwater connection between the Kamačnik and Vitunj springs in the Ogulinska Dobra River basin, but also with the spring in the Krakar polje, which undoubtedly gravitates towards the Drežnica polje and the Zagorska Mrežnica and Bistrac Sabljaki springs. Conversely, during low water conditions, only connectivity with the springs of the Zagorska Mrežnica and the Bistrac was observed, with no tracers appearing in the Krakar polje (1986).

At the foot of the mountain, the Jurassic dolomites and Triassic clastic rocks form a hydrogeological barrier and through Quaternary deluvial–proluvial sedimentary rocks direct the groundwater and cause abundant springing along the Ogulin polje and the Dobra valley [36,42,57]. The low permeability of carbonate rocks and nearly impermeable clastic formations facilitate surface runoff and allow retention within hydropower reservoirs. In the west part of the Ogulin polje, surface water sinks underground in the area of highly permeable limestone or the shallow karst zone. This area exhibits a high density of sinkholes and extensive underground karst formations, indicating the most karstified area of the Dinaric karst [34]. The caves extend horizontally for several kilometers, with height differences of less than 80 m. After 5 to 15 km, the groundwater resurfaces at the karst plateau approx. 100 m lower in elevation, forming direct tributaries of the Kupa River, the Dobra, and the Mrežnica River. This part of the Dinaric karst in Croatia, situated north of the Kapela, is significantly different from the rest of the Dinaric karst. While much of the Croatian Dinaric karst is tectonically "accumulated", reaching depths of kilometers, this northern region exhibits limited karstification confined to the recent erosional base of major rivers in the area (Kupa, Mrežnica, Korana, and Dobra) at the groundwater level. This area is known as a shallow karst or typical fluviokarst.

2.3. Methods and Data

Hourly data are indispensable for analyzing the dynamic characteristics of a highly karstified karst system, given its rapid response [40,42]. Precipitation, discharge, and water temperature data were systematically collected at hourly intervals over a five-year period from January 2018 to December 2022. The Croatian Electric Power Company (HEP) provided discharge and water temperature data from six gauging stations, four of which reflect the aquifer characteristics in the mountain catchment area across the Kapela: Vitunj, Draškovac, Zagorska Mrežnica, and Bistrac Sabljaki springs. The remaining two stations, Gojak and Tounjčica, located downstream of the Ogulin polje, represent the zone of shallow karst.

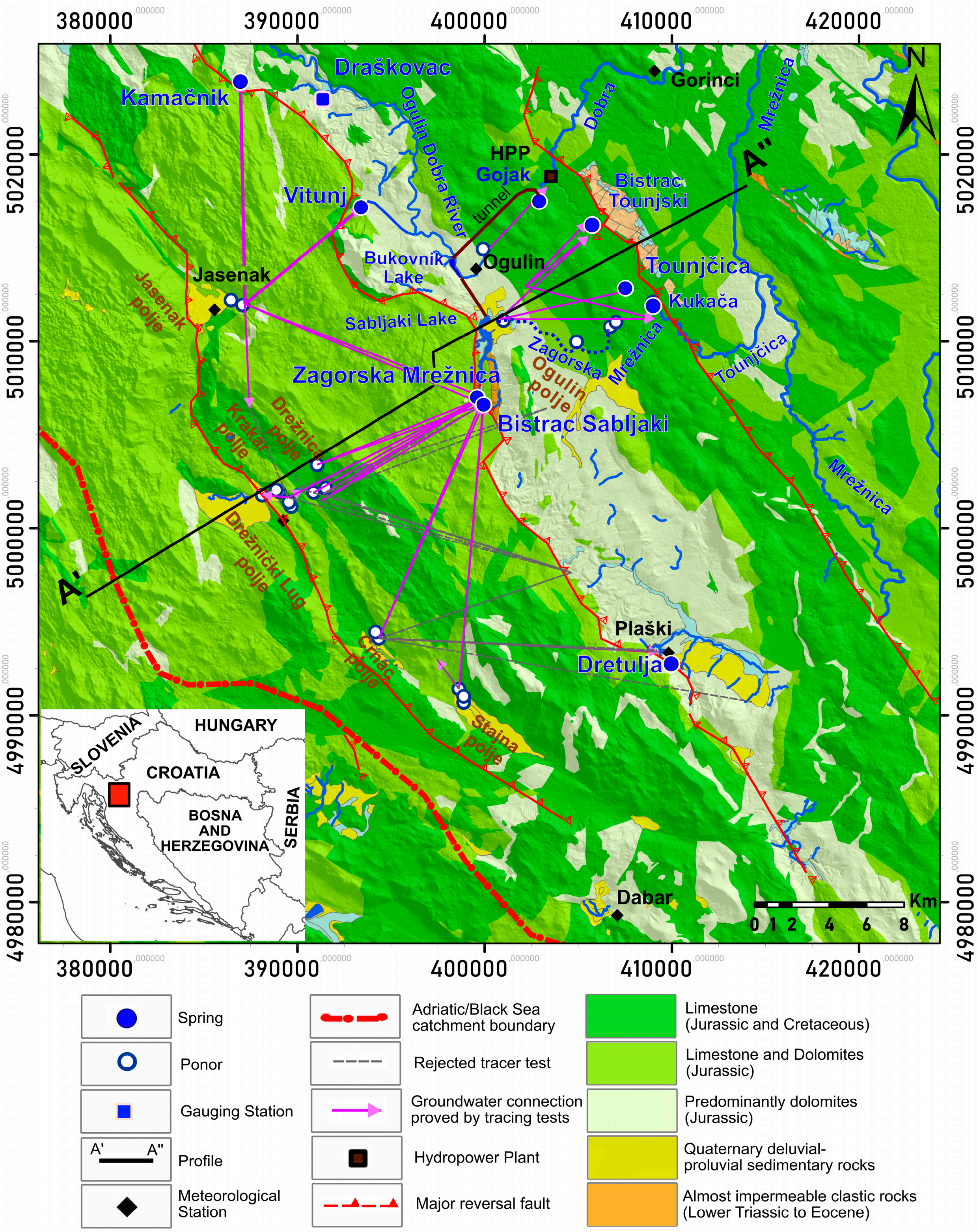


Figure 2. Hydrogeological map of the north Dinaric karst in Croatia (Modified according to [42]).

The Draškovac station, located in the stream formed by two springs, facilitates a clear interpretation of the aquifer's response, due to their close proximity. Flow data expressed in the decimal number were available for all stations from May 2020 to December 2022.

Hence, only this subset was used for detailed hourly analyses. HOBO Water Level Data Loggers (Oneset Computer Corporation, Bourne, MA, USA) were deployed in February 2020 in the Tounjčica and Zagorska Mrežnica springs to minimize atmospheric influences and accurately measure the water temperature. They also served as water level controls.

Groundwater sampling was performed thrice for all monitored springs to determine the main components of the chemical composition of the groundwater, the origin and the comparison between springs. The nitrate, sulphate, and chloride concentrations were utilized to assess the quality of the water. Concentrations of the major anions and cations in the water samples were analyzed using ion chromatography (Thermo Scientific Dionex ICS-6000 HPIC System, Thermo Fisher Scientific Inc., Waltham, MA, USA) in the Croatian Geological Survey.

Hourly precipitation data were obtained from three meteorological stations in the study area by the Croatian Meteorological and Hydrological Service (DHMZ): Jasenak station in Kapela (629 m a.s.l.), Ogulin station (328 m a.s.l.) and Gorinci station (203 m a.s.l.), located 0.5 km from the Gojak spring. Additionally, daily precipitation data from meteorological stations in the Dabar polje (573 m a.s.l.) and the Plaški station (395 m a.s.l.) were utilized to assess the influence of the wider research area. Although Plaški is not within the direct catchment area, it is the closest station on the southern side of the study area, and alongside the Ogulin and Gorinci stations represent the immediate catchment area of the springs (Figure 1).

Time series analyses and spring runoff hydrographs reflect the aquifer's comprehensive reaction to the system's input and output [21], while aquifers behave like a black box. A karst springs' discharge variability is primarily associated with the geometry and physical properties of the system and recharge intensity. To characterize a spring's catchment area, three methods based on discharge data were employed: (1) flow duration curve (FDC) analysis, (2) recession curves analysis (RCA), and (3) autocorrelation function (ACF) analysis. The CCF and water temperature dynamics were used to elucidate the karst system's response to precipitation and the interconnectedness between springs.

FDC analysis of springs assesses the extent and variability of spring discharge, representing the percentage of time during which spring's flow rates exceed a predetermined threshold [4,23]. This analysis entails organizing and plotting discharge values in descending order, irrespective of their chronological sequence. The resulting graph displays discharge along the vertical axis and the percentage of monitored time during which the specified flow-rate threshold is exceeded along the horizontal axis. The steepness of the duration curve indicates deducing key karst systems characteristics; steeper slopes suggest a well-developed system characterized by conduit-dominant flow; conversely, gentler slopes signify systems with slower circulation, greater storage capacity, and lower degrees of karstification [26,58].

RCA is a valuable tool in karst hydrogeological research, focused at understanding the structural characteristics and storage properties of the aquifer based on their response to recharge events. This method involves analyzing the declining limbs of runoff hydrographs, independently of other system parameters, and quantifying the recession coefficient (α) using a simple exponential equation:

$$Q_t = Q_0 e^{-\alpha(t-t_0)} \quad (1)$$

where Q_t is the discharge at time t, Q_0 is the initial discharge at time t_0, and α is the recession coefficient.

The α correlates with the degree of aquifer karstification, including permeability and porosity, but it also depends on the aquifer saturation [3,4,6,11,19,23,59–62]. Due to multiple influences, the α tends to be lower in catchments characterized by lower karstification, thicker deposits, or dense forest cover.

The "matching-strip" tool program was chosen for its ability to utilize all recessionary events, which in the study area's climatic conditions typically lasts no more than 20 days. Developed by Posavec et al. [16,18], the MRCTools v3.1 tool operates on an Excel Visual

Basic for Applications (VBAs) algorithm and is used to assemble the master recession curve (MRC) from the partial recessional limbs observed in each spring's hydrograph. The MRC is further subdivided into typically two or three discharge micro-regimes, each describing distinct reservoirs with varying hydrogeological characteristics. This subdivision is facilitated by the FDC analysis of daily discharges, allowing pinpointing of the crucial discharge points where a sudden and significant shift in the curve's slope occurs [17]. Engineering expertise and a thorough understanding of the terrain are essential for an objective analysis.

The ACF analysis is a statistical tool used to analyze and quantify the degree of similarity between values within a single time series, taking into account their temporal separation [63]. The relation of the autocovariance cov_{xx} can be described as the variance of the signal x for a single event measurement in time t, where $x(t)$ with n data points over lag time, k [31].

$$r(k) = \frac{cov_{xx}(k)}{cov_{xx}(0)} \quad (2)$$

In which:

$$cov_{xx}(k) = \frac{1}{n}\sum_{t=1}^{n-k}(x_t - \overline{x})(x_{t+k} - \overline{x}) \; [k = 0, 1, 2 \ldots (n-1)] \quad (3)$$

$$cov_{xx}(0) = \frac{1}{n}\sum_{t=1}^{n} (x_t - \overline{x})^2 \quad (4)$$

In hydrogeology, the mathematical analysis of discharge data enables the evaluation of a karst system's response to recharge and quantifies the system's memory effect based on decorrelation lag time. It is assumed that the system loses the input impulse once the ACF value attains a predetermined threshold, usually set at 0.2 [7,28,31]. A significant memory effect is frequently associated with a high storage capacity of the system [4,64].

The CCF analysis represents the correlation between two time series data, defining the covariance cov_{xy} and the lag time between them [63]:

$$cov_{xy} = \frac{1}{n}\sum_{t=1}^{n-k}(x_t - \overline{x})(y_{t+k} - \overline{y}) \; [k = 0, 1, 2 \ldots (n-1)]$$

$$cov_{xy} = \frac{1}{n}\sum_{t=1-k}^{n}(x_t - \overline{x})(y_{t+k} - \overline{y}) \; [k = 0, 1, 2 \ldots (n-1)]$$

where $\overline{x}$ and $\overline{y}$ are the average of the input and output parameters. CCF is defined as:

$$r_{xy}\,(\mathrm{k}) = \frac{cov_{xy}(k)}{\sqrt{cov_{xx}(0)cov_{xy}(0)}}$$

This method was used to examine linear relations between input (rainfall) and output (discharge) signals of karst systems [25,31,33], aiming to define the travel time of meteoric water through the vadose zone and discern the similarity between two springs. The ACF and CCF were performed using the XLSTAT (Lumivero, Denver, CO, USA) in the Excel 2021 program (Microsoft, Redmond, WA, USA).

3. Results and Discussion

Figure 3 displays the discharge data of monitored springs spanning from January 2018 to 2022, while Table 1 presents the corresponding basic statistical parameters. The observed lowest, median, and highest discharge ratios are very high, suggesting a rapid water exchange within the system and torrential characteristics. The highest amplitudes are recorded in downstream springs, namely the Gojak and the Tounjčica. However, the increased flow in these springs is caused by the water transfer from their respective catchments to the turbine of the HPP Gojak, primarily during low waters. During dry seasons, the discharge at the Vitunj, Gojak, and Tounjčica springs is significantly reduced, whereas flood events trigger increased activity across the entire spring zone. Notably, the Zagorska Mrežnica spring has the most uniform discharge pattern.

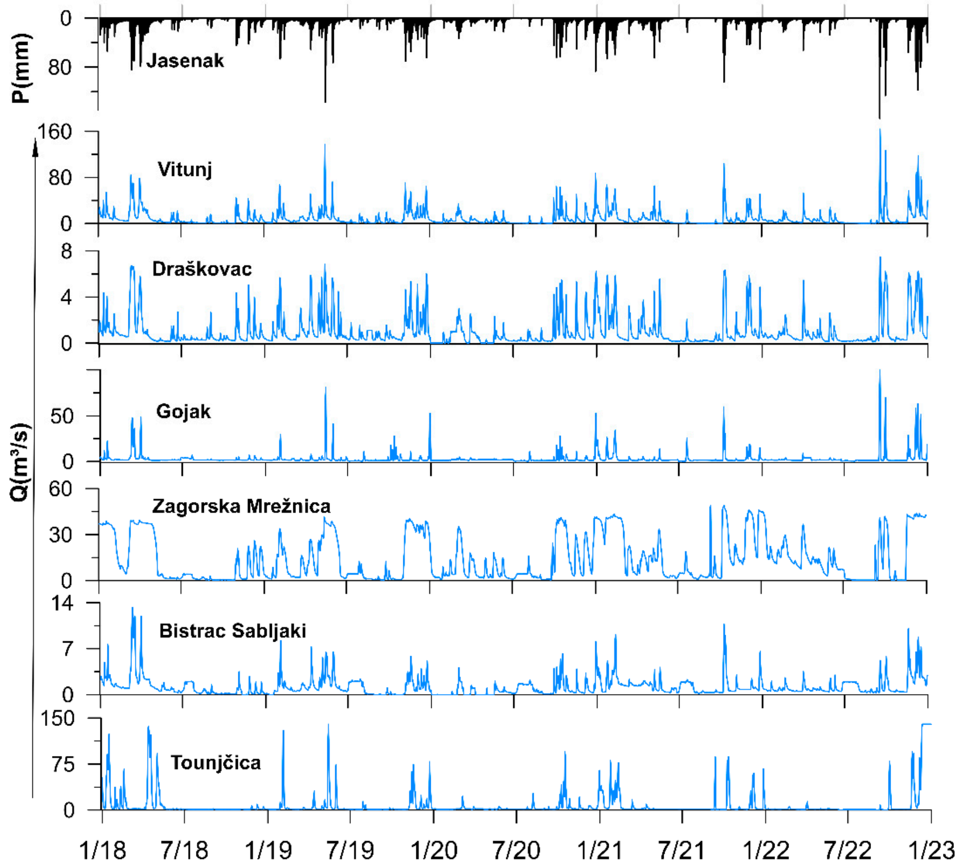


Figure 3. The discharge data of the Vitunj, Draškovac, Gojak, Zagorska Mrežnica, Bistrac Sabljaki and Tounjčica springs from January 2018 to 2022.

Table 1. The basic statistical parameters for the springs' discharge.

	Vitunj (m^3/s)	Zagorska Mrežnica (m^3/s)	Bistrac Sabljaki (m^3/s)	Gojak (m^3/s)	Draškovac (m^3/s)	Tounjčica (m^3/s)
Q_{Min}	0.30	0.30	0.10	0.30	0.10	0.20
Q_{Max}	163.78	49.15	13.30	99.58	7.50	140.00
Q_{avg}	9.07	14.16	1.39	3.13	1.06	7.98
Q_{median}	4.27	7.41	0.85	1.50	0.51	0.54
6 sd	14.07	14.54	1.57	7.22	1.40	21.75
Q_{Min}:Q_{med}:Q_{Max}	1:14:546	1:25:164	1:9:133	1:5:332	1:5:75	1:3:700

The hydrodynamic characteristics of the examined springs are effectively depicted through the configuration of their FDCs, which are based on daily discharge data (Figure 4). FDCs significantly oscillate at the aquifer outflows. The slopes of the FDCs of monitored springs indicate the predominance of two types of flow: a short, mixed time between rapid flow through a well-developed system of karst channels, typical for high-permeability karst, and diffuse flow, typical for low-permeability systems indicating water storage. However, notable differences in behavior are observed among the six springs. The Zagorska Mrežnica spring exhibits the longest duration of high discharge values. Nevertheless, based on earlier research [42], this does not reflect the karstification degree of the catchment area; rather, it signifies the influx of water from the flooded poljes in the hinterland and the limited outflow capacity. The Vitunj spring reaches five or more times the median discharge value of 9.4% for the year, equivalent to 34 days, with a peak discharge of 163 m^3/s. Similarly, the Draškovac spring exceeds this threshold for 40 days throughout the year, with a peak of 7.5 m^3/s, the Bistrac Sabljaki for 17 days with a peak of 13.3 m^3/s, the Gojak for 21 days with a peak of 99.58 m^3/s, the Tounjčica for 49 days with a peak of 140 m^3/s, and the Zagorska Mrežnica for 133 days with a peak of 49.15 m^3/s.

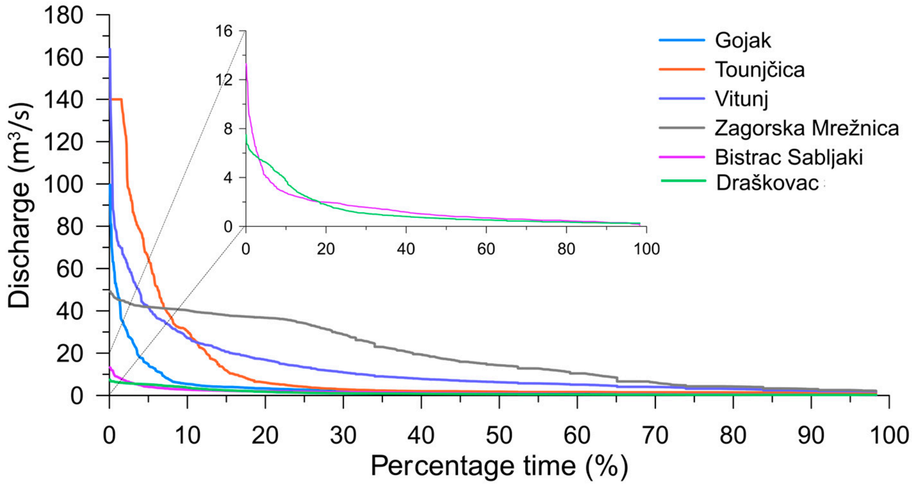


Figure 4. The flow duration curves of daily data for Vitunj, Draškovac, Gojak, Zagorska Mrežnica, Bistrac Sabljaki and Tounjčica springs.

Exponential regression models were developed using the "matching-strip" method to estimate the α, enabling comparative analysis of the hydrogeological characteristics of the monitored springs catchments [65]. In the regression analysis of the Zagorska Mrežnica spring, discharge values exceeding 35 m^3/s were excluded to ensure fidelity of the analyzed data in reflecting the degree of aquifer karstification, independent of the spring outflow capacity's influence. Consequently, the lowest α value obtained for the Zagorska Mrežnica spring should be cautiously considered in interpretation. The recession curves are shown in Figure 5. Generally, the springs have two predominant sub-regimes, first described by α coefficients within the range of 10^{-1}, indicative of rapid discharge through well-developed conduits, and second within the range of 10^{-2}, suggesting an intermediate or mixed to diffuse flow regime with slower circulation in fractured rocks. The MRCs are divided into two or even three sub-regimes to enhance comprehension of the heterogeneous system, although, in these rocks, diffuse flow can be considered as being extremely low. The overview of recession curves in monitored springs are presented in Table 2.

Similarity in the regression models of two smaller springs situated at the foot of Kapela, the Bistrac Sabljaki and the Draškovec is emphasized. The first sub-regime for both springs is characterized by an α of 0.26, and the second is described with an α of 0.112 for the Bistrac Sabljaki and 0.147 for the Draškovac spring, respectively. Bistrac Sabljaki discharge changes regime at the critical point of 2.6 m^3/s, while the Draškovac discharge regime changes at 1.1 m^3/s. Both sub-regimes of the Zagorska Mrežnica aquifer are also characterized by an α higher than 10^{-2}, the first one with 0.134 and the second one with 0.105. We assume that the first value is slightly reduced due to the exclusion of extreme values from the analysis. A regime change occurs at 8.3 m^3/s. For other springs, models comprising three discharge sub-regimes were deemed more appropriate for comparing catchment characteristics. The Vitunj changes flow regime first at 13.2 m^3/s, and subsequently at 4.9 m^3/s, with an α value defined as 0.327 for high, 0.08 for medium, and 0.058 for low waters, as ascertained through automatic regression analysis. The time series for the Gojak and the Tounjčica exhibit the highest α values, suggesting a higher degree of karstification in the shallow karst zone. Discharge from the Gojak spring changes the flow regimes at 4.9 and 1.5 m^3/s, with the highest α value of 0.581 for high, 0.076 for medium, and 0.059 for low waters. At the Tounjčica spring, change in the discharge regime appears at 10.1 and 1.6 m^3/s, with high waters best described by α values of 0.353, medium waters by 0.14, and slower flow by an α value of 0.035.

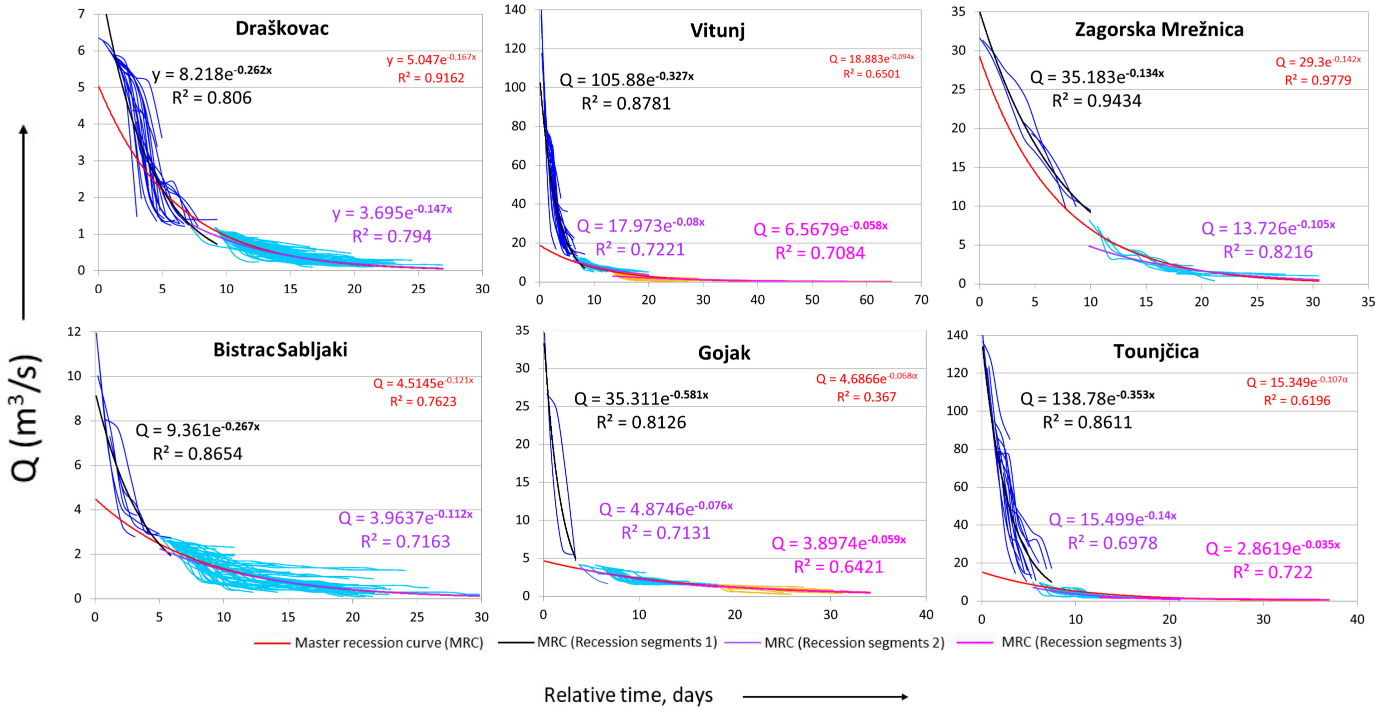


Figure 5. Recession analyses of the Vitunj, Draškovac, Gojak, Zagorska Mrežnica, Bistrac Sabljaki and Tounjčica springs.

Table 2. Recession equations of monitored springs.

Springs	Recession Segment 1 Curve	Recession Segment 2 Curve	Recession Segment 3 Curve	Master Recession Curve
Vitunj	$Q = 105.88e^{-0.327x}$	$Q = 17.973e^{-0.08x}$	$Q = 6.568e^{-0.058x}$	$Q = 18.883e^{-0.094x}$
Zagorska Mrežnica	$Q = 35.183e^{-0.134x}$	$Q = 13.726e^{-0.105x}$	/	$Q = 29.3e^{-0.142x}$
Bistrac Sabljaki	$Q = 9.36e^{-0.27x}$	$Q = 3.96e^{-0.112x}$	/	$Q = 4.51e^{-0.121x}$
Draškovac	$Q = 8.218e^{-0.262x}$	$Q = 3.695e^{-0.147x}$	/	$Q = 5.047e^{-0.167x}$
Tounjčica	$Q = 138.78e^{-0.353x}$	$Q = 15.499e^{-0.14x}$	$Q = 2.862e^{-0.035x}$	$Q = 15.349e^{-0.107x}$
Gojak	$Q = 35.311e^{-0.581x}$	$Q = 4.8751e^{-0.076x}$	$Q = 3.897e^{-0.059x}$	$Q = 4.69e^{-0.068x}$

The α values calculated for the six springs underscore the varying karstification degrees exhibited by the structural tectonic processes and lithologies forming the aquifer reservoirs, thereby indicating a higher karstification within the shallow karst. Furthermore, notable differences in flow velocities observed during distinct recession periods for the Draškovec and Bistrac Sabljaki springs yield different slopes of recession segments, suggesting recharge emanating from different areas within catchments, depending on the precipitation event location and the prevailing saturation levels of the aquifer [18].

Short-term analyses often show a large dispersion of memory effect values due to variations in hydrological conditions [32,42,66]. To avoid this, the precipitation analysis was conducted using 5-year hourly discharge data. The ACF indicates different dynamics of the six monitored springs, characterized by different slopes of ACFs (Figure 6). At the Gojak and Vitunj springs, the ACFs exhibit the quickest decrease within the first 53 h, indicative of well-developed karst conduits facilitating rapid discharge flow. Subsequently, the Gojak spring reaches the threshold value of 0.2, defined as the average duration of the spring's reaction to precipitation or the memory effect. Conversely, a second component is present in the ACF of the Vitunj, denoting a prolonged drainage period lasting from approx. 53 to 146 h before the system loses memory. The Bistrac Sabljaki and the Draškovac reflected similar system dynamics, with generally the same steep slopes of the function and memory loss after approx. 176 h. The Bistrac Sabljaki spring exhibits a short change in dynamics around 65 h, suggesting the activation of an additional system in the hinterland and marking the memory loss observed after 95 h.

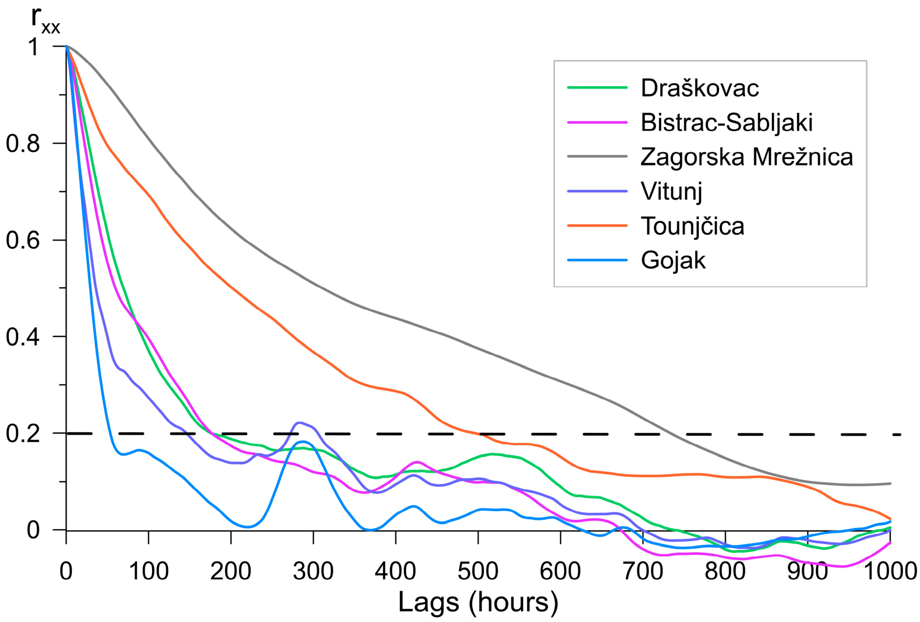


Figure 6. Autocorrelation function in Vitunj, Draškovac, Gojak, Zagorska Mrežnica, Bistrac Sabljaki and Tounjčica springs.

The Zagorska Mrežnica and Tounjčica springs have significantly longer memory effects to the precipitation pulse. Specifically, the Zagorska Mrežnica spring shows memory loss after approx. 730 h or 30.5 days, while the downstream Tounjčica spring exhibits memory loss after approx. 495 h, or 10 days less. Generally, their ACF slopes follow each other without pronounced components. However, in Tounjčica's ACF, a slight increase in discharge is discernible within the first 50 h, with a gentler slope compared to the Vitunj and Gojak springs.

Previous investigation of the ACF of the Zagorska Mrežnica spring, conducted between 2000 and 2013, divided into six-month intervals representing summer and winter seasons [42], resulted in no memory loss during winter periods. In a dataset spanning from 2018 to 2022, the same analysis resulted in memory effect values ranging from 5 to 30 days regardless of the season, probably due to the absence of snow cover during the winter season.

According to the theoretical values [28] and compared with other investigated karst systems within the Dinaric karst [25,30,33], the Gojak spring has an exceptionally rapid loss of memory, reaching 0.2 within 2.5 days. Similarly, the Vitunj, Bistrac Sabljaki and Draškovac springs experience memory loss within 6–7 days. A higher memory effect of 30 days was observed for the Zagorska Mrežnica spring and of 20 days for the Tounjčica spring, likely caused by the existence of intergranular sediment in the catchments and the limited outflow capacity of the Zagorska Mrežnica spring.

Figure 7 illustrates the positive crosscorrelations between precipitation recorded at five meteoric stations and the discharge observed at six springs. The daily response of the monitored springs to precipitation events indicates a very well-drained system.

The correlation between Vitunj spring discharge and precipitations across all stations significantly surpasses that of other springs. The average delay between the Vitunj spring and rainfall in Jasenak is 12–22 h (CCF based on hourly data). The lowest correlation between precipitation and discharge was recorded at the Zagorska Mrežnica spring, with a maximum cov_{xy} of 0.2. The springs in the Dobra River basin, the Vitunj, Draškovac and Gojak, have the highest correlation with rainfall in the mountainous hinterland in the Jasenak polje. Conversely, the southern springs, including the Zagorska Mrežnica, Bistrac Sabljaki and Tounjčica, demonstrate a slightly more pronounced correlation with rainfall in the Dabar polje and Plaški. The Vitunj, Gojak and Bistrac Sabljaki have a simultaneous response to precipitation from all stations within a day of a rainfall event. The Zagorska Mrežnica spring shows positive correlations at a lag of 1 day for rainfall in the Dabar polje, and 2 days for rainfall in Jasenak. The Draškovac spring displays a response within a day to rainfall from its immediate stations and delays of 1 day from hinterland stations, the Dabar polje, and Jasenak. The Tounjčica spring reacts with a 1 day delay for all stations. Despite the lower correlation with precipitation in their immediate catchments, a comprehensive analysis of the hourly precipitation data was conducted due to the high correlation between the discharge of all springs and the precipitation from Jasenak (Figure 8).

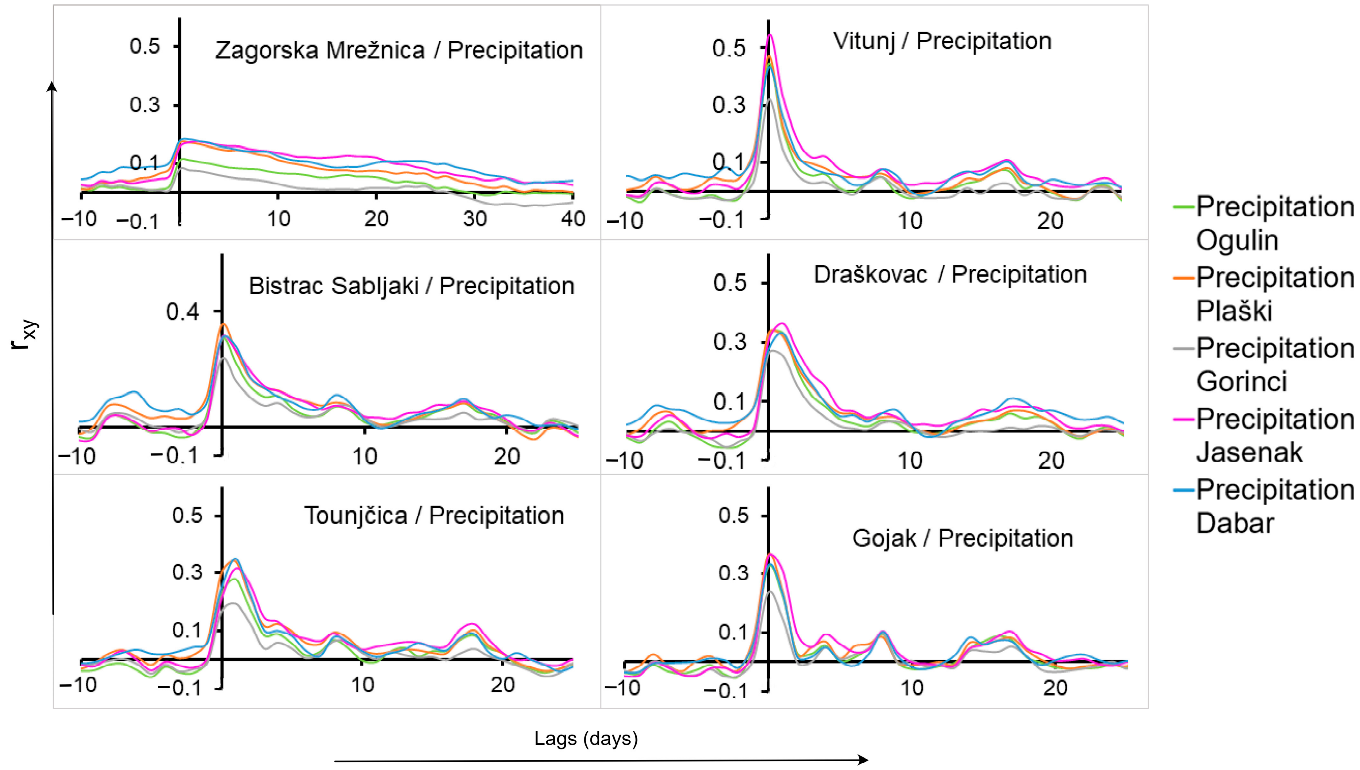


Figure 7. Crosscorrelation between the discharge of six monitoring springs and five meteorological stations in the wider study area between January 2018 and December 2022.

After rainfall, the first hydrograph peak with the highest correlation appears at the Vitunj spring with average delays of 8–16 h, where r_{xy} = 0.18. With the same correlation, the water wave occurs at the Gojak spring after 4–6 h. The Bistrac Sabljaki spring has a slightly higher correlation, with r_{xy} = 0.15, compared to the Draškovac karst system, with a 3–5 h faster response; it reacts approx. 18–26 h following rainfall in Jasenak. The CCF of the Draškovac karst system shows two reactions at the same event, with r_{xy} = 0.1. The first reaction occurs with a delay of 21–30 h and the second one with a delay of 46–55 h. The rationale for this can be traced back to two springs that collectively supply the stream where the measuring station is located. The Tounjčica spring responds to Jasenak precipitation with delays of 37–52 h, with r_{xy} = 0.08; while the Zagorska Mrežnica spring has the lowest correlation, r_{xy} = 0.02, with Jasenak precipitation, with an average delay of 70–83 h.

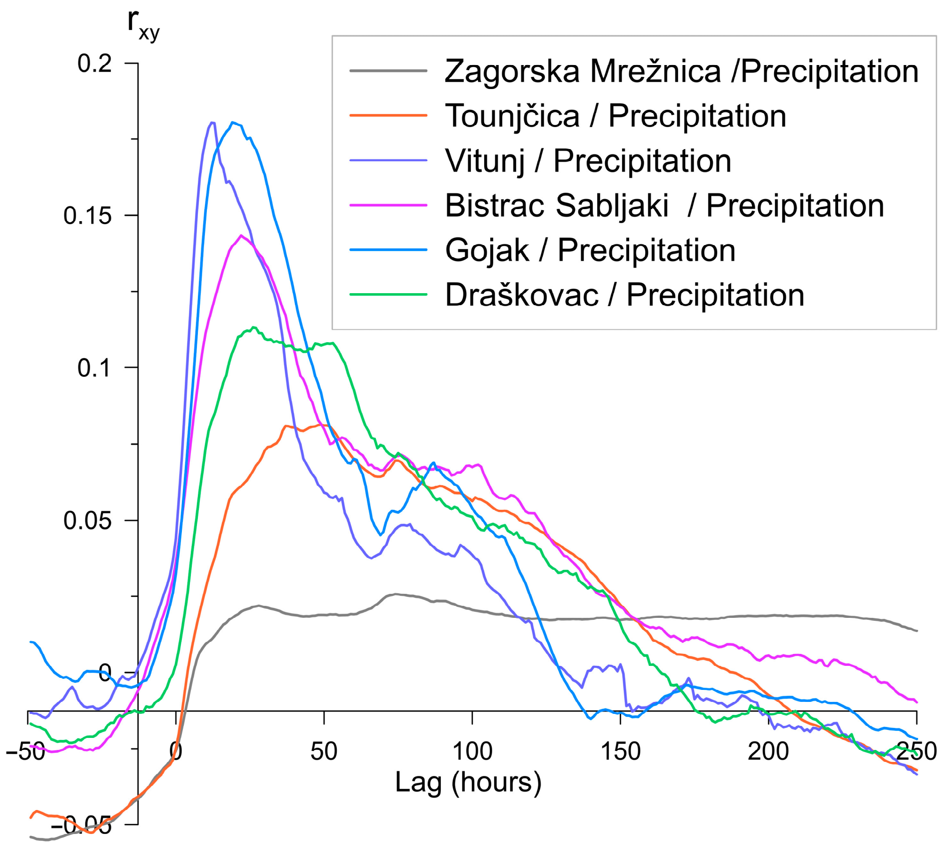


Figure 8. Crosscorrelation function between the discharge of all springs and rainfall in Jasenak.

Since the CCFs between spring discharge depends on environmental variables like vegetation, hydrogeological properties, underground saturation, and precipitation quantity, the time series for the CCFs in different hydrological conditions were conducted between the Vitunj spring, which responds first to rainfall, and the other monitored springs (Figure 9). Regardless of the precipitation distribution and season, the correlation between the Vitunj spring and the downstream Gojak spring is expectedly strong, with a maximum correlation coefficient of r_{xy} = 0.97 in the dry season and r_{xy} = 0.91 in the wet season with a similar delay reaction of 3–6 h. The Draškovac reacts with the high correlation coefficient of r_{xy} = 0.95 approximately 4–8 h after the Vitunj spring in the dry season and with a r_{xy} = 0.88 during the wet season after approximately 8–16 h. The Zagorska Mrežnica and the Bistrac Sabljaki springs have opposite reactions in the same hydrological conditions. The Zagorska Mrežnica spring reacts quite simultaneously with a high r_{xy} = 0.85 during low water conditions with the Vitunj spring, but during the wet season, the correlation is lower, r_{xy} = 0.55, with a delay of 3–6 h. The Bistrac Sabljaki spring has a lower correlation, r_{xy} = 0.44, during the dry season, and a higher correlation during the wet season, r_{xy} = 0.81, with simultaneous reactions with the Vitunj spring. The average delay between the Tounjčica and Vitunj spring hydrograph peaks is 30–45 h with a lower correlation, r_{xy} = 0.73, during low water conditions, while during high water conditions, the correlation is r_{xy} = 0.83 and the average delay between peaks is shorter, 12–22 h.

The water temperature was measured at all gauging stations. However, only at the Zagorska Mrežnica, Bistrac Sabljaki, and Tounjčica springs were the sensors positioned directly within the spring, ensuring that the temperature did not change under atmospheric temperature. The water temperature reflects the thermodynamics of the karst aquifer, giving insight into the dynamics and structural features of the hydrogeological system.

The one-year undisturbed temperature variations are shown in Figure 10 and Table 3. All three aquifers exhibit two distinct patterns: long-term variations following the seasonal oscillations and short-term oscillations resulting from new recharge.

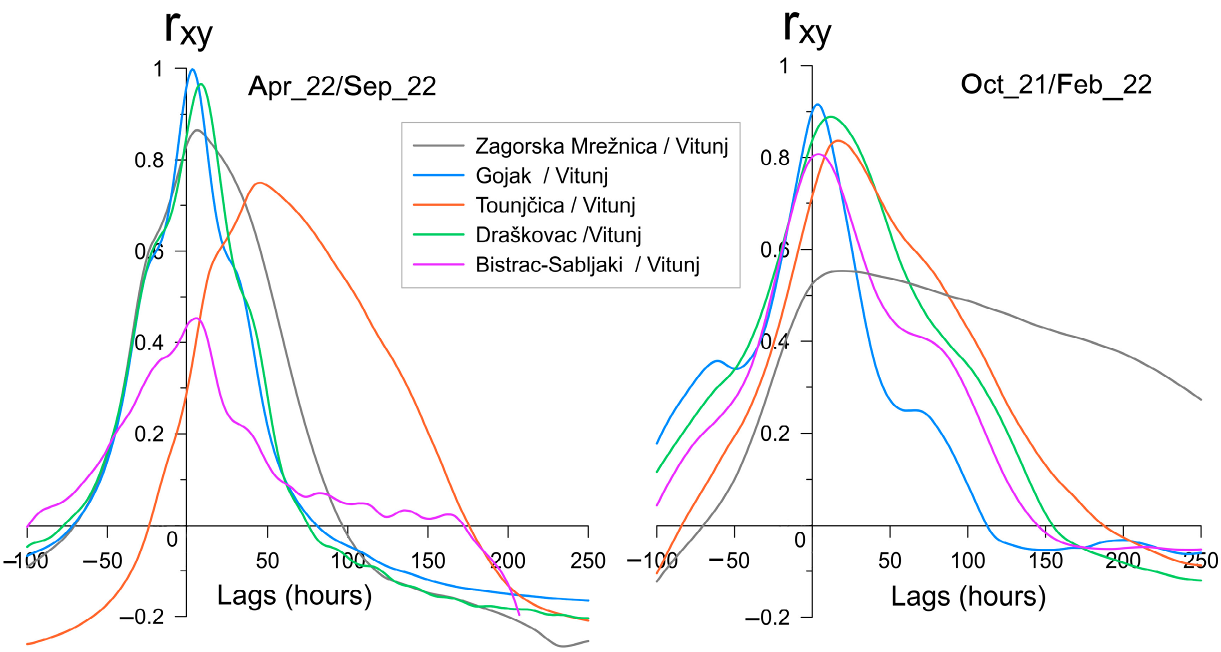


Figure 9. Crosscorrelation between the discharge of the Vitunj spring and Draškovac, Gojak, Zagorska Mrežnica, Bistrac Sabljaki, and Tounčica springs.

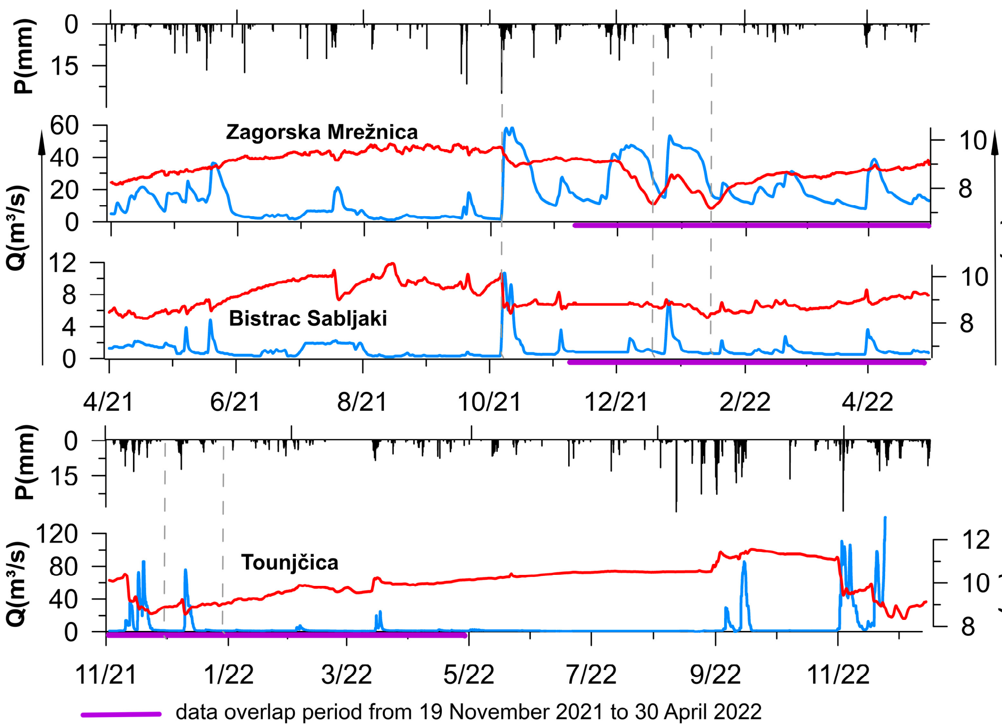


Figure 10. Detailed dynamics of the Bistrac Sabljaki, Zagorska Mrežnica and Tounjčica water springs temperature and discharge.

Table 3. The temperature parameters of groundwater in Zagorska Mrežnica, Bistrac Sabljaki and Tounjčica springs.

	Zagorska Mrežnica	Bistrac Sabljaki	Tounjčica
MIN	7.17	8.20	8.36
MAX	9.85	10.58	11.55
Mean	8.96	8.85	10.09
Average	8.90	9.06	10.03
SD	0.59	0.52	0.78
CV	6.60%	5.92%	7.72%

The water temperature in the Zagorska Mrežnica spring fell within the range from 7.17 to 9.85 °C, with a relatively high variation coefficient of 6.60%. The water flows through the aquifer without total homogenization caused by heat exchange between the rock and water, with a noticeable seasonal oscillation referring to influences of atmospheric conditions. Three flood events were recorded between October 2021 and January 2022. In October, after the dry season, the first heavy rainfall caused a decrease in the temperature before the hydrograph peak, proving that new water reaches the spring still in the rising phase of the hydrograph. The linear lowering of the temperature lasted during the maximum duration of the flow, with a decrease of 0.8 °C.

On 26 November 2021, at the beginning of the second flood event, the aquifer was moderately saturated, and the discharge began to increase six days before the decrease in temperature. The maximum discharge lasted for 16 days, the same as the temperature linearly decreasing, resulting in a temperature reduction of 1.7 °C. The third event started ten days later, with a temperature-decreasing delay of seven days with the same coincidence in the 15 day maximum flow and temperature drop duration with a temperature reduction of 1.4 °C. The minimum water temperature was recorded at the midpoint of the recession, after which the water temperature was rising towards the average temperature of the mountain region.

The hydrogeological structure of the terrain allows us to interpret fluctuations in the water temperature as a clear tracer of spring recharge. In the unsaturated aquifer, new infiltrated precipitation appears in the spring water within the first discharge impulse. In the saturated aquifer, fresh cold water appears with a lag of a few days, depending on the degree of saturation. In the case of complete saturation, the heavy rains caused the flooding of the karst poljes in the hinterland, where ponors are directly connected with the Zagorska Mrežnica spring [41]. The ratio of infiltrated colder surface water at spring outflow increases over time due to a decrease in the hydraulic pressure of the mountain rock mass, and its proportion would finally be insignificant after emptying the accumulation, which can be read in the rising water temperature after the flood event. Similar behavior can be observed in the temperature dynamics of the neighboring Bistrac Sabljaki spring, but only during the third flood event, when the aquifer was the most saturated. The gradual cooling of the spring water started 7 days after the temperature drop in the Zagorska Mrežnica spring, but ended at the exact moment when the accumulation was empty.

The water temperature in the Bistrac Sabljaki spring fluctuated from 8.2 to 10.6 °C. The coefficient of variation is relatively high: 5.92%. The water temperatures measured at the Tounjčica spring ranged from 8.4 to 11.6 °C, with the highest coefficient of variation of 7.7%. In both springs, the seasonal variations are evident, with a maximum temperature recorded at the end of summer or the dry period. The consistent response of the temperature to the change of flow indicates the fast water transfer through the system by well-developed conduits.

The short temperature rises before drops are likely linked to the release of water from narrow cracks with low permeability. This release is triggered by sudden increases in pressure resulting from the infiltration of precipitation, or it could be the activation of deep conduit flow due to a heightened hydraulic gradient within the system [67].

The mean annual groundwater temperature calculated for the Bistrac Sabljaki spring amounts to 8.8 °C, for the Zagorska Mrežnica spring, 9.0 °C, and for the Tounjčica spring waters, 10.1 °C. Calculating the average recharge height should consider the tempering of surface waters in the Zagorska Mrežnica catchment area. However, the mean temperature in the Bistrac Sabljaki is still lower than in the Zagorska Mrežnica spring, which indicates the preferred feed of the Bistrac Sabljaki spring by draining the mountain massif above, while the majority of the Zagorska Mrežnica catchment area is located behind the first mountain peak. The average recharge height of the Tounjčica spring is anticipated to be several hundred meters lower.

3.1. Hydrochemical of Groundwater

The chemical properties of the sampled water are presented in Table 4. All sampled water belongs to the Ca-HCO_3 hydrochemical facies [68], indicating the carbonate aquifer without evaporates and other rocks. A low Mg concentration suggests groundwater has no significant retention in dolomites, which is expected due to large oscillations in the discharge. The bicarbonate is the dominant anion with an average contribution to the anion budget of ~95%. The mineralization of spring water during summer is lower, due to higher groundwater temperature. Lower nitrate and sulphate concentrations were observed during periods of high water levels, perhaps as a result of dilution. Regardless, the amounts of these substances are significantly lower than the maximum allowable limits, suggesting that the water being studied is of excellent quality.

Table 4. The chemical composition of groundwater in Draškovac, Vitunj, Zagorska Mrežnica, Bistrac Sabljaki, Gojak and Tounjčica springs.

Sampled Spring	Date	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	HCO_3^- (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)
Draškovac	10 July 2019 *	58.20	23.64	1.52	254	2.41	6.08	6.09
	12 February 2020 **	58.55	22.76	0.67	272	1.87	5.66	5.42
	28 January 2021 ***	52.49	16.26	0.98	256	1.80	3.50	1.99
Vitunj	10 July 2019 *	55.75	7.1	0.63	166	1.22	4.7	5.69
	12 February 2020 **	55.01	5.77	0.73	199	1.44	5.24	5.18
	28 January 2021 ***	51.37	20.93	0.44	221	1.04	1.35	2.23
Zagorska Mrežnica	10 July 2019 *	73.90	8.01	1.76	262	2.74	4.77	6.76
	12 February 2020 **	71.02	9.41	1.45	254	2.04	4.53	6.47
	28 January 2021 ***	65.80	5.88	2.12	257	3.17	2.19	1.98
Bistrac Sabljaki	10 July 2019 *	64.57	21.69	2.55	325	3.97	5.59	8.30
	12 February 2020 **	67.62	19.13	3.14	290	4.02	4.73	7.09
	28 January 2021 ***	63.00	14.39	2.81	268	4.74	2.79	2.74
Tounjčica	10 July 2019 *	65.61	7.86	1.41	181	2.21	7.45	6.65
	12 February 2020 **	73.89	8.35	1.68	264	2.29	5.64	5.95
	28 January 2021 ***	66.86	7.87	1.99	243	3.12	3.07	2.51
Gojak	10 July 2019 *	68.41	11.04	3.27	183	3.98	5.71	7.20
	12 February 2020 **	59.93	14.12	4.54	239	5.64	6.45	6.74
	28 January 2021 ***	60.66	10.27	5.23	233	7.74	4.87	3.54

Notes: * low water, ** medium water, *** high water.

3.2. Hidrogeological Conceptual Model of Karst System

The time series analyses provide detailed insights into the significant karst system dynamics. The FDC, RCA, and ACF delineated two types of reservoirs in the observed karst systems: well-developed karst conduit systems developed in size compared to fracture-matrix systems without clear diffuse flow. In the mountain massif, the Draškovac, Vitunj, and Bistrac Sabljaki aquifers have a similar behavior, indicating dominant drainage of higher mountain areas, from which the karst conduits are most developed in the Vitunj catchment area, characterized by a higher recession coefficient, discharge ratio, first reaction to the precipitation and a low memory effect. The Bistrac Sabljaki karst network is slightly more developed than the Draškovac aquifer. However, both aquifers respond a few hours after the Vitunj spring, practically simultaneously to precipitation, and lose memory simultaneously. The hydrograph of the Zagorska Mrežnica is not typical for a karst spring as it does not have discharge peaks (Figure 3); the high discharge is rather uniform, with low recession coefficients and a significantly longer memory effect, indicating direct connections with the poljes in the hinterland and a limited spring outflow.

Reviewing all available data and the research results is necessary to define the dynamics of a complex and highly karstified system. In the study area, 23 underground flow tracings have been done in the last 70 years, primarily focused on the Sabljaki catchment area and the Zagorska Mrežnica drinking water supply spring. Table 5 shows 18 tracing tests for which detailed data are available and considered in this interpretation. The results of the tracing tests show interesting and occasionally opposite data. Therefore, tracing tests of the same ponors showed a connection with different springs, but in different hydrological conditions. However, engineers questioned their reliability mainly due to the time lag and outdated techniques.

Table 5. Tracing tests in the north Dinaric karst.

Location of Tracing Test	Injection Location	Spring of the Tracer Detection	Calculate Flow Rate (cm/s)	Emergence of Tracer (h)	Water Conditions
Jasenak polje	South ponor, 1972	Kamačnik Vitunj	2.4 1.6	130 144	High water 100 L/s
	South ponor, 1986	Zagorska Mrežnica Bistrac	0.86 0.85	448 456	Low water 12.8 L/s
Drežnica polje	Kolovoz, 1972	Pećina Bistrac	1.6 1.9	162 146	High water 6 m^3/s
	Potočak, 1980	Zagorska Mrežnica	1.73	167	Low water 17.3 L/s
	Pražića jaruga, 1985	Zagorska Mrežnica Bistrac	2.9 2.9	88 88	High water 3–4 m^3/s
	Zrnića, 1981	Zagorska Mrežnica Pećina	3.4	80	End of the water wave
	Bosanić, 2013	-			Flood
Drežnički Lug	Pećina Maravić Dragi, 1980	Pećina Sušik	0.55	43	Low water
Stajnica polje	Jaruga-Jezerane, 2002	Rokina Bezdani	2.36	24	Medium water
	Jezerane ponor, 1988	Zagorska Mrežnica Bistrac Sabljaki	1.36 1.21	320 344	5 L/s
	Jaruga-Jezerane, 2000	Zagorska Mrežnica Bistrac	1.53 1.38	284 308	80–100 L/s
Crnac polje	1972	Dretulja	2.3	182	High water
	1985	Zagorska Mrežnica Bistrac	2.3 2.16	160 173	Low water 150–200 L/s
Ogulin polje	Đula ponor, 1948	Gojak	5.68	23.45	2 m^3/s
	Zagorska Mrežnica watercours, 1948	Bistrac Sabljaki Tounjčica Kukača	10.2 5.5 11.7	18.45 32.55 18.25	9.37 m^3/s
	Zagorska Mrežnica watercourse, 1948	Bistrac Sabljaki Tounjčica Kukača	11.76 6.97 6.17	15.98 28.45 37.25	13.20 m^3/s

In the hinterland, the tracing tests in low and medium waters have established the connection between the Drežnica polje and a series of karst poljes. On the NW site from the Jasenak and Krakar, via the Drežnicki Lug to the Drežnica poljes; and on the SE site from the Stajnica polje, via Jezerane to the Crnac polje, without detecting the tracer in other springs. In general, during low waters, the shape of the tracer curve of the Zagorska Mrežnica spring was untypically symmetrical, pointing to the significant and uniform dispersion of tracers, longer retention in the underground, and relatively low velocity.

Figure 11 presents dynamics during (a) low and (b) high water conditions. In the dry seasons, the water drains the surrounding mountain from the boundary of the Adriatic/Black Sea catchment, with occasional surface flows in the poljes, and gravitates to the Zagorska Mrežnica springs. In the karst poljes, the vadose zone is not deeper than several tens of meters. Based on time series analysis and tracing results, the Draškovac, Vitunj, and Bistrac Sabljaki springs mainly drain the higher mountain massifs directly above them. On the other hand, during high waters, when the mountain massif is saturated, and the poljes are flooded, the tracers of the same ponors did not appear at the Zagorska Mrežnica spring. In 1972, on the NW, the Jasenak polje established connections in the north with the Kamačnik and Vitunj springs. The high correlation of precipitation in Jasenak with the Vitunj and Draškovac springs and the hydrogeological settings offer compelling evidence for this connection. In the same tracer test, lower tracer concentrations appeared in the Krakar polje in the south of the area, which undoubtedly gravitates towards the Drežnica polje and further towards the Zagorska Mrežnica, but probably due to dilution, it was not detected at the spring.

On the SE, the tracing test during high waters linked the ponor in Crnac polje with the Dretulja spring. The tracings conducted during high waters do not disprove the poljes relationship with the Zagorska Mrežnica spring. However, it is more likely that the absence of tracers is attributed to dilution in retentions, as demonstrated in the tracing experiments conducted in the Drežnica polje on the Kolovoz ponor in 1972 and Bosanić in 2013, when the traced sinkholes started acting as springs. The temperature dynamics of the observed springs show that the hydraulic potential in the mountain massif above the springs is higher than the hydraulic potential from flooded poljes during high water conditions, resulting in the potential runoff of the groundwater towards the peripheral springs, probably incorporating the Jasenak polje as part of the Vitunj catchment area, and the Crnac or Stajnica polje as part of the Dretulja catchment area. Conceptually, the four analyzed karst systems can be considered as a part of the common mountain karst system, in which the catchment area boundaries are zonal, based on the aquifer saturation degree in the high permeability tectonic-formed limestone, which is devoid of the significant hydrogeological barriers and precipitation distribution.

The highest degree of karstification is evident in the karst complex downstream of the Ogulin polje, in the catchment areas of the Gojak and Tounjčica springs. According to the trace tests, the velocity of the groundwater is up to 10 times faster than in the mountain area, which is proved by the recession coefficients and discharge ratios. The CCF and ACF indicate faster water exchange in the Gojak spring system than in the Tounjčica system. If the long pulse of precipitation is taken into account, the fracture-matrix systems component in the Tounjčica system has a significantly higher proportion than the Gojak system. Despite the absence of water in the main entrances to the cave systems throughout the dry season as a result of hydrotechnical interventions, the springs never dry, indicating good hydraulic connections with the immediate hinterland.

Shallow or fluviokarst zone has limited water circulation due to the thinner, highly permeable carbonate deposits than in the deep karst zone. Previously, the boundary between deep and shallow karst was only descriptively defined [69] as a transition zone from deep to shallow karst based on structural geological units. This investigation has shown that the hydrogeological characteristics of the area north of Kapela are significantly different from the deep karst zone, categorizing it as part of the shallow karst zone. This new boundary is depicted on the hydrogeological map (Figure 2).

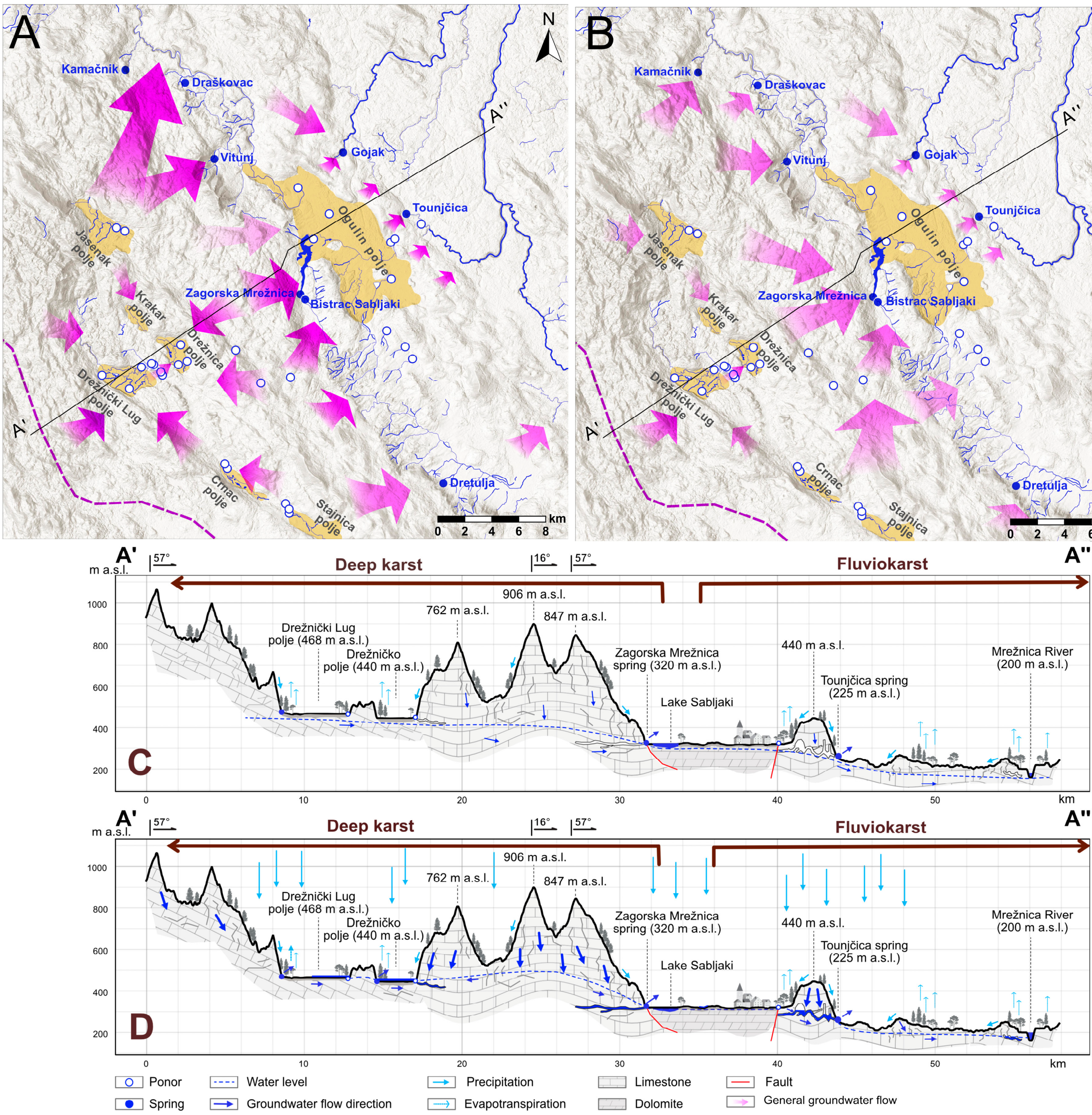


Figure 11. Conceptual map of interpreted regional groundwater flow directions during (**A**) high and (**B**) low water conditions, and a cross-section profile through the study area in low (**C**) and high (**D**) water conditions.

4. Conclusions

By comparing the results of implemented methodologies, differences between two karst types within the study area were determined: (1) deep karst with karstification extending over several hundred meters, and (2) the shallow or fluviokarst with a karstification depth below 200 m.

The Kapela represents the northern part of the typical Dinaric deep karst area and presents the first recharge area formed by substantially fractured Mesozoic limestone and dolomites. The hydrogeological relations are intrinsically complex and caused by compressional tectonics. Due to numerous karstic forms, the area is characterized by rare and ephemeral surface watercourses, with occurrences solely in karst poljes. The geological structure often impedes the vertical movement of groundwater, resulting in the predominantly horizontal development of karst channels. Highly karstified rocks enable the accumulation of groundwater in great amounts. The springs are periodic and have large discharge oscillations, as typical of karst springs. Although numerous tracing tests have been carried out, the catchment areas of the observed springs, and thus the catchments of the main tributaries of the Kupa River, the Dobra and Mrežnica Rivers, have not been unambiguously delineated. The precipitation in the mountains is abundant, resulting in tracer dilution and challenging detection. The time series analyses show that the groundwater dynamics depend on hydrological conditions. The conducted time series analyses indicated that the catchment areas of the monitored springs could be more specifically delineated by obtaining the additional hourly data on water temperature, electrolytic conductivity, and the hourly precipitation data from all meteorological stations.

The zone of shallow karst begins in a sinking area on the NE edge of the dolomite hydrogeological barrier in the Ogulin polje. The watercourses sink in the area of highly permeable limestone and reappear at the surface after 5 to 15 km of around 100 m lower elevation in the recent erosional base of the main rivers in this area. The karst phenomena are highly represented by numerous horizontal caves, sinkholes, springs and river valleys. The conducted time series analyses established a significant difference between the areas of deep and shallow karst, suggesting a more developed karst network, faster water exchange, and shorter retention of groundwater in the shallow karst zone.

The fluvial or shallow karst area in Croatia extended from this study area on the west to the Pannonian basin on the east, without clear and exact defined boundaries. This paper suggests the definition of the western boundary of the shallow karst in Croatia and provides the groundwork for establishing the base for further research of this scientifically not-yet-investigated area.

The practical significance of this research is manifold. Firstly, by delineating the hydrological characteristics of the transition zone from deep to shallow karst, this study offers crucial insights into groundwater flow and storage in one of the most karstified regions of the Dinaric karst. Such insights are essential for effective water resource management in the area. Secondly, the development of a conceptual hydrogeological model that addresses historical discrepancies in groundwater tracing results provides a more accurate depiction of the underground water system. This aids in better management and prediction of groundwater behavior. Thirdly, through the characterization of new hydrogeological relationships concerning long-standing human interventions like dams, tunnels, and reservoirs, this research establishes a baseline condition for the area. This baseline is crucial for evaluating the impacts of these structures on groundwater dynamics and water quality, thus informing future environmental and developmental planning.

While the total capacity of drinking water far exceeds the needs of the population, the region faces challenges during increasingly frequent climatic extremes and rapid water flow through the system. Sustainable management is essential to ensure the long-term availability and quality of water resources. Despite no significant change in total annual precipitation, climatic extremes are becoming more frequent, resulting in longer dry periods and intensified precipitation events. In highly karstified areas, similar to the one in question, intensive precipitation fails to effectively recharge the aquifer and swiftly exits the system. The depletion of the aquifer is further compounded by the absence of snow cover, which gradually melts and fills smaller fractures, thereby promoting longer water retention within the aquifer.

Furthermore, this study highlights the significant quality of groundwater, underscoring the importance of preserving the region's water quality for sustainable development and conservation efforts. Lastly, the integration of various time series analysis techniques, including RCA, FDC, ACF, and CCF, provides a dynamic framework that could serve as a basis for advanced simulations using AI algorithms in the future. This methodological approach can be applied to similar studies in other karst regions globally, significantly contributing to the broader field of hydrogeology.

Author Contributions: All authors contributed to the study conception and design. I.B.: Investigation, Conceptualization, Data curation, Methodology, Visualization, Writing—original draft. J.T.: Investigation, Conceptualization, Methodology, Supervision, Writing—review & editing. J.L.R.: Methodology, Writing—review & editing. Ž.D.: Investigation, Conceptualization, Methodology, Su-

pervision, Writing—review & editing. A.S.: Investigation, Visualization, Writing—review & editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by two projects: Croatian Electric Power Company (B2Z30-76/19), and the Interreg Danube CAMARO-D project (DTPT1-1-096-2.1), co-funded by the European Regional Development Fund.

Data Availability Statement: The datasets presented in this article are not readily available because the data are collected and the ownership of third party. Requests to access the datasets should be directed to the Croatian Electric Power Company and the Croatian Meteorological and Hydrological Service.

Acknowledgments: Authors would like to thank the anonymous reviewers for their careful review, which helped to improve the quality of the manuscript. The Croatian Geological Survey, Department of Hydrogeology and Engineering Geology supported this research (administrative and technical support and utilization of laboratory services). This paper is partly the result in the scope of the internal research project "NONa" at the Croatian Geological Survey, funded by the National Recovery and Resilience Plan 2021–2026 of the European Union—NextGenerationEU, and monitored by the Ministry of Science and Education of the Republic of Croatia. The authors express their gratitude to the Croatian Meteorological and Hydrological Service and the Croatian Electric Power Company for the provided data.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Ford, D.; Williams, P.D. *Karst Hydrogeology and Geomorphology*; John Wiley & Sons: Chichester, UK, 2007; p. 562.
2. Goldscheider, N.; Drew, D. Methods in Karst Hydrogeology. In *IAH International Contributions to Hydrogeology*, 1st ed.; Taylor & Francis: London, UK, 2007; Volume 26, p. 264.
3. Fiorillo, F. The Recession of Spring Hydrographs, Focused on Karst Aquifers. *Water Resour. Manag.* **2014**, *28*, 1781–1805. [CrossRef]
4. Torresan, F.; Fabbri, P.; Piccinini, L.; Dalla Libera, N.; Pola, M.; Zampieri, D. Defining the hydrogeological behavior of karst springs through an integrated analysis: A case study in the Berici Mountains area (Vicenza, NE Italy). *Hydrogeol. J.* **2020**, *28*, 1229–1247. [CrossRef]
5. Fiorillo, F.; Doglioni, A. The relation between karst spring discharge and rainfall by crosscorrelation analysis (Campania, Southern Italy). *Hydrogeol. J.* **2010**, *18*, 1881–1895. [CrossRef]
6. Kovács, A.; Perrochet, P. A quantitative approach to spring hydrograph decomposition. *J. Hydrol.* **2008**, *352*, 16–29. [CrossRef]
7. Panagopoulos, G.; Lambrakis, N. The contribution of time series analysis to the study of the hydrodynamic characteristics of the karst systems: Application on two typical karst aquifers of Greece (Trifilia, Almyros Crete). *J. Hydrol.* **2006**, *329*, 368–376. [CrossRef]
8. Krešić, N. *Quantitative Solutions in Hydrogeology and Ground-Water Modeling*; Lewis Publishers: New York, NY, USA, 1997; 461p.
9. Boussinesq, M.J. *Essai sur la Theories des eax Courantes*; Memoires Presentes par Divers Savants a l'Academie des Sciences de l'Institut National de France; Imprimerie Nationale: Paris, France, 1877; Volume XXIII.
10. Boussinesq, M.J. Recherches the´oriques sur l'e´coulement des nappes d'eau infiltre´es dans le sol et sur le debit des sources. *J. Mathématiques Pures Appliquées* **1904**, *10*, 5–78.
11. Maillet, E. *Mécanique et Physique du Globe: Essai D'hydraulique Souterraine et Fluviale [Mechanics and Physiques of the World: An Essay of Subterranean and Fluviatile Hydraulics]*; Hermann: Paris, France, 1905.
12. Schoeller, H. Hydrodynamique dans le Karst. Hydrogeologie des roches fissure´es. In *Actes du Colloque de Dubrovnik*; IAHS-UNESCO: Paris, France, 1965.
13. Atkinson, T.C. Diffuse Flow and Conduit Flow in Limestone Terrain in the Mendip Hills, Somerset, UK. *J. Hydrol.* **1977**, *35*, 93–110. [CrossRef]
14. Malik, P. Assessment of regional karstification degree and groundwater sensitivity to pollution using hydrograph analysis in the Velka Fatra Mountains. *Slovakia. Environ. Geol.* **2007**, *51*, 707–711. [CrossRef]
15. Krešić, N.; Bonacci, O. Spring discharge hydrograph. In *Groundwater Hydrology of Springs: Engineering, Theory, Management, and Sustainability*; Elsevier: Amsterdam, The Netherlands, 2010; Chapter 4; pp. 129–163. [CrossRef]
16. Posavec, K.; Bačani, A.; Nakić, Z. A visual basic spreadsheet macro for recession curve analysis. *Groundwater* **2006**, *44*, 764–767. [CrossRef]
17. Posavec, K.; Parlov, J.; Nakić, Z. Fully Automated Objective-Based Method for Master Recession Curve Separation. *Groundwater* **2010**, *48*, 598–603. [CrossRef]
18. Posavec, K.; Giacopetti, M.; Materazzi, M.; Birk, S. Method and Excel VBA Algorithm for Modeling Master Recession Curve Using Trigonometry Approach. *Groundwater* **2017**, *55*, 891–898. [CrossRef] [PubMed]
19. Kovács, A. Quantitative classification of carbonate aquifers based on hydrodynamic behaviour. *Hydrogeol. J.* **2017**, *29*, 33–52. [CrossRef]

20. Bailly-Comte, V.; Ladouche, B.; Charlier, J.B.; Hakoun, V.; Maréchal, J.C. XLKarst, an Excel tool for time series analysis, spring recession curve analysis and classification of karst aquifers. *Hydrogeol. J.* **2023**, *31*, 240–2415. [CrossRef]
21. Padilla, A.; Pulido-Bosch, A.; Mangin, A. Relative Importance of Baseflow and Quickflow from Hydrographs of Karst Spring. *Groundwater* **1994**, *32*, 267–277. [CrossRef]
22. Krešić, N.; Stevanović, Z. *Groundwater Hydrology of Springs: Engineering, Theory, Management, and Sustainability*; Butterworth-Heinemann: Oxford, UK, 2010; 573p.
23. Malík, P.; Vojtková, S. Use of recession-curve analysis for estimation of karstification degree and its application in assessing overflow/underflow conditions in closely spaced karstic springs. *Environ. Earth Sci.* **2012**, *65*, 2245–2257. [CrossRef]
24. Kovács, A.; Perrochet, P.; Király, L.; Jeannin, P.Y. A quantitative method for the characterization of karst aquifers based on spring hydrograph analysis. *J. Hydrol.* **2005**, *303*, 152–164. [CrossRef]
25. Kovačič, G. Hydrogeological study of the Malenščica karst spring (SW Slovenia) by means of a time series analysis. *Acta Carsologica* **2010**, *39*, 201–215. [CrossRef]
26. Malík, P. Evaluating Discharge Regimes of Karst Aquifer. In *Karst Aquifers—Characterization and Engineering. Professional Practice in Earth Sciences*; Stevanović, Z., Ed.; Springer: Cham, Switzerland, 2015. [CrossRef]
27. Verma, R.K.; Murthy, S.; Verma, S.; Kumar Mishra, S. Design flow duration curves for environmental flows estimation in Damodar River Basin, India. *Appl. Water Sci.* **2017**, *7*, 1283–1293. [CrossRef]
28. Mangin, A. Pour une meilleure connaissance des systèmes hydrologiques a partir des analyses correlatoire et spectrale. *J. Hydrol.* **1984**, *67*, 25–43. [CrossRef]
29. Chung, S.Y.; Senapathi, V.; Sekar, S.; Kim, T.H. Time series analyses of hydrological parameter variations and their correlations at a coastal area in Busan, South Korea. *Hydrogeol. J.* **2018**, *26*, 1875–1885. [CrossRef]
30. Jemcov, I.; Petrič, M. Measured precipitation vs. effective infiltration and their influence on the assessment of karst systems based on results of the time series analysis. *J. Hydrol.* **2009**, *379*, 304–314. [CrossRef]
31. Zhang, Z.; Chen, X.; Chen, X.; Shi, P. Quantifying time lag of epikarstspring hydrograph response to rainfall using correlation and spectral analyses. *Hydrogeol. J.* **2013**, *21*, 1619–1631. [CrossRef]
32. Paiva, I.; Cunha, L. Characterization of the hydrodynamic functioning of the Degracias-Sicó Karst Aquifer, Portugal. *Hydrogeol. J.* **2020**, *28*, 2613–2629. [CrossRef]
33. Stroj, A.; Briški, M.; Oštrić, M. Study of Groundwater Flow Properties in a Karst System by Coupled Analysis of Diverse Environmental Tracers and Discharge Dynamics. *Water* **2020**, *12*, 2442. [CrossRef]
34. Pahernik, M. Prostorna gustoća ponikava na području Republike Hrvatske. *Hrvat. Geogr. Glas.* **2012**, *74*, 5–26. [CrossRef]
35. Selak, A.; Boljat, I.; Reberski, J.L.; Terzić, J.; Čenčur, B.C. Impact of land use on Karst water resources—A case study of the Kupa (Kolpa) transboundary river catchment. *Water* **2020**, *12*, 3226. [CrossRef]
36. Bahun, S. Geološka osnova hidrogeoloških odnosa krškog područja između Slunja i Vrbovskog (Geological basis of the hydrogeological relations in the karst area between Slunj and Vrbovsko). *Geološki Vjesn.* **1968**, *21*, 19–82.
37. Lukač Reberski, J.; Kapelj, S.; Terzić, J. An estimation of groundwater type and origin of the complex karst catchment using hydrological and hydrogeochemical parameters: A case study of the Gacka river springs. *Geol. Croat.* **2009**, *62*, 157–178. [CrossRef]
38. Lukač Reberski, J.; Marković, T.; Nakić, Z. Definition of the river Gacka springs subcatchment areas on the basis of hydrogeological parameters. *Geol. Croat.* **2013**, *66*, 39–53. [CrossRef]
39. Biondić, B.; Biondić, R.; Kapelj, S. Karst groundwater protection in the Kupa River catchment area and sustainable development. *Environ. Geol.* **2006**, *49*, 828–839. [CrossRef]
40. Pavlić, K.; Parlov, J. Crosscorrelation and Cross-Spectral Analysis of the Hydrographs in the Northern Part of the Dinaric Karst of Croatia. *Geosciences* **2019**, *9*, 86. [CrossRef]
41. Terzić, J.; Stroj, A.; Frangen, T. Hydrogeological investigation of karst system properties by common use of diverse methods: A case study of Lička Jesenica springs in Dinaric karst of Croatia. *Hydrol. Process* **2012**, *26*, 3302–3311. [CrossRef]
42. Buljan, R.; Pavlić, K.; Terzić, J.; Perković, D. A Conceptual Model of Groundwater Dynamics in the Catchment Area of the Zagorska Mrežnica Spring, the Karst Massif of Kapela Mountain. *Water* **2019**, *11*, 1983. [CrossRef]
43. Bonacci, O.; Andrić, I. Impact of an inter-basin water transfer and reservoir operation on a karst open streamflow hydrological regime: An example from the Dinaric karst (Croatia). *Hydrol. Process* **2010**, *24*, 3852–3863. [CrossRef]
44. *HGI-CGS Arhive*; Croatian Geological Survey: Zagreb, Croatia, 1948.
45. Gajić-Čapka, M.; Perćec Tadić, M.; Patarcic, M. Digitalna godisnja oborinska karta Hrvatske. (A Digital Annual Precipitation Map of Croatia-m Croatian). *Hrvat. Meteorološki Časopis (Croat. Meteorol. J.)* **2003**, *38*, 21–33.
46. Zaninović, K.; Srnec, L.; Perčec-Tadić, M. Digitalna godišnja temperaturna karta Hrvatske [A Digital Annual Temperature Map of Croatia—In Croatian]. *Hrvat. Meteorološki Časopis (Croat. Meteorol. J.)* **2004**, *39*, 51–58.
47. Korbar, T. Orogenic evolution of the External Dinarides in the NE Adriatic region: A model constrained by tectonostratigraphy of Upper Cretaceous to Paleogene carbonates. *Earth-Sci. Rev.* **2009**, *96*, 296–312. [CrossRef]
48. Tari, V. Evolution of the northern and western Dinarides: A tectonostratigraphic approach. *Eur. Geosci. Union Stephan. Mueller Spec. Publ.* **2002**, *1*, 223–236. [CrossRef]
49. Schmid, S.M.; Bernoulli, D.; Fügenschuh, B.; Matenco, L.; Schefer, S.; Schuster, R.; Tischler, M.; Ustaszewski, K. The Alpine-Carpathian-Dinaridic orogenic system: Correlation and evolution of tectonic units. *Swiss J. Geosci.* **2008**, *101*, 139–183. [CrossRef]

50. Vlahović, I.; Tišljar, J.; Velić, I.; Matičec, D. Evolution of the Adriatic Carbonate Platform: Palaeogeography, main events and depositional dynamics. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2005**, *220*, 333–360. [CrossRef]
51. Prelogović, E.; Aljinović, B.; Bahun, S. New data on structural relationships in the Northern Dalmatian Dinaride Area. *Geol. Croat.* **1995**, *48*, 167–176.
52. Velić, I.; Sokač, B. *Basic Geological Map of the Republic of Croatia 1:100.000; Sheet Ogulin*; Croatian Geological Survey: Zagreb, Croatia, 1982.
53. Šušnjar, M.; Bukovac, J.; Nikler, L.; Crnolatac, I.; Milan, A.; Šikic, D.; Griman, I.; Vulić, Ž.; Blašković, M. *Basic Geological Map of the Republic of Croatia 1:100.000; Sheet Crikvenica*; Croatian Geological Survey: Zagreb, Croatia, 1970.
54. Bukovac, J.; Šušnjar, M.; Poljak, M.; Čakalo, M. *Basic Geological Map of the Republic of Croatia 1:100.000; Sheet Črnomelj*; Croatian Geological Survey: Zagreb, Croatia, 1983.
55. Stroj, A.; Paar, D. Water and air dynamics within a deep vadose zone of a karst massif: Observations from the Lukina jama–Trojama cave system (−1,431 m) in Dinaric karst (Croatia). *Hydrol. Process* **2019**, *33*, 551–561. [CrossRef]
56. Bočić, N.; Pahernik, M.; Mihevc, A. Geomorphological significance of the palaeodrainage network on a karst plateau: The Una–Korana plateau, Dinaric karst, Croatia. *Geomorphology* **2015**, *247*, 55–65. [CrossRef]
57. Kovačević, A. Hydrogeological Features of Karlovac County. Master's Thesis, University of Zagreb, Zagreb, Croatia, 2006.
58. Karlović, I.; Pavlić, K.; Posavec, K.; Marković, T. Analysis of the hydraulic connection of the Plitvica stream and the groundwater of the Varaždin alluvial aquifer. *Geofizika* **2021**, *38*, 15–35. [CrossRef]
59. Baedke, S.J.; Krothe, N.C. Derivation of effective hydraulic parameters of a Karst Aquifer from discharge hydrograph analysis. *Water Resour. Res.* **2001**, *37*, 13–19. [CrossRef]
60. Milanović, P. Water regime in deep karst—Case study of the Ombla Spring drainage area. In *Karst Hydrology and Water Resources, Proceedings of the U.S.-Yugoslavian Symposium, Dubrovnik, Croatia, 2–7 June 1975*; Yevjevich, V., Ed.; Water Resources Publication: Littleton, CO, USA, 1981; pp. 165–191.
61. Tallaksen, L.M. A review of baseflow recession analysis. *J. Hydrol.* **1995**, *165*, 349–370. [CrossRef]
62. Urumović, K.; Duić, Ž.; Hlevnjak, B. Hydrogeological significance of recession coefficients at the example of Istrian springs. *Rud.-Geološko-Naft. Zb.* **2009**, *21*, 25–34.
63. Trauth, M.H. *MATLAB Recipes for Earth Sciences*; Springer: Berlin/Heidelberg, Germany, 2015.
64. Liu, L.; Chen, X.; Xu, G.; Shu, L. Use of hydrologic time-series data for identification of hydrodynamic function and behavior in a karstic water system in China. *Hydrogeol. J.* **2011**, *19*, 1577–1585. [CrossRef]
65. Taylor, C.J.; Green, E.A. Hydrogeologic characterization and methods used in the investigation of karst hydrology. In *Field Techniques for Estimating Water Fluxes Between Surface Water and Groundwater*; Techniques and Methods 4–D2; U.S. Geological Survey: Reston, VA, USA, 2008; pp. 75–114.
66. Guo, Y.; Wang, F.; Qin, J.D.; Zhao, F.Z.; Gan, F.P.; Yan, B.K.; Bai, J.; Muhammed, H. Hydrodynamic characteristics of a typical karst spring system based on time series analysis in northern China. *China Geol.* **2021**, *4*, 433–445. [CrossRef]
67. Kuhta, M.; Stroj, A.; Brkić, Ž. Hydrodynamic characteristics of Mt. Biokovo foothill springs in Croatia. *Geol. Croat.* **2012**, *65*, 41–52. [CrossRef]
68. Boljat, I.; Terzić, J.; Duić, Ž.; Lukač Reberski, J.; Selak, A.; Briški, M. Tracing Hydrological Processes: Insights from Hydrochemical and Isotopic Investigations in the Northern Part of Croatian Dinaric Karst. *Geol. Croat.* 2024, *in progress*.
69. Herak, M.; Bahun, S.; Magdalenić, A. Pozitivni i negativni utjecaji na razvoj krša u Hrvatskoj (Positive and negative influences on the development of the Karst in Croatia). *Jugosl. Akad. Znan. I Umjet. Odjel Za Prir. Nauk.* **1969**, *6*, 45–71.

Paper 3 (P3)

Tracing Hydrological Processes: Insights from Hydrochemical and Isotopic Investigations in the Northern Part of Croatian Dinaric Karst

By

Boljat, Ivana; Terzić, Josip; Duić, Željko; Lukač Reberski, Jasmina; Selak, Ana; Briški, Maja

Geologia Croatica
Journal of the Croatian Geological Survey and the Croatian Geological Society
2024 | 77/2 | 127–144 | 11 Figs. | 5 Tabs. | 2 Supplements |
www.geologia-croatica.hr

Tracing hydrological processes: insights from hydrochemical and isotopic investigations in the northern part of Croatian Dinaric karst

Ivana Boljat[1], Josip Terzić[1], Željko Duić[2,*]; Jasmina Lukač Reberski[1], Ana Selak[1] and Maja Briški[1]

[1] Croatian Geological Survey, Department of Hydrogeology and Engineering Geology, Sachsova 2, 10000 Zagreb, Croatia
[2] University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Department of Geology and Geological Engineering, Pierottijeva 6, Zagreb, 10000, Croatia; (*corresponding author: zeljko.duic@rgn.unizg.hr)

doi: 10.4154/gc.2024.09

Article history:
Manuscript recieved: January 13, 2024
Revised manuscript accepted: April 18, 2024
Available online: June 21, 2024

Abstract

This study presents the findings derived from a three-year monitoring programme focusing on the hydrochemical composition and stable isotope signatures ($\delta^{18}O$, $\delta^{2}H$) within the vulnerable karst groundwater system in Croatia's northern Dinaric karst region. Covering an area of 1980 km^2 across Kapela Mountain and its foothills, this groundwater system falls within the Kupa River basin and encompasses the catchment areas of the main springs across two spring levels of the Dobra, Mrežnica, and Slunjčica Rivers (namely the Vitunj, Zagorska Mrežnica, Dretulja, Veliko Vrelo, Gojak, Tounjčica, Mrežnica, and Slunjčica springs). Given the complex hydrogeological framework, prior studies have not extensively addressed the hydrochemical characteristics of this region, thereby necessitating a comprehensive investigation to elucidate system dynamics. This paper outlines the first investigation employing stable isotopic analyses within the karst groundwater system of Kapela Mt.

The main results and conclusions of the research include: (i) the aquifers across Kapela Mt. drain mainly limestones, (ii) water–rock interaction and carbonate weathering are significant contributors to water geochemistry, (iii) there is a slight human impact on the Gojak and Tounjčica spring waters, (iv) the mean residence time of water in the observed aquifer is up to 1.5 years, (v) the new LMWL was calculated for Kapela Mt. based on a three-year dataset (June 2018 – May 2021), (vi) in the north Dinaric karst, the predominant origin of precipitation is from the Mediterranean air mass, (vii) Velebit Mt. has a strong influence on the precipitation isotopic composition of the study area.

Keywords: karst hydrogeology, environmental tracer, excess air, mean recharge altitude, local meteoric water line, Kupa River catchment

1. INTRODUCTION

Karst aquifers are challenging to exploit, manage, and protect due to the extreme variability of hydraulic properties (PALMER, 2010). The pathways and residence time of groundwater within the subsurface often depend upon not only the geometry of a complex underground network of conduits and fissures, but also the prevailing hydrological conditions (FORD & WILLAMS, 2007; VASIĆ et al., 2020; MILANOVIĆ et al., 2023; TORRESAN et al., 2020; TERZIĆ et al., 2012; TORKAR & BRENČIČ, 2015; ŽIVANOVIĆ et al., 2022). The Dinaric karst system represents a geologically heterogeneous, south European orogenic belt, developed in highly vulnerable carbonate aquifers, which are the main drinking water resource for the region. The system stretches from the Carso area in Italy in the north and crosses over several countries from Slovenia to Albania (STEVANOVIĆ et al., 2016). The north Dinaric karst in Croatia remains uniquely unaffected by its neighbouring countries, boasting very high groundwater quality (BIONDIĆ 2013; PAVLIĆ & PARLOV, 2019). Hence, it has been declared as part of the first-degree strategic reserve of drinking water by the Croatian Water Management Strategy (Water Management Strategy 2008). These strategic reserves include the Gacka River catchment in the south, aquifers across Kapela Mt., and the mountainous section of the Kupa River's immediate catchment to the north. The catchments of the Gacka River (MANDIĆ et al., 2008; LUKAČ REBERSKI et al., 2009, 2013; STROJ et al., 2023) and Kupa River (BIONDIĆ et al., 2021; PAVLIĆ & PARLOV, 2019; FRANČIŠKOVIĆ-BILINSKI et al., 2013), have been hydrogeological explored. However, there is limited knowledge regarding the hydrogeological and groundwater characteristics of the aquifer spanning Kapela Mt. and the Ogulin-Plaški Valley, with only local studies conducted (BOČIĆ et al., 2015; BONACCI & ANDRIĆ, 2010; BULJAN et al., 2019; GLADOVIĆ et al., 2023; TERZIĆ et al., 2012). This research endeavour is poised to address this gap in knowledge. The local hydrogeological studies, specifically focusing on hydrochemical and stable isotopic analyses were carried out in the neighbouring area of the Plitvice Lakes catchment (BABINKA, 2007; BIONDIĆ et al., 2006, 2010; ČANJEVAC et al., 2023; HUNJAK et al., 2013; MEAŠKI et al., 2016), Krbavica (STROJ et al., 2020) and Velebit Mt. (STROJ & PAAR, 2019).

Long-term hydrochemical monitoring provides valuable insights into the mechanisms governing water-rock interactions, dissolution processes, groundwater flow pathways, and anthropogenic impacts in karst aquifers (GIBBS, 1970;

MEYBECK 1987; AKTER & AHMED, 2019; MARKOVIĆ et al., 2022). Moreover, stable isotopes, such as oxygen-18 ($\delta^{18}O$) and deuterium (δ^2H), serve as natural tracers, offering clues about the origin (VREČA et al., 2007; HUNJAK, 2013; MEZGA et al., 2014), mean residence time (KRALIK, 2015), mean recharge altitudes (MOHAMMED et al., 2014; FIKET et al., 2021), mixing patterns (TERZIĆ et al., 2014), and the groundwater dynamic (MANCE et al., 2022) within the karst system. We conducted a comprehensive analysis using a three-year dataset, examining hydrochemical and physical parameters alongside the $\delta^{18}O$ and δ^2H stable isotope content of the groundwater. The investigation spanned eight distinct locations (Vitunj, Zagorska Mrežnica, Dretulja, Veliko Vrelo, Gojak, Tounjčica, Mrežnica, and Slunjčica springs) within two spring zones situated in the area of Kapela Mt. We integrated insights from the neighbouring catchments to interpret our research findings. This integration enriches the depth and scope of the analysis. The research holds significant value as it marks the inaugural regional study of its kind within the northern part of the Dinaric karst in Croatia.

2. SETTINGS

2.1. Study area

The study area belongs to the Black Sea basin and is located in the northern part of the Croatian Dinaric karst, spanning an approximate area of 1980 km^2. It encompasses the catchments of the main springs of the Dobra, Mrežnica, and Slunjčica Rivers catchments (Fig 1). The northern boundary of the investigated area is demarcated by the interface between the immediate catchments of the Kupa and Dobra Rivers. The western boundary coincides with the watershed between the Adriatic and Danube River basins, while the southern boundary extends from the Plitvice Lakes to Slunj. The eastern boundary is defined by the springs of the Dobra, Mrežnica, and Slunjčica Rivers. Catchment boundaries for the Zagorska Mrežnica, Dretulja, Veliko Vrelo, and Slunjčica springs were defined during the establishment of sanitary protection zones. However, it should be noted that these boundaries are zonal and depend upon the hydrological conditions prevailing within the respective watershed (TERZIĆ et al., 2012; BIONDIĆ, 2013; BULJAN et al., 2019).

The area falls within the continental climatic belt, characterized by mountain climate elements. Kapela Mt., with a peak of 1534 m a.s.l., acts as a barrier to moisture-laden air masses from the west, causing significant precipitation. This area lacks dry periods. Annual precipitation levels vary between 1750 and 2500 mm, conditioned by both vertical and horizontal relief divisions, generally increasing from SE to NW. The snow cover duration averages 50 days per annum over the period from 1949 to 2022, as per Croatian Meteorological and Hydrological Service (DHMZ) records. Average annual air temperatures oscillate between 3 to 6°C. The Ogulin-Plaški Valley, located at an altitude of 300 to 400 m a.s.l., experiences dry and hot summers contrasting with wet and cold winters. Average annual precipitation varies from 1250 to 1750 mm, and air temperature between 10 to 11°C. DHMZ records from 1949 to 2022 indicate an average yearly duration of snow cover lasting 39 days.

The northern part of the Dinaric karst in Croatia is predominantly composed of karstified carbonate rocks, which were deposited from the Triassic to Lower Cenozoic periods. Non-karstic rocks occupy small and scattered areas, often surrounded by karst terrain (BAHUN 1968; BULJAN et al. 2019). The typical orientation in a NW-SE direction can be attributed to thrust-related deformation between the Palaeogene and the Eocene or Miocene epochs (TARI, 2002; SCHMID et al., 2008; KORBAR, 2009). However, the region's evolution is still an essential subject of investigation (DRAGIČEVIĆ & VELIĆ, 2002; VLAHOVIĆ et al., 2005; VELIĆ, 2007; KORBAR, 2009;).

A comprehensive Basic geological map, at the 1:100,000 scale, was created for the entire research area, covered by six sheets, each accompanied by interpretations. The sheets include: Delnice (SAVIĆ & DOZET, 1983), Crikvenica (ŠUŠNJAR et al., 1970), Črnomelj (BUKOVAC et al., 1983), Ogulin (VELIĆ & SOKAČ, 1982), Otočac (VELIĆ et al., 1974) and Slunj (KOROLIJA et al., 1980). According to the structural-geological position and lithology, the rocks within the area were divided into the following distinct hydrogeological groups (Fig. 1):

Quaternary deposits – encompass heterogeneous depostits, mostly mixtures of rock fragments and fine-grained material. The soil covers the carbonate base across the entire area, but their hydrogeological significance is only notable within morphological depressions such as karst poljes: Ogulin, Plaški, Lička Jesenica.

High permeability carbonates – represented predominantly by limestones. These formations were deposited between the Jurassic and Eocene periods.

Permeable carbonate rocks – represented predominantly by dolomitic limestone to thinner beds or interbeds of dolomite, deposited during the Jurassic and Cretaceous periods.

Low permeability carbonates – characterized by lower karstification intensity, mainly composed of dolomite, dolomitized limestone, or dolomite/limestone exchange, with dissolution cavities often filled with secondary materials including silt, sand and rock fragments. Deposition occurred from the Upper Triassic to Lower Cretaceous periods.

The hydrogeological relationships in the study area result from compressional tectonics (TARI, 2002) and are intrinsically complex. The mountainous terrain of Kapela Mt. serves as the first recharge area formed by substantially fractured Mesozoic limestones and dolomites exhibiting high secondary porosity. Due to numerous karstic forms, the area is characterized by rare, ephemeral surface watercourses limited to karst poljes. Highly karstified rocks enable the substantial accumulation of groundwater. The monitored springs Vitunj, Zagorska Mrežnica, Dretulja, and Veliko Vrelo emerge at the foot of the mountain, where permeable carbonate rocks meet with less permeable dolomites. The hydrogeological barrier is represented by several karst poljes with short watercourses. Geomorphologically, the hydrogeological barrier is represented by the Una-Korana karst plateau, the largest plateau in Dinaric karst (BOČIĆ et al, 2003, 2015; 2010). Among these, the largest are Ogulin, Plaški, and Ličko-jeseničko polje, and smaller Begovac and Saborsko poljes.

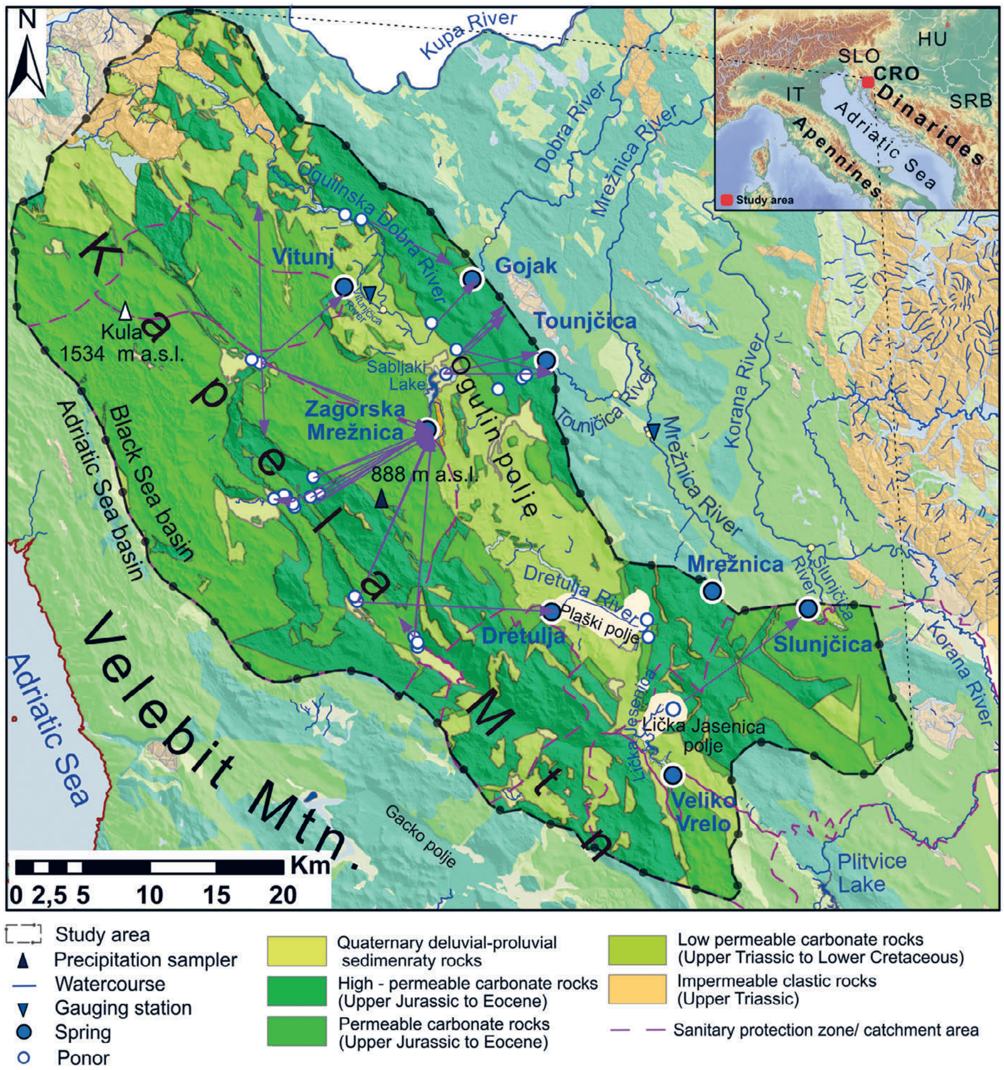


Figure 1. Hydrogeological map of the north Dinaric karst region in Croatia.

Watercourses of the Zagorska Mrežnica, Dretulja, and Lička Jesenica Rivers flow across the karst plateau, where they sink into the highly permeable limestones. They resurface at an elevation around 100 m lower than the plateau, eventually forming the Kupa River tributaries: Dobra, Mrežnica, and Slunjčica Rivers.

Eight springs have been strategically selected for monitoring, considering their spatial distribution and contribution to the hydrological network of the three Kupa River tributaries. The first spring zone encompasses four springs located at the foot of Kapela Mt. namely the Vitunj, Zagorska Mrežnica, Dretulja, and Veliko Vrelo springs. The second spring zone is represented by the Gojak, Tounjčica, Mrežnica, and Slunjčica springs, serving as the main outlets of the sinking rivers, which are formed by the springs in the first spring zone. The second spring area marks the transition between deep (classical) and shallow karst (fluviokarst) (BAHUN, 1968; KOVAČEVIĆ, 2005). Although this border is primarily descriptive and based solely on structural units, 1the entirety of the area east of the Kapela Mt. differs greatly from the rest of the Croatian Dinaric karst in terms of karstification depth.

The Vitunj spring forms the Vitunjčica River, a main tributary of the sinking Ogulinska Dobra River, which resurfaces at the Gojak spring, initiating the Dobra River's watercourse. The Zagorska Mrežnica spring is the main spring in the Ogulin polje, which feeds the catchment area of the Tounjčica River, or the west tributary of the Mrežnica River. The Dretulja spring forms the eponymous sinking river, which emerges through the Mrežnica spring, serving as the starting point of the Mrežnica River. The Veliko Vrelo spring forms the Lička Jesenica sinking river, proven to be connected with the Slunjčica spring (Engineering Project Institute, 1948).

The discharge regime of springs and rivers in the study area shows a distinctly karstic nature, characterized by notable differences in minimum and maximum discharges and fast responses (within a day) to precipitation in the hinterland (BULJAN et al., 2019). An illustration of substantial fluctuations in discharge under low and high hydrological conditions is shown in Figure 2. The supplementary material (1 and 2) presents all monitored springs during varying water levels. The available literature data shows that the ratio of the lowest, medium, and maximum discharges in Veliko Vrelo spring is 1:6.75:100 (TERZIĆ et al., 2012), in Vitunjčica River

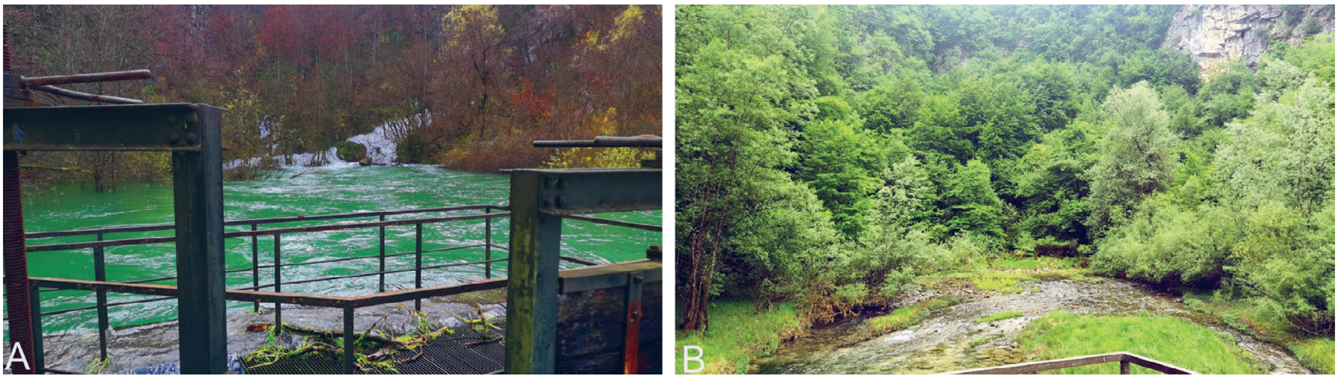


Figure 2. The Mrežnica spring during high (A) and low water conditions (B). The spring is located within the military training area "Eugen Kvaternik" and is inaccessible to the general population.

1:14:143 (PAVLIĆ & PARLOV, 2020), and the ratio of minimum and maximum discharge of the Zagorska Mrežnica spring is 1:222 (BIONDIĆ, 2013); 1:6:64 Slunjčica (DHMZ).

3. MONITORING, SAMPLING, AND DATA ANALYSIS

Hydrochemical and isotopic investigations have been conducted within the study area, focusing on eight springs: the Vitunj, Zagorska Mrežnica, Dretulja, Veliko Vrelo, Gojak, Tounjčica, Mrežnica, and Slunjčica springs. Table 1 provides details regarding the geographic position, sample numbers for chemical and isotopic analyses, and *in situ* measurements at selected sampling locations (Fig 1). Monthly observations of chemical and physicochemical parameters were undertaken over a span of 33 monitoring campaigns between September 2018 and May 2021. Stable isotopes were observed in spring waters during 40 campaigns, from February 2018 to May 2021. Additionally, isotopic precipitation analyses were performed in 36 campaigns, at monthly intervals from June 2018 to May 2021. The precipitation sampler was located at Kapela Mt.

The physico-chemical parameters (water temperature, pH, specific electrolytic conductivity (SEC), and oxygen concentration) were measured *in situ* using a WTW (Multi 3630 IDS SET G) multi-parameter probe. The HCO_3^- ion concentration or alkalinity was measured in the field through volumetric titration using 1.6N H_2SO_4 to pH 4.5, employing a HACH digital titrator.

The groundwater and precipitation samples were analysed in the hydrochemical laboratory of the Department of Hydrogeology and Engineering Geology of the Croatian Geological Survey. The concentrations of the major anions (Cl^-, NO_3^-, and SO_4^{2-}) and cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) were measured using ion chromatography (Thermo Scientific Dionex ICS-6000 HPIC System). The ion analyses balance was checked by the relative deviation from the charge balance ($\Delta meq = 100 \times (\Sigma meq+ - \Sigma meq-)/(\Sigma meq+ + \Sigma meq-) < \pm5\%$) (MANDEL & SHIFTAN, 1981; DOMENICO & SCHWARTZ, 1990). Stable isotopes of oxygen and hydrogen were analyzed with a Picarro L2130-i Isotope and Gas Concentration Analyzer (Picarro, Santa Clara, CA, USA), using the Secondary Water Isotopes Standard Kit (Picarro) for calibration of the results. The results are presented in delta notation (‰), normalised to the international measurement standard VSMOW (Vienna Standard Mean Ocean Water) (CRAIG, 1961a).

Precipitation was collected using oil-free Palmex® rain collectors (Palmex d.o.o., Zagreb, Croatia) that effectively prevent evaporative isotopic enrichment (MICHELSEN et al., 2018). The sampler was positioned at the observation station of Croatian Roads (HAC) (45°05'3422 N, 15°12'42'' E) on Kapela Mt, at 888 m a.s.l. The direct distance by air between the sampler and the Adriatic coast is about 25 km. Out of 36 samples collected, three were excluded from further interpretation due to technical difficulties. Specifically, during the months of August 2018, May 2020, and January 2021, the precipitation collector funnel encountered blockages, causing

Table 1. Sampling location, altitude, type, and number of samples per analysis.

Location	Lat. (deg N)	Long. (deg w)	Altitude (m a.s.l.)	No. of samples for analysis of δ^2H and δ^{18}O isotopes	No. of samples for chemical analysis	*In situ* measurements of physical parameters
Vitunj spring	45.291221	15.140482	345	39	32	32
Zagorska Mrežnica spring	45.195624	15.221742	326	40	33	32
Dretulja spring	45.074659	15.342673	359	40	32	33
Veliko Vrelo spring	44.966213	15.460677	484	38	33	33
Gojak spring	45.297340	15.262693	197	40	33	33
Tounjčica spring	45.248871	15.322711	225	40	33	33
Mrežnica spring	45.090260	15.495816	320	29	29	28
Slunjčica spring	45.078297	15.588019	258	40	33	33
Kapela Mt. (precipitation)	45.092973	15.211796	888	36(33*)	-	-
			Total	339	258	257

* number of samples taken in the interpretation

inadequate data. The recorded values deviated by more than 200% from the obtained maximal/minimum value, necessitating exclusion from the analyses.

Daily discharge data were acquired from the Croatian Meteorological and Hydrological Service (DHMZ) and the Croatian Electric Power Company (HEP).

To delineate the hydrochemical facies of springs, monthly water samples were subjected to major anion and cation analyses. The results were used to construct a Piper diagram (PIPER, 1944) that graphically represents the major ion ratios. The interactions among the chemical and physicochemical parameters were further analyzed using Pearson's correlation coefficient (r). This statistical measure is widely employed to explore relationships between the various parameters within hydrochemical samples. The dimensionless number in question falls between the range of +1 to –1, where +1 signifies a perfect positive correlation, 0 indicates no linear relationship, and –1 denotes a perfect negative correlation between the parameters. More precisely, parameters with a correlation coefficient $r > 0.7$ are considered to have a strong correlation, while values between 0.5 and 0.7 indicate a moderate correlation (FREEDMAN et al. 2007). The molar ratio Mg^{2+}/Ca^{2+} was utilized to derive information regarding the source, evolution, and geochemical processes influencing water chemistry in aquifers (APPELO & POSTMA, 2005).

Analyses of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) stable isotopes in spring water and precipitation samples were used to define spring water origin by comparing it with local precipitation characteristics. The local meteoric water line (LMWL) was calculated using the ordinary least square

Table 2. Main statistical descriptors of *in situ* measured parameters and major ion concentrations at the eight locations in catchment areas of Dobra, Mrežnica, and Slunjčica Rivers.

Site	statistic	T	pH	SEC (µS/cm)	O_2 (mg/l)	Na^+ (mg/l)	Mg^{2+} (mg/l)	K^+ (mg/l)	Ca^{2+} (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	HCO_3^- (mg/l)
Vitunj	MAX	9.4	8.36	407	12.3	1.76	29.64	0.94	64.64	2.14	8.36	8.05	285.4
	MIN	7.6	7.0	272	10.9	0.0	4.5	0.0	42.4	0.7	1.4	1.6	165.9
	MEDIAN	7.8	7.9	319	11.6	0.6	7.0	0.3	55.5	1.3	5.2	5.4	203.7
	AVERAGE	7.9	7.9	326	11.3	0.6	9.2	0.3	55.4	1.3	4.9	4.9	208.4
	SD	0.4	0.2	33	2.0	0.3	5.7	0.2	5.4	0.3	1.7	1.9	27.2
Zagorska Mrežnica	MAX	10.9	8.3	437	14.6	5.0	23.6	1.0	82.8	4.1	7.9	11.1	295.2
	MIN	7.6	7.4	336	7.7	0.6	5.2	0.0	41.0	1.8	0.5	1.9	184.2
	MEDIAN	9.1	7.6	409	10.6	1.8	8.4	0.4	71.3	2.8	4.5	6.0	252.5
	AVERAGE	9.2	7.7	405	10.5	1.9	9.6	0.4	70.2	2.8	4.4	5.8	250.8
	SD	0.8	0.2	22	2.4	0.7	4.1	0.2	8.7	0.7	1.5	2.2	24.0
Dretulja	MAX	10.2	8.1	488	14.3	1.8	16.7	2.0	93.9	2.6	7.4	11.6	339.2
	MIN	8.2	0.0	423	9.0	0.0	7.2	0.0	61.8	0.5	1.3	2.3	219.6
	MEDIAN	8.7	7.4	462	10.4	0.6	10.7	0.3	83.5	1.1	4.4	6.4	292.8
	AVERAGE	8.9	7.2	461	10.2	0.6	11.1	0.4	82.6	1.3	4.4	6.4	292.1
	SD	0.7	1.3	11	2.0	0.3	2.3	0.4	6.1	0.5	1.5	2.3	22.2
Veliko Vrelo	MAX	8.7	8.1	506	14.3	1.7	22.9	0.8	84.8	2.3	8.5	8.3	347.7
	MIN	7.0	7.4	278	10.0	0.3	8.5	0.1	48.1	0.7	2.5	2.3	253.8
	MEDIAN	7.8	7.5	439	11.4	0.6	14.1	0.3	73.0	1.3	5.2	5.7	285.5
	AVERAGE	7.7	7.5	439	11.4	0.7	14.8	0.3	73.1	1.3	5.2	5.4	284.1
	SD	0.3	0.1	33	0.7	0.3	3.5	0.2	6.4	0.4	1.3	1.7	19.9
Gojak	MAX	16.9	8.4	432	12.8	5.2	24.0	2.8	75.7	10.6	10.4	10.3	273.3
	MIN	7.7	7.5	344	9.5	1.7	8.0	0.2	40.5	2.1	3.3	3.0	178.1
	MEDIAN	10.0	7.9	391	11.2	3.4	13.1	0.8	60.7	5.1	6.3	6.6	235.5
	AVERAGE	11.1	7.9	392	10.6	3.5	13.1	0.9	60.7	5.1	6.5	6.5	233.8
	SD	2.5	0.2	22	2.8	0.9	3.4	0.5	6.4	1.7	1.7	2.1	18.0
Tunjčica	MAX	16.1	8.2	659	12.1	34.9	15.0	2.4	88.3	67.1	17.6	10.9	305.0
	MIN	6.9	7.5	355	1.9	0.8	4.5	0.2	53.0	1.8	2.7	2.5	180.6
	MEDIAN	9.5	7.8	393	9.5	1.8	7.5	0.6	70.1	2.8	5.9	6.2	240.3
	AVERAGE	9.8	7.8	407	8.4	4.0	7.8	0.7	71.1	6.5	7.2	6.2	239.8
	SD	1.6	0.2	55	3.3	6.1	2.2	0.4	7.6	11.5	3.9	2.3	26.3
Mrežnica	MAX	13.7	8.1	470	12.6	1.2	18.0	1.8	86.0	2.8	7.7	9.2	324.5
	MIN	6.4	6.8	387	9.6	0.1	6.3	0.1	45.8	1.1	0.5	2.6	169.6
	MEDIAN	9.7	7.7	446	10.4	0.8	12.4	0.7	76.7	1.7	4.3	6.0	278.2
	AVERAGE	9.9	7.7	443	10.3	0.7	12.5	0.8	74.8	1.8	4.4	5.9	278.8
	SD	1.7	0.2	17.5	2.1	0.3	2.6	0.5	8.2	0.5	1.5	1.7	27.8
Slunjčica	MAX	10.9	8.0	460	14.2	2.2	15.7	1.4	94.9	3.1	7.8	10.5	345.3
	MIN	8.7	0.0	390	9.2	0.4	4.4	0.1	53.8	0.7	1.6	2.4	213.5
	MEDIAN	9.5	7.5	443	10.8	1.0	9.7	0.4	78.4	1.8	4.7	6.3	273.3
	AVERAGE	9.7	7.3	438	10.8	1.1	9.9	0.4	78.8	1.8	4.5	6.3	278.2
	SD	0.6	1.3	17	0.8	0.4	2.9	0.3	7.1	0.5	1.4	2.1	21.3

regression (OLSR), excluding improperly collected samples. Spring water isotope values were plotted and compared with the LMWL, and the groundwater lines (GWL) were calculated for the monitored springs (CLARK & FRITZ, 1997).

The d-excess was calculated for each sample following the equation: d-excess = $\delta^2H - 8\delta^{18}O$ (DANSGAARD, 1964). The d-excess can be used as an indicator of the origin of precipitation and conditions during the vapour formation (CLARK et al., 2015).

Isotopic analyses also enabled a rough estimation of spring water mean residence time (MRT) in the aquifer by using a simple equation based on observed annual oscillation amplitudes in rainwater and spring water samples. The MRT in the karst aquifers were a rough estimation using an exponential model by the following equation:

$$T=\omega^{-1}[(A/B)^{-2}-1]^{0.5} \qquad (1)$$

where T is the mean residence time, A is the amplitude of precipitation $\delta^{18}O$, B is the amplitude of the spring water and the ω is the angular frequency. The theoretical background of the applied equation is elaborated upon in the works by MAŁOSZEWSKI et al. (1983), McGUIRE & McDONNELL (2006), and RODGERS et al. (2005). The calculation examines the sinusoidal oscillation of the stable isotope content in precipitation and the subsequent reduction of this oscillation in observed springs due to the mixing and retention of water in the karst aquifers.

4. RESULTS

The descriptive statistics of the physico-chemical and chemical parameters of the sampled waters are summarised in Table 2 and shown in Figure 3.

The pH ranges between 6.8 and 8.2, which indicates the slightly alkaline water, typical for karst aqifers. The most dispersed and highest values were observed in the Gojak spring

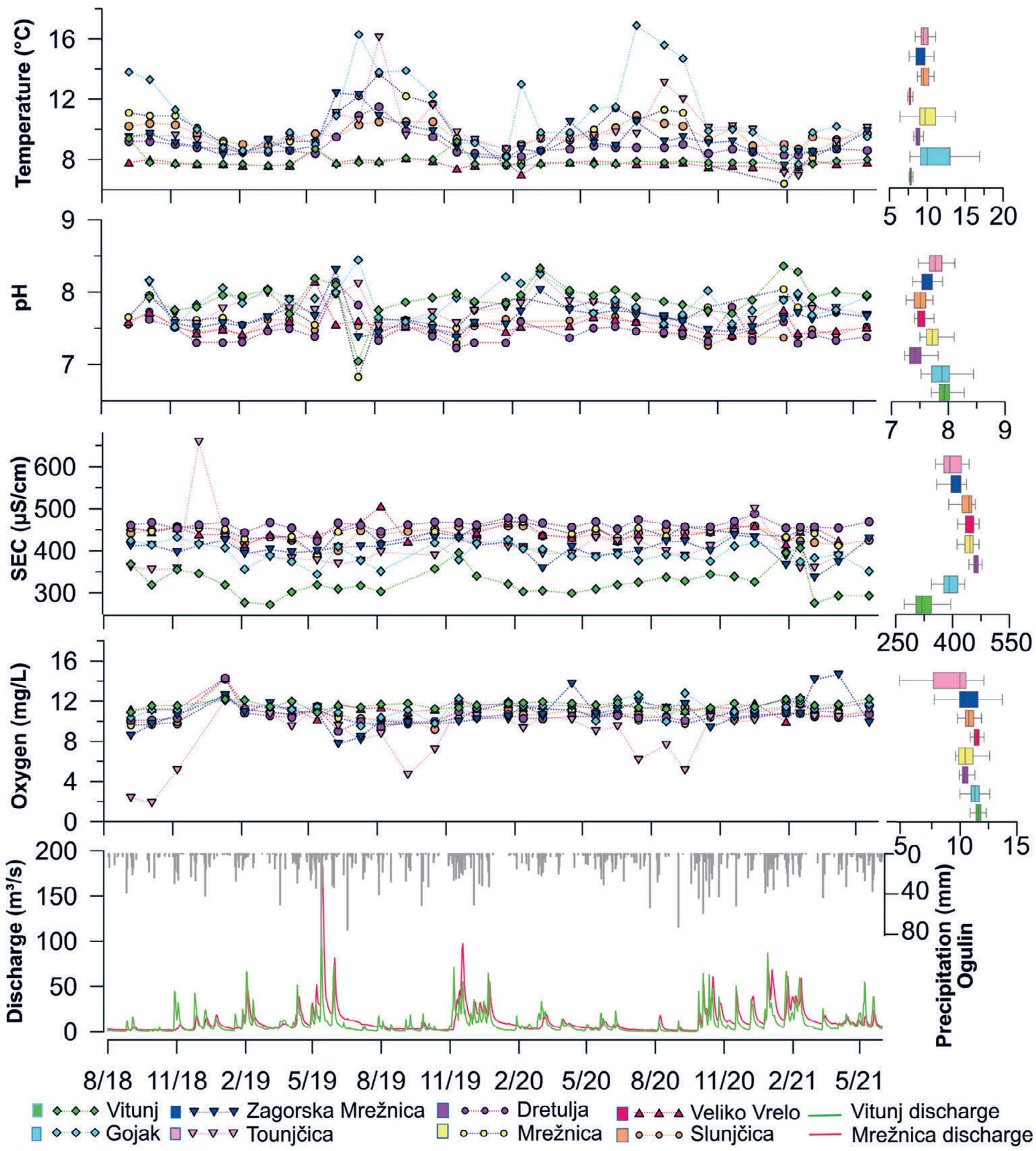


Figure 3. Dissolved oxygen, precipitation, pH, water temperature, and SEC compared with daily discharge and precipitation data, which represent hydrological conditions.

water. In general, the Dretulja spring water has the lowest, while the Vitunj spring water has the highest pH values.

The water temperature of the monitored springs ranges from 6.4 to 16.9°C, with pronounced temperature homogenization of the springs at the foot of the Kapela Mt. The most consistent water temperature was recorded in the Veliko Vrelo (Δ 1.7°C) and Vitunj (Δ 1.8°C) springs, while the water temperature in the Dretulja spring oscillates around 2.4°C, and in Zagorska Mrežnica spring around 2.8°C. The temperature oscillations in the spring water at the second spring level are more pronounced. Within the area of shallow karst, the temperature of the Slunjčica spring amounts to only 2.2°C. However, the springs to the north, such as Mrežnica, Tounjčica, and Gojak exhibit much larger temperature oscillations of Δ 7.3°C, Δ 9.2°C, and Δ 9.2°C, respectively.

The SEC in spring waters ranges between 272 and 506 µS/cm, with an anomaly noted in December 2019 in the Tounjčica spring, when the SEC measured 659 µS/cm. The observed anomaly is further explained in the discussion. In general, there is a trend of increasing SEC values in springs from the north to the south of the study area. The Vitunj spring water has the highest degree of oscillation, with the lowest overall values (median of 319 µS/cm). The median SEC value in Zagorska Mrežnica spring water was 409 µS/cm. However, at the foot of the Kapela Mt. slightly higher SEC values were detected in Dretulja (median of 462 µS/cm) spring waters than in the Veliko Vrelo spring (median of 439 µS/cm). This pattern is mirrored in the second spring zone, in Mrežnica (median of 446 µS/cm) and Slunjčica (median of 443 µS/cm) springs. The Tounjčica spring water (median of 393 µS/cm) has similar SEC values to the Gojak spring waters (median of 391 µS/cm), but with a higher degree of oscillation.

The oxygen concentration in the monitored spring waters ranges between 7.73 to 14.63 mg/l, except for Tounjčica spring water, where extremely low values up to 1.88 mg/l were observed. The median values of oxygen concentration showed the following order: Vitunj (11.6 mg/l) > Gojak (11.2 mg/l) > Veliko Vrelo (11.4 mg/l) > Slunjčica (10.8 mg/l) > Zagorska Mrežnica (10.6 mg/l) > Dretulja (10.4 mg/l) > Mrežnica (10.4 mg/l) > Tounjčica (9.5 mg/l).

The results of the chemical analysis indicated Ca^{2+} as a dominant cation in monitored spring waters, followed by Mg^{2+}, Na^{+}, and K^{+}. The average contribution of Ca^{2+} to the cation budget is 84 – 87% in all spring water, except Gojak spring water, which is 78%. The dominant anion in monitored spring waters is HCO_3^- followed by Cl^-, NO_3^-, and SO_4^{2-}. The average contribution of HCO_3^- is 96% to the anion budget in the Mrežnica, Veliko Vrelo, and Slunjčica springs, 95% in the Vitunj and Zagorska Mrežnica springs, and 93% in the Dretulja and Tounjčica springs. Spring water mineralization was calculated from a chemical analysis of major anions and cations. The mineralization during the monitoring period was in the range of 236 – 370 mg/L for the Vitunj spring, 267 – 430 mg/L for the Mrežnica spring, 273 – 378 mg/L for the Gojak spring, 273 – 495 mg/L for the Tounjčica spring, 281 – 395 mg/L for the Zagorska Mrežnica spring, 306 – 450 mg/L for the Dretlja spring, 317 – 455 mg/L for the Slunjčica spring, and 342 – 453 mg/L for the Veliko Vrelo spring.

The minimum, maximum, and median isotopic composition of $\delta^{18}O$ and $\delta^{2}H$ in monitored springs and precipitation collected on Kapela Mt. are reported in Table 3. In spring waters, the measured $\delta^{18}O$ values ranged from –10.65 to –8.01‰, and the $\delta^{2}H$ values ranged from –70.46 to –50.48‰. The results align with the previous study in Lika and Gorski Kotar regions (BRKIĆ et al., 2020; STROJ et al., 2020; PAAR et al., 2019; HUNJAK, 2013). The amplitude in precipitation is expectedly much higher; the measured $\delta^{18}O$ values ranged from –12.33 to –4.99‰, and the $\delta^{2}H$ varied from –88.00 to –25.55‰.

The higher amplitude of $\delta^{18}O$ was observed in the spring water of Vitunj spring (2.39‰), followed by the Gojak (2.08‰), Tounjčica (2.06‰), Zagorska Mrežnica (1.84‰), Slunjčica (1.80‰), Mrežnica (1.55‰), Veliko Vrelo (1.41‰) and Dretulja (1.30‰) springs. The amplitude of the observed isotope

Table 3. Minimum, maximum, median, and amplitude values of the $\delta^{18}O$, $\delta^{2}H$ and d-excess isotope compositions for Vitunj, Zagorska Mrežnica, Dretulja, Veliko Vrelo, Gojak, Tounjčica, Mrežnica and Slunjčica springs, and Kapela Mt. precipitation.

Location	Values	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	d-excess
Vitunj	Maximum	-10.65	-70.46	15.86
	Minimum	-8.26	-51.83	13.06
	Median	-9.12	-59.52	14.62
	Amplitude	2.39	18.63	2.80
Zagorska Mrežnica	Maximum	-10.28	-67.75	15.29
	Minimum	-8.43	-53.39	13.11
	Median	-9.50	-61.92	14.48
	Amplitude	1.84	14.36	2.18
Dretulja	Maximum	-10.60	-70.49	15.46
	Minimum	-9.30	-60.26	13.46
	Median	-10.20	-67.08	14.48
	Amplitude	1.30	10.22	2.00
Veliko Vrelo	Maximum	-10.48	-69.10	15.49
	Minimum	-9.07	-57.57	11.96
	Median	-10.10	-66.09	14.69
	Amplitude	1.41	11.53	3.53
Gojak	Maximum	-10.10	-67.40	14.69
	Minimum	-8.01	-50.48	12.84
	Median	-9.26	-60.23	12.84
	Amplitude	2.08	16.92	1.85
Tounjčica	Maximum	-10.51	-70.27	15.06
	Minimum	-8.46	-53.65	12.47
	Median	-9.49	-62.25	13.76
	Amplitude	2.06	16.62	1.85
Mrežnica	Maximum	-10.44	-68.75	15.39
	Minimum	-8.89	-57.23	12.80
	Median	-9.95	-65.69	14.08
	Amplitude	1.55	11.52	2.58
Slunjčica	Maximum	-10.58	-70.38	14.86
	Minimum	-8.78	-55.73	13.16
	Median	-9.94	-65.57	14.15
	Amplitude	1.80	14.64	1.70
Kapela Mt. Precipitation	Maximum	-12.33	-88.00	18.56
	Minimum	-4.99	-25.55	8.75
	Median	-7.87	-47.52	15.00
	Amplitude	7.34	62.45	9.81

indicates the residence time of water in the aquifer, characterizing the lowest amplitude with the highest homogenization, i.e., the longest retention (CLARK & FRITZ, 1997).

5. DISCUSSION

5.1. Major ion chemistry

The chemical composition analysis of spring waters was plotted on a Piper diagram (Fig. 4) to define their hydrochemical facies. All water samples from the monitored springs exhibited the Ca–Mg–HCO_3 hydrogeochemical facies, indicating the dissolution and weathering of carbonates (limestone and dolomite), with no discernible interaction between groundwater and non-carbonate rocks such as evaporites. The spring waters from Tounjčica, Veliko Vrelo, Slunjčica, and Dretulja displayed a more uniform and clearly defined Ca–HCO_3 facies, while the samples from Zagorska Mrežnica, Vitunj, Gojak, and Mrežnica showed mixed facies ranging from Ca–HCO_3 to Ca–Mg–HCO_3.

The pH indicates alkaline waters, which are vital for the dissolution of carbonate rocks within the watershed. The molar Mg^{2+}/Ca^{2+} ratio (Fig. 5) was used to determine the predominant dissolution of carbonate minerals. In all spring waters, the Mg^{2+}/Ca^{2+} ratio indicated the predominant presence of limestone rocks in the study area (Fig. 5a). Specifically, the calcite dissolution results in water characterized by a Mg^{2+}/Ca^{2+} ratio below 0.1. However, the simultaneous dissolution of calcite and dolomite results in a Mg^{2+}/Ca^{2+} ratio of about 0.33. If the Mg^{2+}/Ca^{2+} ratio is equal to 1, this indicates that the pure dolomite dissolution is in equilibrium with the water (MAYO & LOUCKS, 1995; SZRAMEK et al., 2011).

The ratio was higher during recession periods and lower during high water conditions in all monitored spring waters (Fig. 5b). Regardless of hydrological conditions, in the groundwaters of the Dretulja, Slunjčica, Tounjčica, and mainly Zagorska Mrežnica springs, the Mg^{2+}/Ca^{2+} ratio consistently indicates the dissolution of limestone rocks. In contrast, during recession periods in the Vitunj, Gojak, Mrežnica, and Veliko Vrelo spring waters, the increase in the Mg^{2+}/Ca^{2+} ratio was significantly more pronounced. This could be attributed to a higher proportion of dolomite in their respective catchment areas or to the extended water residence time within small aquifer fractures (STROJ et al., 2020).

The correlation analysis of physico-chemical and chemical parameters, conducted on 258 samples, is presented in Table 4. A strong positive correlation was observed between the dominant Ca^{2+} cation and the dominant HCO_3^- anion, indicating a robust linear relationship. Furthermore, the SEC showed a strong positive correlation with both Ca^{2+} and HCO_3^- ions, while its correlation with Mg^{2+}, Cl^-, Na^+, and K^+ was weak to moderate. This is attributed to an interaction between the groundwater and mainly limestone. No correlation was present with the NO_3^- ion. Conversely, the NO_3^- ion displayed a strong positive correlation with SO_4^{2-} ions and moderate correlation with Cl^- and Na^+ ions, indicating the anthropogenic source of those ions. Moreover, Na^+ ions had a strong positive correlation with Cl^-, and weak correlation with K^+, NO_3^-, and SO_4^{2-}. The temperature values positively correlated with K^+ and SO_4^{2-} ions. pH did not display any conspicuous correlations with any of the studied parameters.

Despite the high quality of the spring waters in the study area, with all parameter values falling significantly below their Maximum Allowable Concentrations (MAC), there is a

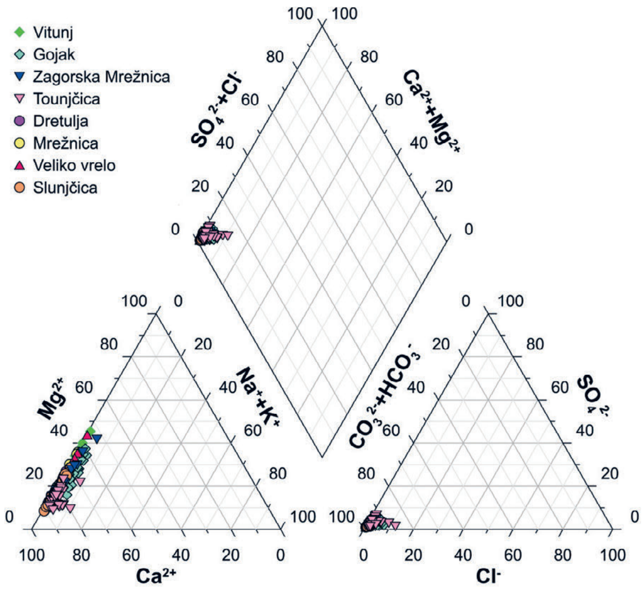


Figure 4. The Piper diagram of hydrochemical facies within the study area.

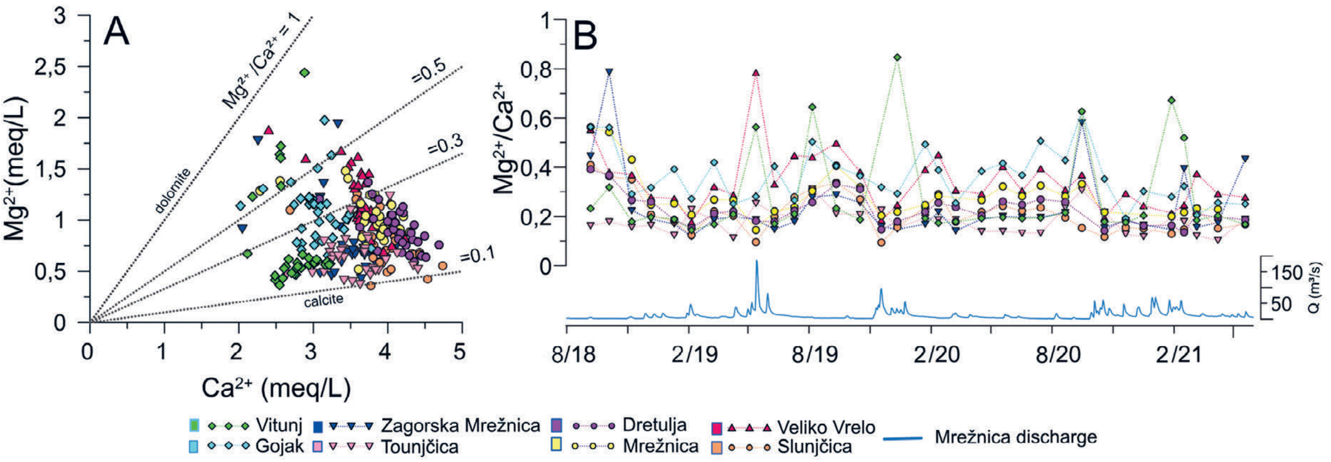


Figure 5. The Mg^{2+}/Ca^{2+} ratio in monitored springs.

Table 4. Pearson correlation analysis of physico-chemical and chemical parameters in the eight karst spring waters in the north Dinaric region of Croatia.

Variables	T	pH	EC	O_2 (mg/l)	Na^+ (mg/l)	Mg^{2+} (mg/l)	K^+ (mg/l)	Ca^{2+} (mg/l)	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	HCO_3^- (mg/l)
T	1											
pH	0.033	1										
EC	0.094	−0.245	1									
O_2 (mg/l)	−0.265	0.016	−0.042	1								
Na^+ (mg/l)	0.243*	0.061	0.234*	−0.061	1							
Mg^{2+} (mg/l)	0.193	0.009	0.279*	0.086	−0.040	1						
K^+ (mg/l)	0.330*	0.078	0.197*	−0.164	0.473*	0.053	1					
Ca^{2+} (mg/l)	−0.085	−0.282	0.687	0.012	−0.029	−0.147	0.061	1				
Cl^- (mg/l)	0.184	0.049	0.261*	−0.052	0.975	−0.050	0.458*	−0.013	1			
NO_3^- (mg/l)	0.166	0.091	−0.053	−0.432	0.313*	−0.053	0.145	−0.296	0.346*	1		
SO_4^{2-} (mg/l)	0.342*	−0.024	0.192	−0.364	0.158	0.286*	0.174	−0.171	0.166	0.688	1	
HCO_3^-(mg/l)	−0.050	−0.208	0.737	0.088	−0.080	0.262	−0.027	0.643	−0.050	−0.251	−0.005	1

*week correlation

noticeable anthropogenic impact. The natural sources of sulfates are the dissolution of gypsum and anhydrite, as well as the oxidation of sulfide minerals (FERNANDO et al., 2018; LUKAČ REBERSKI et al., 2009). However, the strong correlation with nitrate (r=0.69) and weak correlation with Cl^- (r=0.17) and K^+(r=0.17) and its spatial distribution and seasonal variation indicate human impact, such as inputs from wastewater, agriculture, or fertilizer usage. In general, it can be observed that the concentration of nitrates and sulphates is diluted in all springs during periods of higher water levels, e.g. in February and May as well as November 2019 and October 2020. (Fig. 6). The slightly higher sulfate, nitrate, and chloride concentrations are determined in the Gojak and Tounjčica spring waters, located downstream from the Ogulin urban area

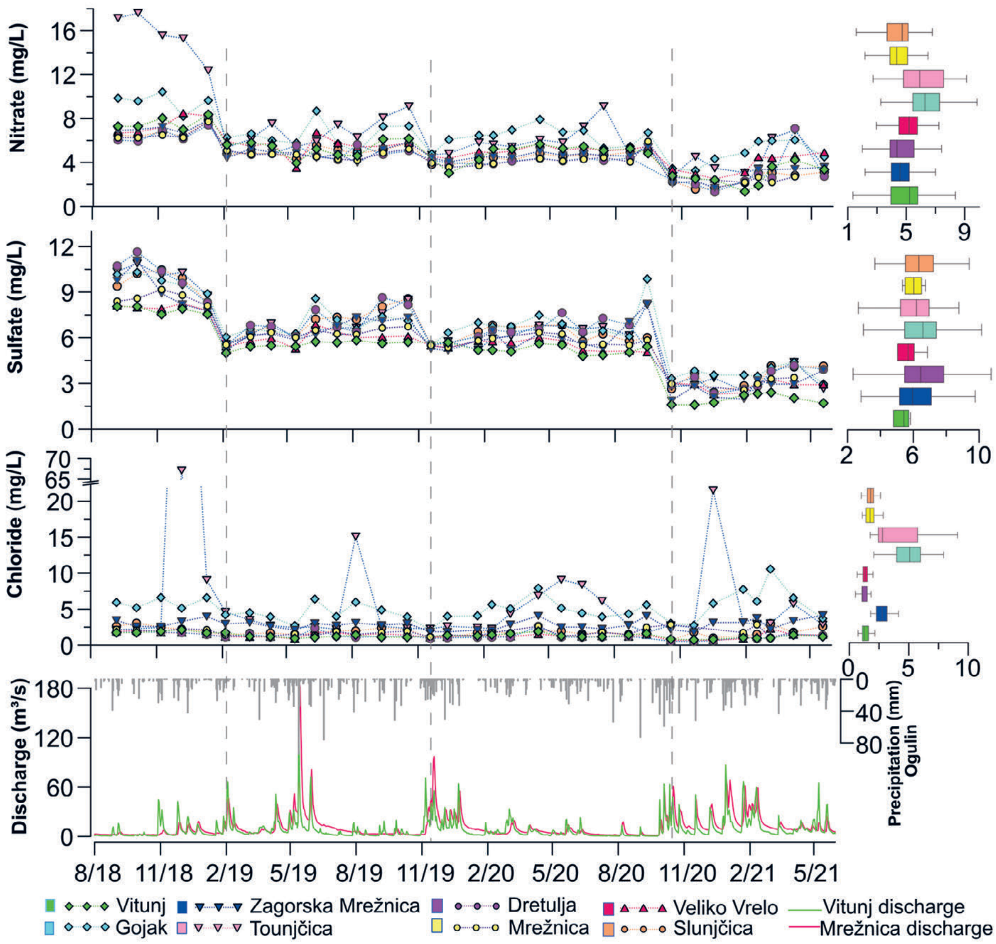


Figure 6. Time series of sulfates, nitrates and chlorides in Vitunj, Zagorska Mrežnica, Dretulja, Veliko Vrelo, Gojak, Tounjčica, Mrežnica and Slunjčica spring waters.

and Ogulin polje, where agriculture activities are prevalent. In both springs, a slight increase in the chloride content was observed during recession periods. Furthermore, three monitoring campaigns determined extremely high concentrations of Na^+ and Cl^-, as well as elevated SEC values in the Tounjčica spring water. While these occurrences in December of 2018 and 2019 could be attributed to road salting practices, it is not the case for August 2018. The data suggests that the cabbage pickling plants, located between the Sabljaki Lake dam and the southern part of the Ogulin City urban area, are within the Tounjčica catchment area, and anecdotal evidence suggests overflow from salty water tanks may end up in the underground under certain conditions. In addition, in the springs of Tounjčica, unusual movements of dissolved oxygen can be observed, which drops to very low values during the recession periods. Hydrogeological relationships do not explain this phenomenon; it is more likely due to the impact of wastewater, particularly water from a wastewater treatment plant situated within the catchment area.

5.2. Stable isotopes

The isotopic composition of spring waters displays muted seasonal fluctuations in contrast to the isotope composition of precipitation collected at the Kapela Mt. (Fig. 7c). The changes in discharge exerted a stronger influence on the $\delta^{18}O$ and δ^2H content in spring waters than the seasonal variations. The noticeable enrichment in stable isotopes is observed in two water waves, in December of 2019 and November of 2020, indicating the sampling of spring water with a noteworthy component of freshly infiltrated precipitation. Conversely, a noticeable decrease in the isotope content was observed in April 2018, likely caused by the impact of melted snow cover on the Kapela Mt. Therefore, samples collected during the hydrograph peaks should be discarded if seasonal variations are considered, as well as in the mean residence time and mean recharge altitude calculations.

The precipitation isotope data were plotted in a binary $\delta^{18}O$– δ^2H diagram to create the LMWL of Kapela Mt (Fig. 7A) based on three-year series of $\delta^{18}O$ and δ^2H values, as follows:

$$\delta^2H = 7.81\ \delta^{18}O + 13.72$$

The obtained relationship coincides well with the regional Western Mediterranean Meteoric Water Line (WMMWL) established by CELLE-JEANTON et al. (2001), suggesting that the air mass has predominant Mediterranean sources. Calculated d-excess values (Fig. 7B) of monthly precipitation mixtures in almost all samples also indicate a predominant origin from the Mediterranean air mass, (d-excess value higher than 10‰ taken as a reference as suggested by MERLIVAT & JOUZEL (1979)). Considering the precipitation amount and frequency, only two monthly precipitation samples could be predominantly originating from the Atlantic, collected in July 2019 and February 2020 (Fig. 7B).

Monthly values of $\delta^{18}O$ and δ^2H isotopic composition in spring waters are plotted in Figure 8 and compared with the Kapela Mt. LMWL. The plotted δ values for all springs construct the Groundwater Lines (GWLs).

The GWLs of the monitored springs conform to the Kapela LMWL, veryfing the meteoric origin of groundwater (Fig. 8). Based on the GWLs, we observed two distinct isotopic fingerprints of precipitation influencing the Vitunj and

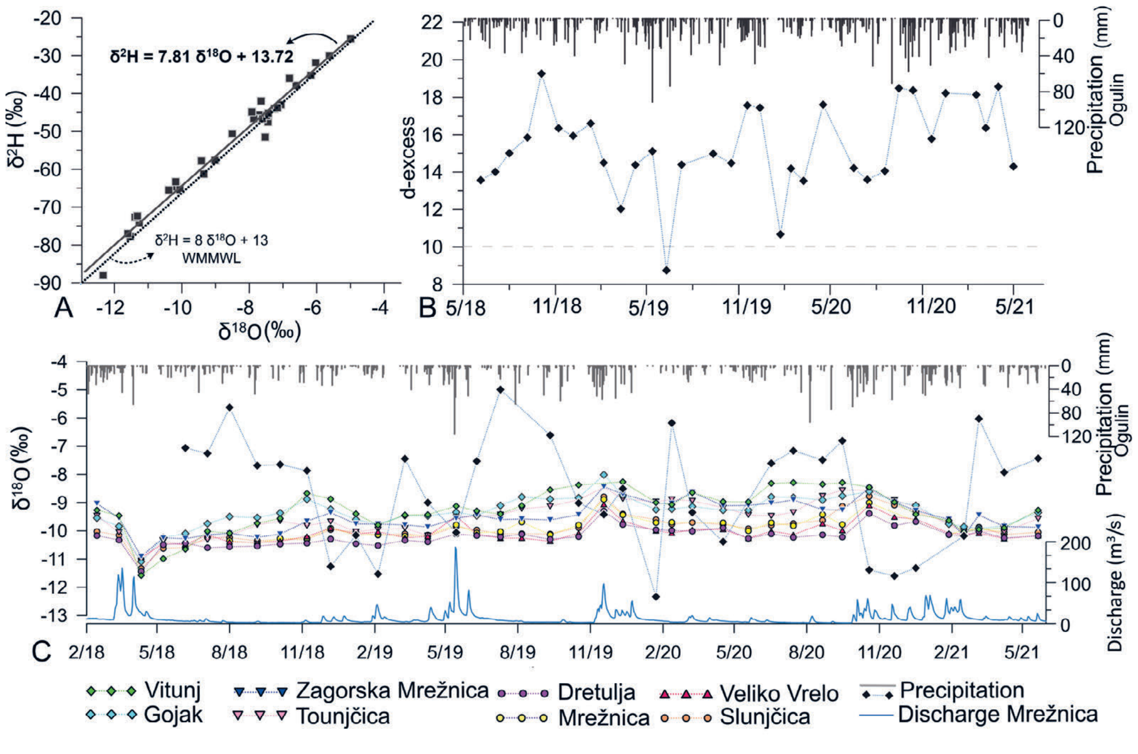


Figure 7. A. Local meteoric water line (LMWL) for the Kapela Mt vs. Western Mediterranean meteoric water line (WMMWL) (CELLE-JEANTON et al. 2001); **B.** d-excess of precipitation; **C.** Time series of the isotope composition of a $\delta^{18}O$ in monitored springs, compared with precipitation of the Ogulin station and discharge data for the Mrežnica River station.

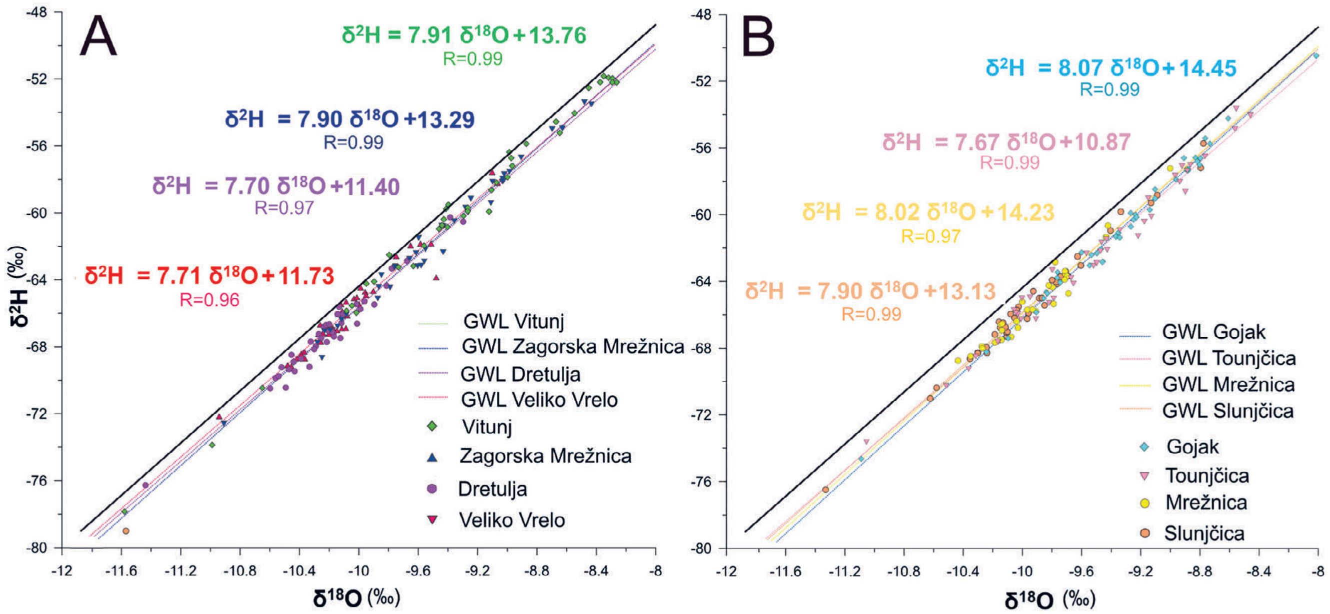


Figure 8. Correlation diagram of $\delta^{18}O$ and $\delta^{2}H$ values and Groundwater Lines for four springs in the first spring zone, situated at the foot of the Kapela Mt (A), and four springs in the second spring zone situated in the shallow karst zone (B).

Zagorska Mrežnica springs vs. the Veliko Vrelo and Dretulja springs. The Veliko Vrelo and Dretulja springs generally have more negative values of $\delta^{18}O$ and $\delta^{2}H$ than the Vitunj and Zagorska Mrežnica water springs. The GWLs of monitored springs across the Kapela Mt. coincide well with the Kapela Mt. LMWL showing the lack of precipitation evaporation before infiltration to the subsurface. During periods of elevated water levels, the Zagorska Mrežnica spring is fed from surface waters originating from flooded poljes in the hinterland (BULJAN et al., 2019). However, the impact of evaporation is insignificant due to the relatively short duration of flooding and the low temperature, which render the evaporation effect negligible (CLARK & FRITZ, 1997).

In the second spring zone, the content of stable isotopes in the spring waters follows the trend across Kapela Mt.; decreasing in heavy isotopes from north to south. In the north, the Gojak spring is generally enriched in heavy isotopes in relation to the upstream Vitunj spring, which was especially noticeable during the recession period of 2018, indicating a large proportion of water from other directions and the lower immediate hinterland. This corroborates the results of tracer testing linking the Gojak spring with sinkholes in the Ogulin Dobra watercourse (known only from unpublished reports, as the original reports are unavailable).

The slope of the Tounjčica GWL (Fig 8.) indicates a slight evaporation effect in the spring waters, probably caused by a more lengthy atmospheric influence on the spring water, which suggests that Sabljaki Lake belongs to its catchment area.

The Mrežnica and Gojak springs have interesting, similar GWLs, with the same slope and intercept. Still, the observed isotope values in Mrežnica spring waters have more negative values than those of the Gojak spring water.

In the southern part of the study area, the $\delta^{18}O$ average contents of spring waters exhibited the most negative values in Dretulja, followed by the Veliko Vrelo, Mrežnica, and Slunjčica springs. The impact of precipitation impoverishment is clearly visible in this area, since the Dretulja spring is 110 metres lower in elevation but located 11 kilometres north of the Veliko Vrelo spring.

The dynamic of stable isotopes in spring waters in the south is similar, but seasonal fluctuations depend on hydrological conditions (Fig. 7). In the summer of 2018, during the recession period, the water of Dretulja spring had a noticeably lower stable isotopic content compared to the Veliko Vrelo spring. In contrast, differences were relatively minor during the moderate water levels. This observation suggests a greater influx of water into the Veliko Vrelo spring. The Mrežnica and Slunjčica springs were enriched in heavy isotopes compared to the upstream Veliko Vrelo and Dretulja springs.

Possible interpretations of the spatial distribution and general depletion of the stable isotope content from north to south can be interpreted as follows: (1) the precipitation continental effect (KERN et al., 2020; MEZGA et al., 2014), (2) the more significant influence of the Atlantic air mass, evident in the neighbouring area of Plitvice Lake (BABINKA, 2008), (3) the potential impact of lake water evaporation on precipitation composition (HUNJAK, 2015). Although the calculated gradients for the continental effect in the Adriatic-Pannonian region are much lower than those observed in this area (KERN et al., 2020); it is essential to consider the significant altitude effect caused by the rugged terrain. In the south, the Mediterranean air masses must cross the Velebit Mt., with a peak of 1754 m a.s.l, before reaching the Kapela Mt., or ~ 60 km to the catchment areas of Dretulja and Veliko Vrelo. Conversely, in the north, the Kapela Mt. is the first significant barrier for Mediterranean air masses, affecting the catchment areas of Vitunj and Zagorska Mrežnica, with an aerial distance to the Adriatic coast of ~20 km. In addition, the d-excess value depends on humidity, sea temperature, and wind speed during primary evaporation (or geographic location of forming air masses). The three-year data set reveals

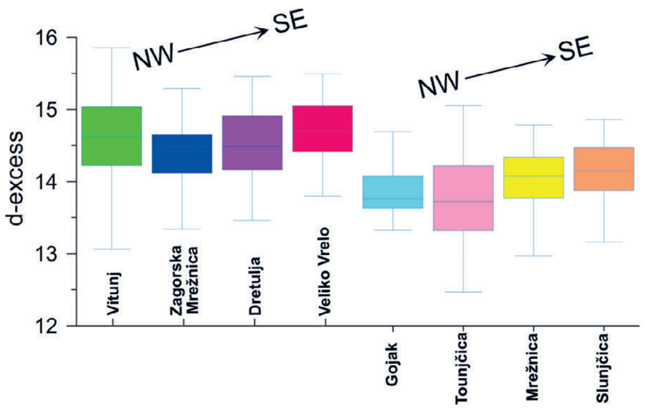


Figure 9. The box plots of the d-excess values observed in monitored spring waters.

average d-excess values ranging between 14.48 and 14.69 in aquifers within the Kapela Mt., or in the spring water of the first spring zone. Conversely, in the second spring zone, the d-excess values range from 13.72 to 14.15 (Fig. 9, Table 3). The calculated d-excess values are very similar in the observed groundwater and undoubtedly suggest the spring being fed predominantly from the Mediterranean air masses. Slightly lower values were expected in the second spring zone, as its immediate catchment area is located on the NE side of Kapela Mt. The mountain obstructs air masses with a lower d-excess coming from the north, which are emptied before crossing the mountain range. Similar d-excess values were calculated for the Plitvice Lakes area (HUNJAK, 2015), but with a different interpretation emphasizing the impact of lake water evaporation on precipitation composition.

A detailed interpretation of the origin of the precipitation origin is beyond the scope of this research. However, the authors lead towards understanding the intricate interplay between the influence of relief and continental effect on the isotopic signatures observed in the region (Fig. 10).

The stable isotopes and spring water temperature are widely recognized natural tracers for assessing groundwater's origin, retention time, and dynamics. Higher groundwater residence times result in greater homogenisation of the observed parameters (CLARK & FRITZ, 1997). To estimate groundwater mean residence times (MRT) and elevation of the recharge area, only $\delta^{18}O$ values are considered due to the strong correlation between $\delta^{18}O$ and $\delta^{2}H$ values (R >0.96) (Fig.8)

5.3. Estimation of the groundwater mean residence times

In determining MRTs, it is crucial to be careful due to established variations in spring GWLs caused by differences in the composition of stable isotopes in precipitation. However,

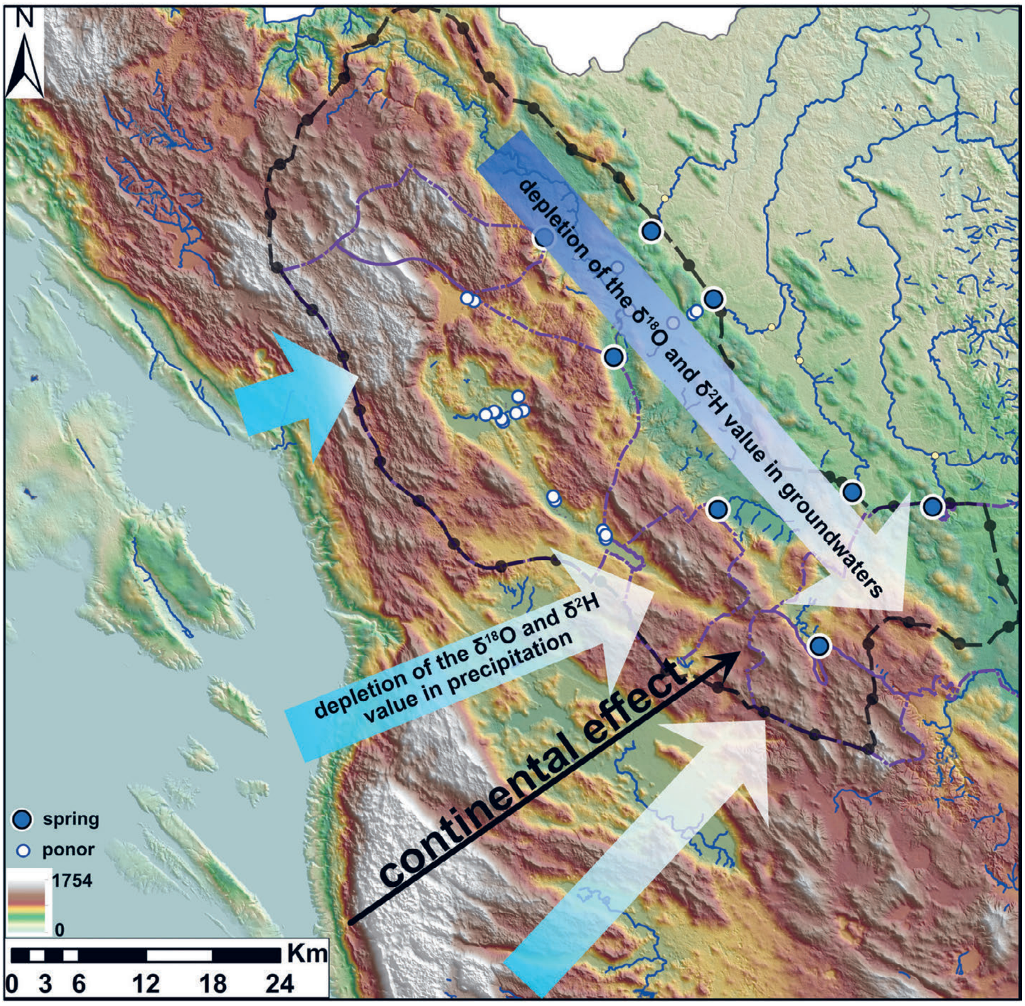


Figure 10. Interplay between relief and continental effect on depletion of the $\delta^{18}O$ and $\delta^{2}H$ composition across the north Dinaric karst region.

Table 5. Average recharge altitudes and mean residence times for the monitored springs.

Spring	Average recharge altitude (m a.s.l.)	Average temperature (3-year data set)	Mean residence times (month)	$\delta^{18}O$ Amplitude (‰)	Temperature amplitude (°C)
Vitunj	1080	7.9	16	0.81	1.8 (1.2*)
Zagorska Mrežnica	840	8.9	15	0.83	2.3
Dretulja	840	8.9	13	0.97	1.6
Veliko Vrelo	1120	7.7	12	1.19	1.7 (1.4*)
Gojak	400	11.1	10	1.25	9.2
Tounjčica	660	9.8	13	0.97	9.2
Mrežnica	440	9.9	11	1.12	7.3
Slunjčica	680	9.7	9	1.32	2.2

*the amplitude without two measurements in the highest hydrogram peaks

given that the precipitation sampler was situated in the middle of the study area, the MRTs could be calculated since the calculation does not consider absolute but relative values (Eq. 1).

The MRTs of groundwater were determined based on Equation 1 using the amplitudes of $\delta^{18}O$ isotopes in precipitation as input data and amplitudes of spring waters as output data, (without extreme values caused by a single event and assumed high proportion of freshly infiltrated water). The data in Table 5 represent the average MRT values of three calculations, one per monitored year.

The MRT for monitored springs is between 9 and 16 months (Table 5), indicating a system with significantly low storage capacity, similar to the nearby regions in the Dinaric karst: in Northern Velebit ≤ 1 year (PAAR et al., 2019); in Postojna, the established MRT in the systems was 7 months to 10 years (MANDIĆ, et al., 2013); in the catchment area of Plitvice lakes 1.3–2.9 year (MEAŠKI, 2011). The MRT for the water that drains Kapela Mt. (in the aquifers of Vitunj, Zagorska Mrežnica, Veliko Vrelo, and Dretulja springs) was ascertained over one year, and the established average retention of water in aquifers in shallow karst area is for less than one year. The temperature fluctuations are correlated with the obtained values in spring waters as a water retention indicator. The pronounced temperature fluctuation in the water of the Zagorska Mrežnica springs may be attributed to the recharge of spring with water from flooded poljes during high water conditions (Fig.3).

5.4. Estimation of the mean recharge altitude

The precipitation isotope content is linearly depleted with increasing altitude due to the water's physical characteristics, known as the altitude effect, meaning that spring waters fed from higher altitudes are more depleted in heavy isotopes (CLARK & FRITZ, 1997). In the study area, anomalies are detected by comparing the isotopic content in spring water (Fig.11B.). Based on the mean $\delta^{18}O$ value, the Tounjčica and Gojak catchment areas are situated at higher elevations compared to the upstream Zagorska Mrežnica and Vitunj springs within their respective catchment areas. The obtained data indicates the impact of evaporation from surface waters within the immediate catchment of springs and the intake from other directions in the Gojak spring.

Furthermore, geomorphology attributed to mean spring temperature data contradicts the isotope data's assertion that the Dretulja catchment area is at a higher elevation than the Veliko Vrelo watershed. (Fig. 11 A). These anomalies are in line with the interpreted continental effect (Fig. 10).

Therefore, the spring's MRA is determined based on the mean spring water temperature as a reliable indicator and compared with isotope content. The spring water temperature reflects the annual air temperature of the spring catchment area. Vertical temperature gradients in continental Croatia, including the study area, amount to 0.5°C/100 m (ZANINOVIĆ et al., 2008). Therefore, based on water temperature, the MRA of the monitored springs spreads within 710 metres from the lowest positioned catchment area of Gojak to the highest

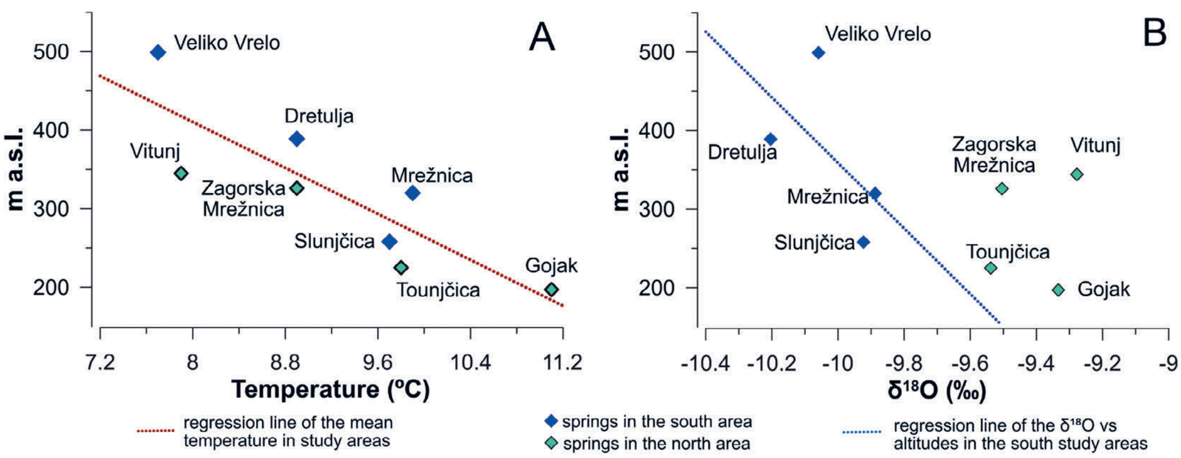


Figure 11. The mean spring water temperature vs. springs' elevation (A), the $\delta^{18}O$ value vs. springs' elevation (B).

situated at Veliko Vrelo. The lowest elevation of the Gojak catchment area corresponds to the previously mentioned northward connection. According to the morphological characteristics, the estimated mean recharge altitude of the Gojak catchment is approximately 400 m a.l.s. The springs MRA in shallow karst areas of Tounjčica, Mrežnica, and Slunjčica, extends to ~640–680 m a.s.l. In the Kapela Mt, the Zagorska Mrežnica and Dretulja springs feed from similar average altitudes ~840 m a.s.l, as well as the Vitunj and Veliko Vrelo springs ~1080–1120 m a.s.l.

6. CONCLUSION

Here, the hydrochemical and isotopic fingerprints have been used to gain insight into the highly karstified aquifers situated across Kapela Mt. These aquifers play a pivotal role in the provision of drinking water within the region. The study area comprises two spring zones: the first one is represented by four springs located at the foot of Kapela Mt., with the Vitunj spring to the north, and Zagorska Mrežnica, Dretulja, and Veliko Vrelo spings to the south. The second spring zone is represented by the Gojak, Tounjčica, Mrežnica, and Slunjčica springs.

The results of major ion analysis reveal a monolithological drainage basin. All eight springs exhibit calcium–hydrogen carbonate (Ca–HCO_3) to calcium-magnesium hydrogen carbonate (Ca–Mg–HCO_3) hydrochemical facies, indicating the dissolution and weathering of carbonates (limestone and dolomite), with the absence of evaporites and other non-carbonate rocks. From the Mg^{2+}/Ca^{2+} ratio and the Piper diagram, we observed a higher proportion of dolomite component in the Vitunj and Gojak springs which belong to the Dobra River catchment, and in the Veliko Vrelo and Mrežnica spring waters. Groundwater mineralization generally increases from the north to the south of the area, with the lowest mineralization observed in the Vitunj spring and the highest in the Dretunja and Veliko Vrelo springs. The concentrations of nitrates, sulfates, and chlorides are low, indicating the relatively unpolluted quality of the groundwater, but the human impact is still observed in the Gojak and Tounjčica springs located downstream from the urban area and Ogulin polje. Although the observed concentrations are not alarming, it is crucial to consider the aquifers' high vulnerability when planning the spatial development of the region.

The new LMWL calculated for Kapela Mt. based on a three-year dataset (June 2018 – May 2021) can be used as a background for investigating precipitation, groundwater, and surface water origin and their interrelationships. From the new LMWL we observed a predominant origin of precipitation from the Mediterranean air mass regardless of the season, in contrast to earlier studies which suggested a much more significant influence of Atlantic air masses on winter precipitation in the neighbouring areas.

The isotopic composition of spring waters indicates the meteoric origin of groundwater, rapid dynamics, and a mean residence time in the aquifer of up to 1.5 years. The seasonal fluctuations of isotopic composition are muted in spring waters due to water mixing in the subsurface. However, all calculated d-excess values in the monthly spring samples indicate a dominant reach from the Mediterranean air masses. Based on the spatial distribution of monitored springs, a significant continental (altitude) effect is detected on the isotopic composition of spring waters in the southern area, which are depleted of the heavier isotopes. The air masses from the Mediterranean have to cross Velebit Mt. and several smaller massifs to the Dretulja and Veliko Vrelo catchment areas. On that path, the heavier isotopes are broken down by the high mountain's obstruction of the air masses, resulting in depletion of the $\delta^{18}O$ and $\delta^{2}H$ in the groundwaters. Due to the significant enrichment of stable isotopes from south to north, the mean recharge altitude calculation based on stable isotopes is not applicable in the study area. The MRA was calculated based on the average spring water temperature as a reliable indicator, the MRA of the monitored springs ranges over 710 metres from the lowest positioned catchment area of Gojak to the highest situated at Veliko Vrelo.

ACKNOWLEDGEMENT

The authors express their gratitude to the Croatian Meteorological and Hydrological Service and the Croatian Electric Power Company for the provided data. This work was financially supported by Interreg Danube CAMARO-D project co-funded by the European Regional Development Fund, project B2Z30-76/19 funded by the Croatian Electric Power Company, and NONa project funded by the National Recovery and Resilience Plan 2021–2026 of the European Union – NextGenerationEU, and monitored by the Ministry of Science and Education of the Republic of Croatia. The field investigations and analysis were funded and supported by the Croatian Geological Survey, Department of Hydrogeology and Engineering Geology.

REFERENCES

AKTER, S. & AHMED, K.R. (2019) Water chemistry and water quality of a tidal river system in relation with riverbank land use pattern and regional climate in the southwest Bengal Delta of Bangladesh.– Sustain. Water Resour. Manag. 5, 1259–1279. doi: 10.1007/s40899-019-00308-3

APPELO, C.A.J & POSTMA, D. (1994): Geochemistry, groundwater and pollution.– Balkema, Rotterdam, 536 p.

BABINKA, S. (2007): Multi-Tracer Study of Karst Waters and Lake Sediments in Croatia and Bosnia and Herzegovina: Plitvice Lakes National Park and Bihać Area.– Doctoral Thesis, Universität Bonn, 168 p., Bonn.

BABINKA, S. (2008): Environmental isotopes as a tool for hydrological characterisation of karsta aquifer , groundwater protection and estimation of groundwater reserves – case study: Plitvice lakes and Bihać area.– In: Savjetovanje hidrološka mjerenja i obrada podataka, Nacionalni park Plitvička jezera, 232–255.

BAHUN, S. (1968): Geološka osnova hidrogeoloških odnosa krškog područja između Slunja i Vrbovskog (Geological basis of the hydrogeological relations in the karst area between Slunj and Vrbovsko).– Geološki vjesnik, 21, 19–82.

BIONDIĆ, B., BIONDIĆ, R. & KAPELJ, S. (2006): Karst groundwater protection in the Kupa River catchment area and sustainable development.– Environ. Geol., 2006, 49/6, 828–839. doi: 10.1007/s00254-006-0178-4

BIONDIĆ, B., BIONDIĆ, R. & MEAŠKI, H. (2010): The conceptual hydrogeological model of the Plitvice Lakes.– Geol Croat, 63/2, 195 – 206. doi: 10.4154/gc.2010.17

BIONDIĆ, R. (2013): Zones of sanitary protection of springs in the Ogulin area (in Croatian).– Unpublished, the archive of University of Zagreb, Faculty of Geotechnical Engineering.

BIONDIĆ, R., MEAŠKI, H., BIONDIĆ, B. & LOBOREC, J. (2021): Karst Aquifer Vulnerability Assessment (KAVA) Method – A Novel GIS-Based

Method for Deep Karst Aquifers.– Sustainability, 13/6, 3325, 20. doi: 10.3390/su13063325

BOČIĆ, N. (2003): Relation between Karst and Fluviokarst Relief on the Slunj Plateau (Croatia).– Acta Carsologica, 32/2, 11, 137–146. doi: 10.3986/ac.v32i2.343

BOČIĆ, N., PAHERNIK, M. & MIHEVC, A. (2015): Geomorphological significance of the palaeodrainage network on a karst plateau: The Una–Korana plateau, Dinaric karst, Croatia.– Geomorphology, 247, 55–65. doi: 10.1016/j.geomorph.2015.01.028

BOČIĆ, N., PAHERNIK, M. & MARADIN, M. (2016): Temeljna geomorfološka obilježja Karlovačke županije.– Prirodoslovlje, 16/1–2, 153–172.

BONACCI, O. & ANDRIĆ, I. (2010): Impact of an inter-basin water transfer and reservoir operation on a karst open streamflow hydrological regime: an example from the Dinaric karst (Croatia).– Hydrol Process, 24/26, 3852–3863. doi: 10.1002/hyp.7817

BRKIĆ, Ž., KUHTA, M., HUNJAK, T. & LARVA, O. (2020): Regional Isotopic Signatures of Groundwater in Croatia.– Water, 12, 1983. doi: 10.3390/w12071983

BUKOVAC, J., ŠUŠNJAR, M., POLJAK, M. & ČAKALO, M. (1983): Osnovna geološka karta 1:100 000, List Črnomelj [(*Basic Geological Map scale 1:100.000 sheet Črnomelj), L 33 – 91*].– Geološki Zavod Zagreb i Geološki Zavod Ljubljana, Savezni geološki zavod, Beograd, 63 p.

BULJAN, R., PAVLIĆ, K., TERZIĆ, J. & PERKOVIĆ, D. (2019): A Conceptual Model of Groundwater Dynamics in the Catchment Area of the Zagorska Mrežnica Spring, the Karst Massif of Kapela Mountain.– Water, 11/10. doi: 10.3390/w11101983

CLARK, M., FAN, Y., LAWRENCE, D.M., ADAM, J.C., BOLSTER, D., GOCHIS, D., HOOPER, R., KUMAR, M., LEUNG, L.R., MACKAY, D.S., MAXWELL, R.M., SHEN, C., SWENSON, S.C. & ZENG, X. (2015): Improving the representation of hydrologic processes in Earth System Models.– Water Resources Research, 51, 5929–5956. doi:10.1002/2015WR017096

CLARK, I. & FRITZ, P. (1997): Environmental Isotopes in Hydrogeology.– Lewis, 328 p.

CRAIG, H. (1961a): Isotopic variations in meteoric waters.– Science, 133, 1702 – 1703. doi: 10.1126/science.133.3465.1702

CELLE-JEANTON. H., TRAVI. Y. & BLAVOUX. B. (2001): Isotopic typology of the precipitation in the Western Mediterranean region at three different time scales.– Geophysical Research Letters, 28, 1215–1218. doi:10.1029/2000GL012407

CROATIAN PARLIAMENT (2008): Water Management Strategy.– Official Gazette of Croatia, Zagreb, 91 p.

ČANJEVAC, I.,MARTINIĆ, I., RADIŠIĆ, M., RUBINIĆ, J. & MEAŠKI, H. (2023): Hydrology, Hydrogeology and Hydromorphology of the Plitvice Lakes Area, Plitvice Lakes.– In: MILIŠA, M. & IVKOVIĆ, M. (eds): Plitvice Lakes. Springer Water. Springer, Cham., 17–64. doi: 10.1007/978-3-031-20378-7_2

DANSGAARD, W. (1964): Stable isotopes in precipitation.– Tellus, 16, 436–468. doi: 10.1111/j.2153-3490.1964.tb00181.x

DOMENICO, P.A. & SCHWARTZ. F.W. (1990): Physical and Chemical Hydrogeology.– John Willey and Sons, New York, 824 p.

DRAGIČEVIĆ, I. & VELIĆ, I. (2002): The Northeastern Margin of the Adriatic Carbonate Platform.– Geologia Croatica, 55/2, 185–232.

FERNANDO. W.A.M., ILANKOON. I., SYED. T.H. & YELLISHETTY. M. (2018): Challenges and opportunities in the removal of sulphate ions in contaminated mine water: A review.– Miner. Eng., 117, 74–90. doi: 10.1016/j.mineng.2017.12.004

FIKET, Ž., FURDEK TURK M., IVANIĆ, M. & KNIEWALD , G. (2021): Non-traditional stable isotope signatures in geological matrices as a tool for interpreting environmental changes – a review. – Geol. Croat., 74/2, 177–187. doi: 10.4154/gc.2021.12

FRANČIŠKOVIĆ-BILINSKI, S., CUCULIĆ, V., BILINSKI, H., HÄUSLER, H. & STADLER, P. (2013): Geochemical and stable isotopic variability within two rivers rising under the same mountain, but belonging to two distant watersheds.– Chemie Der Erde, Geochemistry, 73/3, 293–308. doi: 10.1016/j.chemer.2013.02.004

FREEDMAN, D., PISANI, R., & PURVES, R. (2007): Statistics (international student edition).– WW Norton &amp Company, New York.

FORD, D. & WILLIAMS, P. (2007): Karst Hydrogeology, in: Karst Hydrogeology and Geomorphology.– John Wiley & Sons Ltd, 103–144. doi: 10.1002/9781118684986.ch5

GIBBS R.J. (1970): Mechanisms controlling world water chemistry.– Science, 170, 1088–1090. doi: 10.1126/science.170.3962.1088

GLADOVIĆ, D., PARLOV, J., PEROKOVIĆ, D., NAKIĆ, Z. & KOVAČ, Z. (2023): The role of slope inclination, doline density and water budget analysis in delineation of complex karst catchment area of Slunjčica River (Croatia).– Geofizika, 40. doi: 10.15233/gfz.2023.40.1

HUNJAK, T. (2015): Spatial Distribution of Oxygen and Hydrogen Stable Isotopes from Precipitation in Croatia.– Unpubl. PhD Thesis, University of Zagreb, 75 p.

HUNJAK, T., LUTZ, H. O. & ROLLER-LUTZ, Z. (2013): Stable isotope composition of the meteoric precipitation in Croatia.– Isot. Environ. Healt S., 49/3, 336–345. doi: 10.1080/10256016.2013.816697

KERN, Z., HATVANI, I.G., CZUPPON, G., FÓRIZS, I., ERDÉLYI, D., KANDUČ, T., PALCSU, L. & VREČA, P. (2020): Isotopic 'Altitude' and 'Continental' Effects in Modern Precipitation across the Adriatic–Pannonian Region.– Water, 12, 1797. doi: 10.3390/w12061797

KOROLIJA, B., ŽIVALJEVIĆ, T. & ŠIMUNIĆ, A. (1980): Osnovna geološka karta SFRJ 1: 100.000: List Slunj [*Basic Geological Map of SFRY: Sheet Slunj*].– Savezni geološki zavod, Beograd

KORBAR, T. (2009): Orogenic evolution of the External Dinarides in the NE Adriatic region: A model constrained by tectonostratigraphy of Upper Cretaceous to Paleogene carbonates.– Earth-Sci. Rev., 96, 296–312. doi: 10.1016/j.earscirev.2009.07.004

KOVAČEVIĆ, A. (2005): Hydrogeological features of Karlovac County.– Unpubl. Master Thesis, Faculty of Mining, Geology and Petroleum Engineering, Department of Geology and Geological Engineering, University of Zagreb, Croatia, 126 p.

KRALIK, M. (2015): How to Estimate Mean Residence Times of Groundwater.– Proced Earth Plan. Sc., 13, 301–306. doi: 10.1016/j.proeps.2015.07.070

LUKAČ REBERSKI, J., KAPELJ, S. & TERZIĆ J. (2009): An estimation of groundwater type and origin of the complex karst catchment using hydrological and hydrogeochemical parameters: A case study of the Gacka river springs.– Geologia Croatica, 62/3, 157–178. doi: 10.4154/GC.2009.14

LUKAČ REBERSKI, J., MARKOVIĆ, T. & NAKIĆ Z. (2013): Definition of the river Gacka springs subcatchment areas on the basis of hydrogeological parameters.– Geologia Croatica, 66/2, 39–53. doi: 10.4154/BC.20I3.04

MAŁOSZEWSKI, P., RAUERT, W., STICHLER, W., HERRMANN, A. (1983): Application of flow models in an alpine catchment area using tritium and deuterium data.– Journal of Hydrology, 66, 1–4, 319–330. doi: 10.1016/0022-1694(83)90193-2

MANCE, D., RADIŠIĆ, M., LENAC, D. & RUBINIĆ, J. (2022): Hydrological Behavior of Karst Systems Identified by Statistical Analyses of Stable Isotope Monitoring Results.– Hydrology, 9, 82. doi: 10.3390/hydrology9050082

MANDIĆ, M., MIHEVC, A., LEIS, A., LOJEN, S. & KRAJCAR BRONIC, I. (2013): Mean residence time of drip water in Postojna cave, Slovenia.- In: 3rd International Conference "Waters in Sensitive & Protected Areas". Zagreb, Croatia, 171–174.

MANDEL., S. & SHIFTAN., Z.L. (1981): Groundwater Resources: Investigation and Development.– Academic Press, New York, 269 p.

MANDIĆ, M., BOJIĆ, D., ROLLER LUTZ, Z., LUTZ, H. & BRONIĆ KRAJCAR, I. (2008): Note on the spring region of Gacka River (Croatia).– Isot. Environ. Health Stud., 44, 201–208.

MARKOVIĆ, T.,SLADOVIĆ, Ž., DOMITROVIĆ, D., KARLOVIĆ, I. & Larva, O. (2022): Current utilization and hydrochemical characteristics of geothermal aquifers in the Bjelovar sub-depression.– Geol. Croat., 75/2, 223-233. doi: 10.4154/gc.2022.21

MAYO A.L. & LOUCKS M.D. (1995): Solute and isotopic geochemistry and ground water flow in the central Wasatch Range, Utah.– Journal of Hydrology, 172/1, 31–59. doi: 10.1016/0022-1694(95)02748-E

McGUIRE, K. & McDONNELL, J. (2006): A Review and Evaluation of Catchment Transit Time Modeling.– Journal of Hydrology, 330, doi: 10.1016/j.jhydrol.2006.04.020

MEZGA, K., URBANC, J. & CERAR, S. (2014): The isotope altitude effect reflected in groundwater: a case study from Slovenia.– Isot. Environ. Healt S., 50/1, 33–51, doi: 10.1080/10256016.2013.826213

MEAŠKI, H. (2011): Model of the karst water resources protection on the example of the Plitvice Lakes national park [in Croatian].– Unpubl. PhD Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, 211 p.

MEAŠKI, H., MARCIUŠ, M. & PTIČEK SIROČIĆ, A. (2016): Hidrogeološke značajke vodotoka Plitvica na području Plitvičkih jezera, Hrvatska.– Environmental engineering = Inženjerstvo okoliša, 3, 21–32.

MERLIVAT, L. & JOUZEL, J. (1979): Global climatic interpretation of the deuterium-oxygen 18 relationship for precipitation.– J. Geophys. Res, 84, 5029 – 5033

MEYBECK, M. (1987): Global chemical weathering of surficial rocks estimated from river dissolved loads.– Am. J. Sci., 287, 401–428. doi: 10.2475/ajs.287.5.401

MICHELSEN, N., GELDERN, V.R., ROßMANN, Y., BAUER, I., SCHULZ, S., BARTH, J.A.C. & SCHÜTH, C.(2018): Comparison of precipitation collectors used in isotope hydrology.– Chemical Geology, 488, 171–179. doi:10.1016/j.chemgeo.2018.04.032

MILANOVIĆ, S., VASIĆ, L., PETROVIĆ, B., DAŠIĆ, T., MARINOVIĆ, V. & VOJNOVIĆ, P. (2023): The Impact on Karst Aquifer Regimes Induced by a Surface Reservoir in Karst through Multiparametric Analyses (Reservoir Bileća – Herzegovina).– Sustainability, 15, 11968. https://doi.org/10.3390/su151511968

MOHAMMED, N., CELLE-JEANTON, H., HUNEAU F., LE COUSTUMER, P., LAVASTRE, V., BERTRAND, G., CHARRIER, G. & CLAUZET, M.L. (2014): Isotopic and geochemical identification of main groundwater supply sources to an alluvial aquifer, the Allier River valley (France).– J Hydrol., 508, 181–196. doi: 10.1016/j.jhydrol.2013.10.051

PAAR, D., MANCE, D., STROJ, A. & PAVIĆ, M. (2019): Northern Velebit (Croatia) karst hydrological system: Results of a preliminary 2H and 18O stable isotope study.– Geol. Croat., 72/3, 205–213. doi: 10.4154/gc.2019.15

PALMER, A.N. (2010): Understanding the Hydrology of Karst.– Geol. Croat., 63/2, 143–148. doi: 10.4154/gc.2010.11

PAVLIĆ, K. & PARLOV, J. (2019): Crosscorrelation and Cross-Spectral Analysis of the Hydrographs in the Northern Part of the Dinaric Karst of Croatia.– Geosciences; 9/2, 86 p. doi: 10.3390/geosciences9020086

PIPER, A.M. (1944): A graphic procedure in the geochemical interpretation of water-analyses.– Trans. Am. Geophys. Union, 25, 914–928. doi: 10.1029/TR025i006p00914

RODGERS, P., SOULSBY, C., WALDRON, S. & TETZLAF, D. (2005): Using stable isotope tracers to assess hydrological flow paths, residence times and landscape influences in a nested mesoscale catchment.– Hydrology and Earth System Sciences, 9, 139–155. doi:10.5194/hess-9-139-2005

SAVIĆ, D. & DOZET, S. (1983): Osnovna geološka karta SFRJ 1: 100.000: List Delnice [(*Basic Geological Map of SFRY, sheet Delnice) L 33–90*]. – Geološki zavod; OOUR za geologiju i paleontologiju, Zagreb; Geološki zavod, Ljubljana (1970.–1983.); Savezni geološki institut, Beograd.

SCHMID, S.M., BERNOULLI, D., FÜGENSCHUH, B., MATENCO, L., SCHEFER, S., SCHUSTER, R., TISCHLER, M. & USTASZEWSKI, K. (2008): The Alpine-Carpathian-Dinaridic orogenic system: Correlation and evolution of tectonic units.– Swiss J. Geosci., 101, 139–183. doi: 10.1007/s00015-008-1247-3

STEVANOVIC, Z., KREŠIĆ, N., & KUKURIC, N. (2016): Karst without Boundaries (1st ed.).– CRC Press. doi: 10.1201/b21380

STROJ, A., BRIŠKI, M., LUKAČ REBERSKI, J. & FRANGEN, T. (2023): Regional Analysis of Tracer Tests in the Karstic Basin of the Gacka River (Croatian Dinaric Karst).– Hydrology, 10, 106. doi: 10.3390/hydrology10050106

STROJ, A., BRIŠKI, M. & OŠTRIĆ, M. (2020): Study of Groundwater Flow Properties in a Karst System by Coupled Analysis of Diverse Environmental Tracers and Discharge Dynamics.– Water, 12/9, 2442. doi: 10.3390/w12092442

STROJ, A. & PAAR, D. (2019): Water and air dynamics within a deep vadose zone of a karst massif: Observations from the Lukina jama–Trojama cave system (−1,431 m) in Dinaric karst (Croatia).– Hydrol Process, 33, 551–561. doi: 10.1002/hyp.13342

SZRAMEK, K., WALTER, L., KANDUČ, T. & OGRINC, N. (2011): Dolomite Versus Calcite Weathering in Hydrogeochemically Diverse Watersheds Established on Bedded Carbonates (Sava and Soča Rivers, Slovenia).– Aquatic Geochemistry, 17, 357–396. doi: 10.1007/s10498-011-9125-4

ŠUŠNJAR, M., BUKOVAC, J., NIKLER, L., CRNOLATAC, I., MILAN., A., ŠIKIĆ, D., GRIMANI, I., VULIĆ, Ž. & BLAŠKOVIĆ, I. (1970): Osnovna geološka karta SFRJ 1:100.000: list Crikvenica [*Basic Geological Map of SFRY, sheet Crikvenica, L 33–102*].– Inst. geol. istraž. Zagreb, 1970., Sav. geol. zavod Beograd.

TARI, V. (2002): Evolution of the northern and western Dinarides: a tectonostratigraphic approach.– Stephan Mueller Spec. Publ. 1, Eur. Geosci. Union, 1, 223–236.

TERZIĆ J., STROJ, A. & FRANGEN, T. (2012): Hydrogeological investigation of karst system properties by common use of diverse methods: a case study of Lička Jesenica springs in Dinaric karst of Croatia.– Hydrological Processes, 26/21, 3302–3311. doi: 10.1002/hyp.9194

TERZIĆ, J., MARKOVIĆ, T. & LUKAČ REBERSKI, J. (2014): Hydrogeological properties of a complex Dinaric karst catchment: Miljacka Spring case study.– Environ. Earth., Sci, 72, 1129–1142. doi: 10.1007/s12665-013-3031-6

TORKAR, A. & BRENČIČ, M. (2015): Spatio-temporal distribution of discharges in the Radovna River valley at low water conditions.– Geologija, 58/1, 47–55. doi: 10.5474/geologija.2015.003

TORRESAN, F., FABBRI, P., PICCININI, L., LIBERA, N. D., POLA, M. & ZAMPIERI, D. (2020): Defining the hydrogeological behavior of karst springs through an integrated analysis: a case study in the Berici Mountains area (Vicenza, NE Italy).– Hydrogeol. J., 28, 1229–1247. doi: 10.1007/s10040-020-02122-0

UNKNOWN AUTHOR (1948): Basic project of Dobra-Mrežnica, Hydrological substrata; trecer tests, Engineering Project Institute, Zagreb, (In Croatian). Osnovni projekt Dobra-Mrežnica, Hidrološke podloge; bojadisanje ponornica, Inženjerski projektni zavod, Zagreb.

VASIĆ, L., MILANOVIĆ, S., STEVANOVIĆ, Z. & PALCSU, L. (2020): Definition of groundwater genesis and circulation conditions of the complex hydrogeological karst system Mlava–Belosavac–Belosavac-2 (eastern Serbia).– Carbonate Evaporite, 35, 16 p. doi: 10.1007/s13146-020-00550-3

VELIĆ, I., BAHUN, S., SOKAČ, B. & GALOVIĆ, I. (1974): Osnovna geološka karta SFRJ, list Otočac 1:100 000, L 33–115; [*Basic Geological Map SFRJ, sheet Otočac 1:100 000*].– Institute of geology Zagreb, Federal institute of geology, Beograd.

VELIĆ, I. & SOKAČ, B. (1982): Basic Geological Map of the Republic of Croatia 1:100.000; Sheet Ogulin.– Croatian Geological Survey, Zagreb, Croatia.

VELIĆ, I. (2007): Stratigraphy and Palaeobiogeography of Mesozoic Benthic Foraminifera of the Karst Dinarides (SE Europe) – PART 1..– Geol. Croat., 60/1, 1–60.

VLAHOVIĆ, I., TIŠLJAR, J., VELIĆ, I. & MATIČEC, D (2005): Evolution of the Adriatic Carbonate Platform: Palaeogeography. main events and depositional dynamics.– Palaeogeography, Paleoclimatology, Palaeoecology, 220, 333–360. doi: 10.1016/j.palaeo.2005.01.011

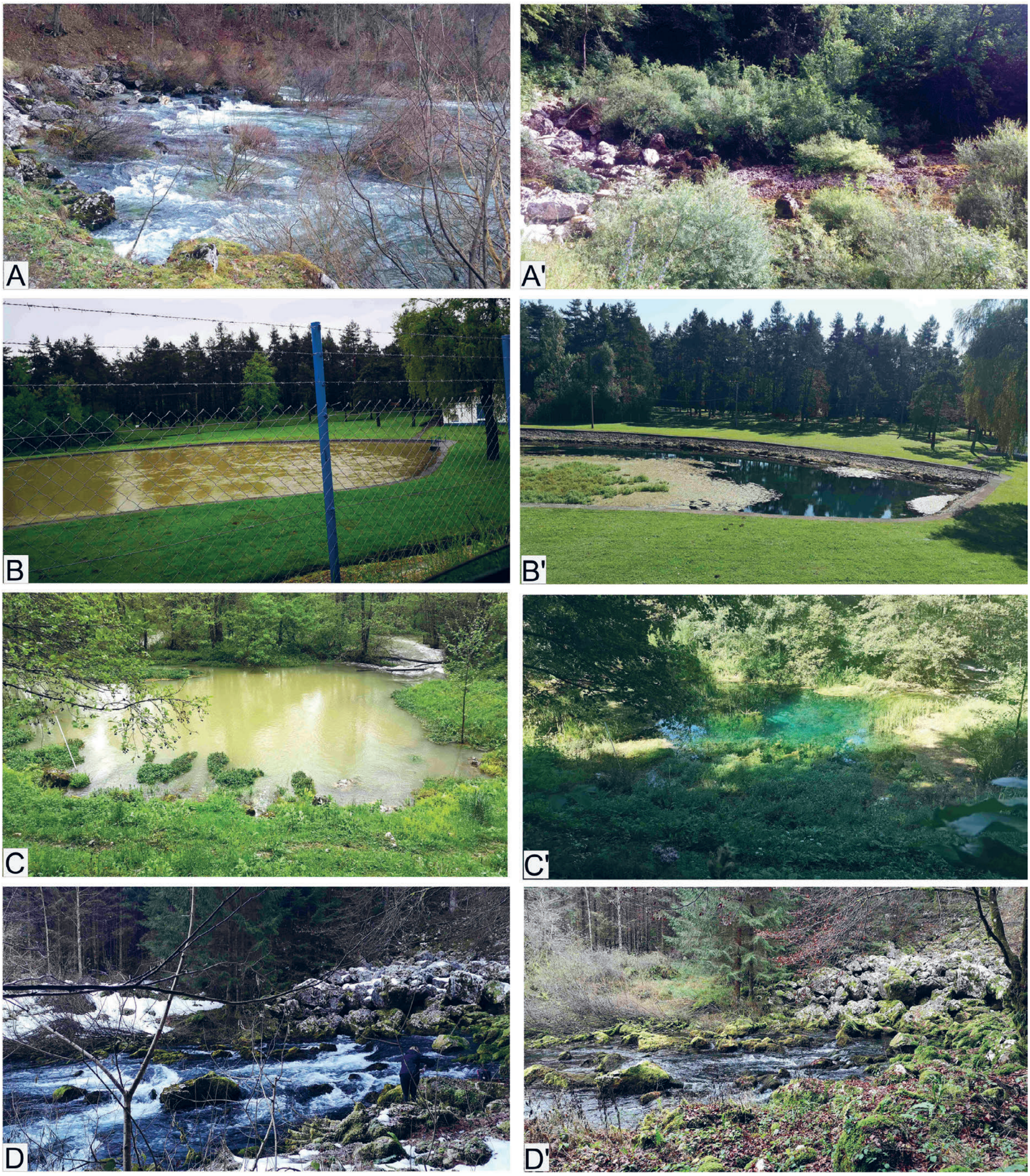
VREČA, P., BRENČIČ, M. & LEIS, A. (2007): Comparison of monthly and daily isotopic composition of precipitation in the coastal area of Slovenia.– Isot. Environ. Health Stud., 43, 307–321. doi: 10.1080/10256010701702739

ZANINOVIĆ, K., SRNEC, L. & PERČEC-TADIĆ, M. (2004): Digitalna godišnja temperaturna karta Hrvatske [*Digital map of the air temperature in Croatia*].– Hrvatski meteorološki časopis, 39, 51–58.

ZANINOVIĆ, K., GAJIĆ-CAPKA, M., PERČEC TADIĆ, M. & VUČETIĆ, M. (2008): Klimatski Atlas Hrvatske = Climate Atlas of Croatia 1961–1990. –Državni hidrometeorološki zavod: Zagreb.

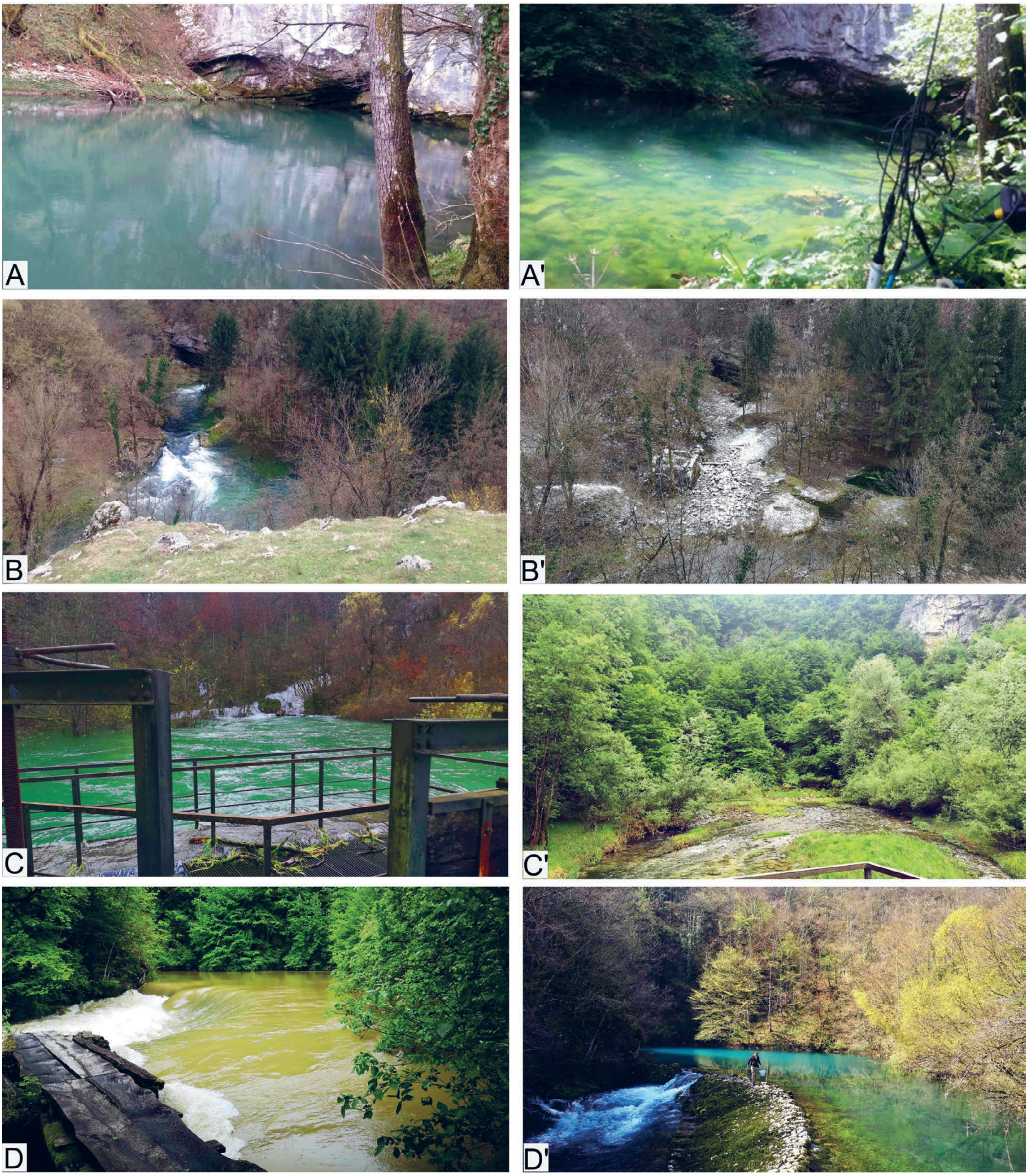
Supplement 1. – The karst springs at the foot of the Kapela mountain

The Vitunj spring during high (A) and low water conditions (A'); The Zagorska Mrežnica spring during high (B) and low water conditions (B'); The Dretulja spring during high (C) and low water conditions (C'); The Veliko Vrelo spring during high (D) and low water conditions (D')



Supplement 2. – The main karst springs of the Kordun rivers

The Gojak spring during high (A) and low water conditions (A'); The Tounjčica spring during high (B) and low water conditions (B'); The Mrežnica spring during high (C) and low water conditions (C'); The Slunjčica spring during high (D) and low water conditions (D')



3. DISCUSSION

The main goal of this research was to define the hydrogeological relationships in the northern part of the Croatian Dinaric karst, an area that has not previously been examined on a regional scale. Consequently, the following objectives were established: (1) to characterise the study area using hydrochemical and isotopic research, including defining groundwater retention times, age, and mean elevation of recharge area; (2) to identify the baseline state of system dynamics as a foundation for monitoring new hydrotechnical interventions in the study area; (3) to improve the methodology for investigating regional karst systems, with an emphasis on defining the transition zone between deep karst and shallow or fluviokarst, which significantly differs from other Dinaric karst areas; (4) to develop a conceptual model of springs sharing catchment areas based on dynamics and hydrochemical properties.

An interdisciplinary approach was employed to investigate four hypotheses using different hydrogeological methods to accomplish the research goals. Spatial data analysis was conducted across the karst part of the Kupa River catchment area to identify regions under the highest pressure. Based on the obtained data, the most questions arose for the central part of the area, which feeds the main springs of the Dobra, Mrežnica, and Slunjčica rivers, and encompasses two springing levels. An applied hydrogeological investigation was conducted across Kapela Mtn. and the downstream karst poljes, including the determination of studied aquifers dynamics through time series analysis and content of stable isotopes of oxygen and deuterium, as well as determining the hydrochemical properties of the groundwater.

Hypothesis #1: Land use and hydrogeological properties of catchment directly influence the quality of karst groundwater.

In northern Dinaric karst in Croatia, the aquifers are developed primarily in Mesozoic carbon rocks. Rainwater, which is naturally slightly acidic, interacts with the rocks and, in the study area, dissolves mainly limestone and dolomite. The physicochemical and chemical parameters were determined on 258 spring water samples in eight springs across the study area monthly from August 2018 to June 2021. The dominant cation in monitored spring waters indicated Ca^{2+} as a dominant cation in monitored spring waters, followed by Mg^{2+}, Na^{+}, and K^{+}. The average contribution of Ca^{2+} to the cation budget is 84 – 87% in all spring water. Groundwater exhibited the Ca–Mg–HCO_3 hydrogeochemical facies, with no discernible interaction between groundwater and non-carbonate rocks such as evaporites. The spring waters from Tounjčica, Veliko Vrelo, Slunjčica, and Dretulja displayed a more uniform and clearly defined Ca–HCO_3 facies, while the samples from Zagorska Mrežnica, Vitunj, Gojak, and Mrežnica showed mixed facies ranging from Ca–HCO_3 to Ca–Mg–HCO_3 (Boljat, 2024b, P3). The mineralization of spring waters was calculated from a chemical analysis of major anions and cations (Figure 3A), and Total Dissolved Solids (TDS) generally increases towards the southeast of the study area (Figure 3B).

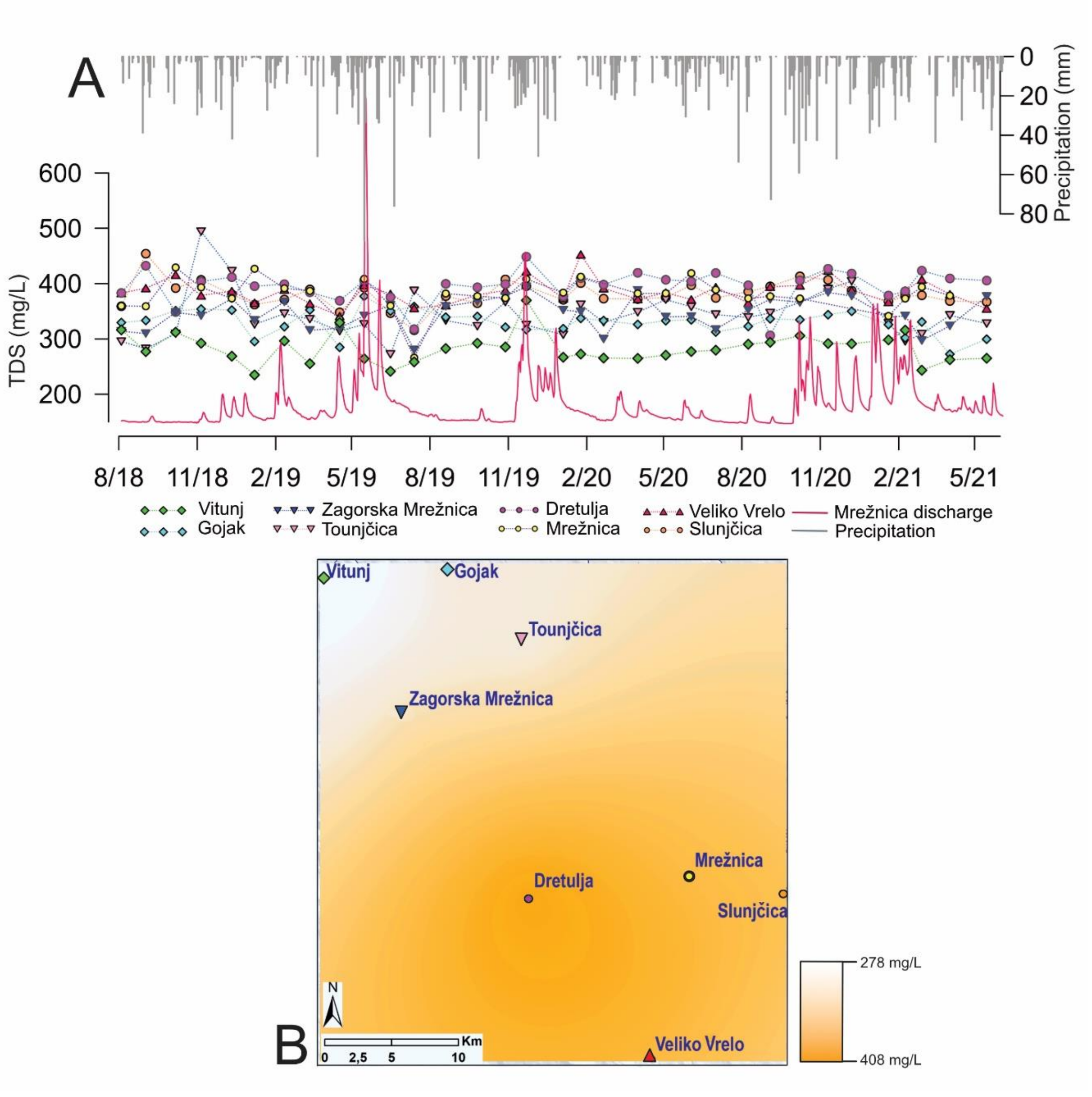


Figure 3. (A) TDS compared with daily discharge and precipitation data (B) Spatial distribution of TDS in the monitored spring in northern Dinaric karst in Croatia

The waters in the study area are rich in oxygen due to rapid movement through systems of cavities and channels, which also contributes to the high water quality. The oxygen concentration in the monitored spring waters ranges between 7.73 to 14.63 mg/l

The activities and practices within a catchment area - such as agriculture, urban development, forest management, and industrial activities - play a significant role in determining groundwater quality. In karstic areas of the Kupa River catchment, the natural groundwater vulnerability is substantial due to aquifers' development in highly permeable Mesozoic carbonate rocks. Consequently, rapid infiltration and movement of water through fractures and conduits can quickly transport surface contaminants to the groundwater and springs used in drinking water supply. Beyond the direct use of land and localised land covers, it is important to highlight water transfer from one catchment area to another. This can facilitate the increase of pollutant concentrations in water ecosystems that are receiving water from distinct catchments.

The water quality is generally very good due to the high percentage of forest and natural areas combined with a sparse population and low industrial development. The spatial data analysis identified the highest pressure on groundwater quality downstream of the Ogulin, Plaški, and Lička Jasenica poljes, which was confirmed by slight increases of nitrate, sulfate, and chloride concentrations in the Gojak, Tounjčica, Dretulja, and Slunjčica springs water (Boljat, 2024b, P3). The positive correlation observed between ions indicates the anthropogenic sources. The time series analyses indicated a well-developed karst system without apparent diffuse flow in the shallow karst zone (Boljat, 2024a, P2), meaning a lack of natural contaminant attenuation and reduced water retention in the aquifer. Despite all parameter values falling significantly below their Maximum Allowable Concentrations, MAC (EU Directive 2020/2184), it is important to notice that the networks of fractures and large conduits in the karst system enable the rapid and unfiltered flow of water, increasing the susceptibility of the groundwater to rapid contamination.

An example of pollution from the point source is the Zdiška Spring in Turković Ogulinski, located at the foot of the Kapela Mtn., about 3 km SE from Vitunj Spring. Based on data from the Ogulin waterworks, this spring is frequently excluded from the water supply network due to the presence of substances exceeding the MAC or unsatisfactory microbiological quality. The catchment area is sparsely populated, with only animal husbandry polluters, but obviously with a direct groundwater connection.

The evidence of possible significant contamination was determined in the Tounjčica Spring waters. In three monitoring campaigns, high concentrations of harmless dissolved halite were observed. The halite source is most likely overflowing from salty water tanks in the production facility of sour cabbage located in Ogulin polje. It should be noted that spring monitoring was conducted monthly, and due to the very high karstification, the contaminated water pulse often goes undetected. The spring waters of Tounjčica also have unusually low oxygen concentrations during the low waters. The interpretation of this phenomenon cannot be explained by applied hydrogeological methods. Still, we can speculate that the cause is natural biological processes in the aquifer or the influence of wastewater, particularly water from a wastewater treatment plant (probably) situated within its catchment area. The spring was not included in the observation network in the tracer test done at the sinkhole, which is presently used as an outlet for treated waters from the wastewater treatment plant (**Ivičić, 1994**). This is illogical since the tracer was detected at the nearby springs Bistrac and Kukača, and Tounjčica is situated between them. The wastewater treatment plant Ogulin has been in operation for 25 years, and it is one of Croatia's first wastewater treatment plants. It consists of open basins and was designed to handle 100-year rainfall events and uses advanced technology of ultrafiltration as a final step of wastewater treatment. However, we are increasingly experiencing frequent extreme rain events, resulting in wastewater overflow before complete treatment and the direct recharge of untreated waters into the aquifer.

In the study area, water use for hydropower indirectly impacts water quality, especially in the case of the Mrežnica River catchment, where water is redirected to the Dobra River catchment area. **Bonacci and Andrić (2010**) calculated that the average annual discharge of Mrežnica River's west tributaries dropped to 11.9 m^3/s after the construction of HPP Gojak's. The consequent reduction in volume increases the concentration of pollutants, changes the biological conditions, slows the flow, and thus raises the water temperature. While the current situation does not pose an immediate concern, the potential for a significant decline in water quality could arise with the climate extremes, leading to prolonged periods of drought coupled with the ongoing industrial development in the region.

The negative impact on land use is noticed in the Gojačka Dobra River after the construction of the HPP Lešće in 2010, impacting its hydrology, ecology, and geomorphology. The dam's construction has resulted in the saturation subsurface upstream, while downstream, the 12h - operation regime changes river morphology and downstream habitats. The new hydrogeological condition has not been investigated, but 12 kilometres of river retention certainly changed the recharge area and moved the water bodies' watersheds. In the last decade, additional changes in the regime of the neighbouring Mrežnica River have been observed; however, without field research, these cannot be linked to either changes in the rainfall regime or the construction of the accumulation. Inadequate water management practices may have adverse consequences in the eastern portion of the study area.

The municipalities of Rakovica and Plitvice Lakes are currently supplied with surface water from Kozjak Lake (one of the Plitvice Lakes), which is unsatisfactory and has a negative impact on the Plitvice Lakes system, which is under UNESCO protection. The issue of water supply is nearing resolution, with an agreed-upon water intake at the mouth of two streams forming the Lička Jesenica River. This project aims to connect several settlements, which currently lack a secure water supply, to the water distribution network. Current estimates for water supply needs are a maximum pumping capacity of 93 l/s (**Bakula et al., 2023**), which should not have a hazardous impact on the water system. However, in the future, due to the significant tourism growth and development, the demand for drinking water may substantially increase, especially during the summer recession period, at the height of the tourist season. It is important to consider that this inter-basin transfer could have negative consequences if the biological minimum is not maintained.

Across the entire area, a negative practice of forest clear-cutting has been observed (Figure 4). The areas affected by such forest "regeneration methods "are alarmingly extensive and frequent in Gorski Kotar and Kordun. Clear-cutting removes the vegetation that stabilises soil and increases erosion. Heavy rainfalls lead to extreme soil erosion and significant turbidity in springs and surface waters. Additionally, without the tree canopy and root systems to intercept and absorb rainfall, clear-cut areas experience increased surface runoff. This runoff can rapidly carry pollutants and sediments into aquifers and degrade water quality. Forests act as natural filters, trapping and absorbing pollutants before they reach water sources. Removing trees and vegetation reduces the land's ability to filter out contaminants, leading to increased concentrations of pollutants such as pesticides, fertilisers, and other chemicals in drinking water resources. This method usually creates conditions conducive to invading non-native or aggressive species. These invasive species can outcompete native plants and hinder the natural regeneration of the forest. Thus, specifically in the area shown in Figure 4, beech trees are predominantly replaced by shrubs, conifers, or hornbeam trees.

Figure 4. The clear-cutting in the Kordun (photo by Zoran Pavlović, Croatian waters)

Hypothesis #2: Springs occurring in the study area can be grouped according to dynamics and hydrochemical properties in common sub-catchments.

The northern Dinaric karst is the most karstified area of the Dinarides. The geological structure often impedes the vertical movement of groundwater, leading to the predominantly horizontal development of karst channels. As a result of significant karstification across the study area, groundwater primarily flows orthogonal to the NW-SE oriented Dinaric formations, cascading from the boundary of the Adriatic/Black Sea catchment towards the Pannonian Basin in two or three springing levels, representing the transition zone from deep to shallow karst.

The karstification in the Kapela mountainous area is up to several hundred metres deep and represents the first recharge area formed in the tectonized carbonate mass. Abundant karstic forms result in rare and ephemeral surface watercourses and rapid infiltration of precipitation. The time series analyses of discharge and precipitation data show that well-developed karst conduit systems have developed in size compared to fracture-matrix systems without a clear diffuse flow. The groundwater emerges with large discharge oscillations at a concentrated point at the foot of the mountain, as typical karst springs. In the dry seasons, the water drains the mountain region, with occasional surface flows into the poljes, and gravitates to the main spring of Ogulin polje, Zagorska Mrežnica. Based on time series analysis, stable isotope content, temperature dynamics and tracing results, the Draškovac, Vitunj, and Bistrac Sabljaki springs mainly drain the higher mountain massifs directly above them. During heavy precipitation, due to the limited outflow of the Zagorska Mrežnica Spring, the karst system becomes entirely saturated, changing the direction of hydraulic pressure and groundwater flow. The karst poljes across the mountain are flooded, and sinkholes take on the function of springs, enabling the mountain to discharge on both sides. The conceptual model of interpreted regional groundwater flow directions during high and low water conditions is explained in detail and schematically represented in Boljat et al. (2024a, P2). Saturated underground likely activates non–active channels during low waters, directing water from the area of the Jasenak Polje toward the northern springs and the Crnac or Stajnica Polje toward the southern springs. Conceptually, the karst systems can be considered as a part of the common mountain karst system, in which the catchment area boundaries are zonal and variable regarding precipitation distribution and the aquifer saturation degree in the high permeability tectonic-formed limestone, which is devoid of the significant hydrogeological barriers. The scheme of the sub-catchment areas is shown in Figure 4.

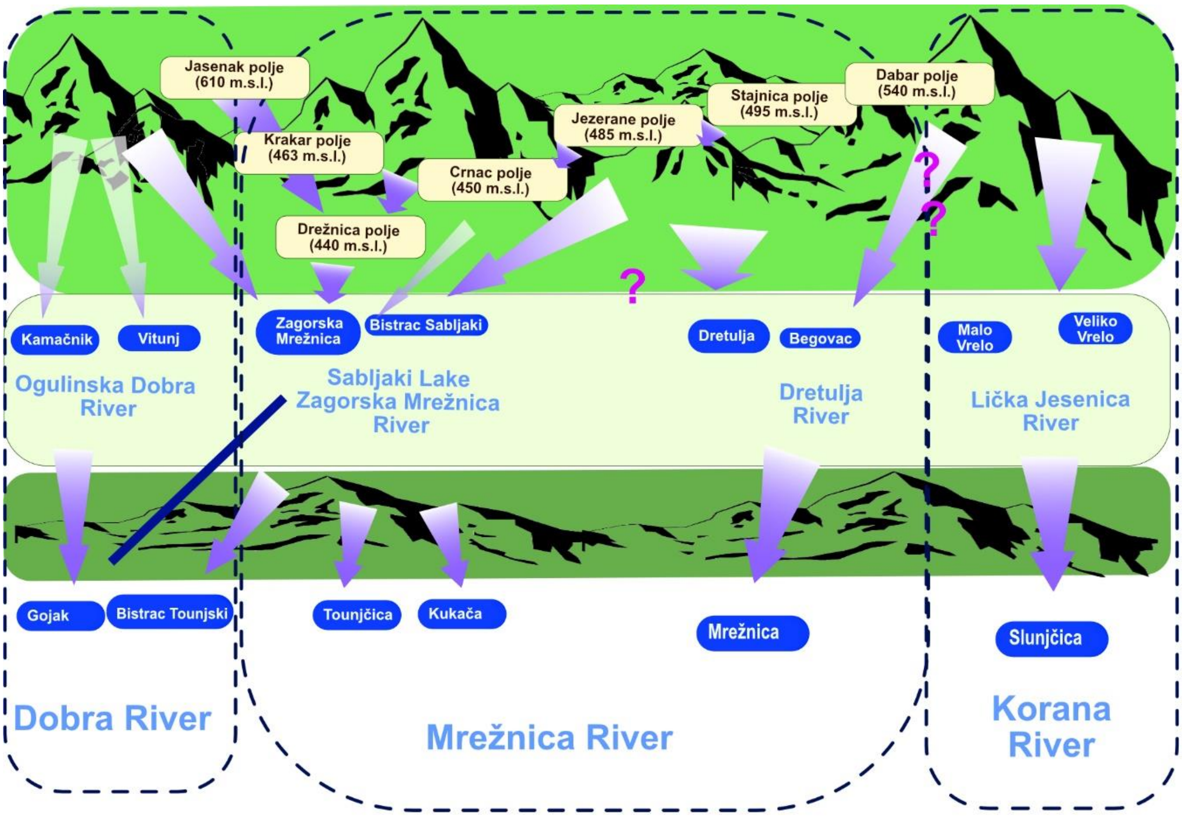


Figure 5. Schematic representation of two springing zones, the first at the foot of Kapela Mtn., and the second in the shallow karst area

Additionally, the catchment areas of springs at the foot of the Kapela Mtn. are part of the catchment areas of the springs of the Kordun Rivers (Figure 5). The hydrogeological barrier directs the springing water into the shallow karst complex downstream of the karst poljes as Ogulin, Plaški, Lička Jesenica. The well-developed karst conduit systems allow the mixing of groundwater and the recharge from the same sinkhole zones. For instance, according to the tracer test, the Zagorska Mrežnica sinkhole zones feed a series of springs in the second springing zone, including the Bistrac Tounjski, which forms a tributary of the Dobra River, and the Tounjčica and Kukača form tributaries of the Mrežnica River (unknown author, HGI-CGS archive, 1948).

Furthermore, the monitored springs can be grouped based on the dynamic properties of deep and shallow karst zone springs. The springs in the shallow karst zone have a faster water exchange, more significant temperature fluctuation, shorter groundwater retention, up to 10 times faster groundwater velocity, and the depth of water circulation, which is limited due to the thinner, more highly permeable carbonate deposits defined by the erosion base of Kordun rivers.

Hypothesis #3: The mean groundwater retention time in Dinaric karst is less than two years.
Groundwater residence time is the duration it takes for a water molecule to travel from the entry point in the aquifer to its discharge point (**Kazemi et al., 2006**). The mean residence time (MRT) represents the average retention time of all water emerging at a specific time. It is a crucial determinant in forming aquifer hydrogeological concepts (**Clark and Fritz, 1997**). Furthermore, contamination and risk assessment are heavily reliant on the estimated groundwater retention and storage capacity.

In a karst system, pinpointing a groundwater retention time can be challenging due to its heterogeneity and dynamic nature, such as karstification degree, geological characteristics primarily referring to the structural and tectonic relationships of permeable and impermeable rocks, climate, hydraulic gradients, amount and spatial distribution of precipitation.

Studies have suggested that MRT in karst aquifers can range from weeks to decades (**Mandić, et al., 2013**), with pronounced local variations. Slow percolation through soil, epikarst and shallower vadose zones, where the tiny pores and fissures may store the recharged water, results in longer retention times. The short-term heavy rainfall causes surface runoff and rapid infiltration through sinkholes and well-developed pathways directly to springs, significantly reducing retention times. Consequently, old water with longer retention time may be observed in base flow, while a high proportion of the young water may be observed during discharge peaks in spring waters.

Isotopic studies are widely used to estimate the MRT (**Maloszewski & Zuber, 1982; Maloszewski et al., 2002; Lauber & Goldscheider, 2014**). This work used stable isotopes oxygen ($\delta^{18}O$) and deuterium ($\delta^{2}H$) as environmental tracers observed in precipitation as input data and in spring waters as output data. The fundamental assumption is that the precipitation isotopic composition remains unchanged upon entering the subsurface. The spring waters result from a mixing process, and the MRT is determined based on the homogenisation degree. The detailed methodology is outlined in Chapter 4 **(Boljat et al., 2024b, P3).**

Considering the study area's geological structure, hydrogeological properties, and data calculated for the Dinaric karst, it is hypothesised that the MRT in northern Dinaric karst is less than two years. The conducted RCA and ACF methods refer to the dominant groundwater movement of groundwater through well-developed conduits, fractures, and channels, without clear diffuse flow in the aquifer of six springs, namely Draškovac, Vitunj, Zagorska Mrežnica, Dretulja, Gojak and Tounjčica **(Boljat et al, 2024a, P2)**. Rapid and significant increase in discharge following a precipitation event indicates a large proportion of young water in the spring waters. This is corroborated by tracing tests and the temperature dynamics of the springs, which clearly determine the arrival time of newly infiltrated water. In the deep karst area, the newly infiltrated water arrived from to the spring after 3 to 18 days, and in the shallow karst zone from half a day to 1.5 day **(Boljat et al, 2024a)**.

The calculated MRT for the study area is between 9 and 16 months, indicating a significantly low storage capacity in general. The MRT of aquifers across Kapela Mtn., developed in the deep karst zone, was ascertained over one year, and the established average water retention in aquifers developed in the shallow karst areas is for less than one year. Notably, the water from the first level partially reemerges in the springs at the second springing level, which likely increases the MRT. Therefore, it can be inferred that the shallow karst has an even lower storage capacity than the calculated one.

Hypothesis #4: Differences in content stabile isotope enable us to distinguish the Mediterranean and continental precipitation influence on spring water in the study area.

The precipitation isotope data defined the LMWL for Kapela Mtn. based on the 3-year dataset of monthly precipitation samples, presented in Boljat et al. 2024b. The calculated regression line coincides very well with the regional Western Mediterranean Meteoric Water Line (WMMWL) established by **Celle-Jeanton et al. (2001)**, suggesting that the Kapela Mtn. precipitation has a predominant origin from Mediterranean air masses. All spring water samples, collected in eight spring waters across the study area were aligned along the LMWL, confirming the meteoric origin of the spring waters and insignificant evaporation of the precipitation prior to infiltration into the subsurface. Additionally, the absence of a surface watercourse and aquifer characteristics established through three papers comprising this dissertation, such as the rapid exchange of water, short mean groundwater residence time, fats arrival of fresh infiltrated water at the springs, and the observed seasonal variations of stable isotopes in the spring waters, allow us to discuss the distribution of precipitation which affecting the study area.

Based on previous isotope studies in the northern Dinaric karst region, it was observed that the aquifers in the northern area are predominantly fed by air masses originating from the Mediterranean (**Hunjak et al., 2013; Francišković-Bilinski et al. 2013**), while the southern area of Plitvice Lakes is predominantly influenced by air masses originating from the Atlantic (**Babinka, 2008; Meaški 2011, Hunjak 2015**). This hypothesis was substantiated by preliminary results showing general depletion from north to south of the stable isotopes $\delta^{18}O$ and $\delta^{2}H$ composition in the monitored springs. However, the interpretation of the final results showed that the air masses in the study area do not differ due to their origin but rather due to the local influence of the rugged terrain. Therefore, the hypothesis could not be confirmed.

The studies in the Plitvice Lake area were conducted based on data collected from 2003 to 2005 (**Babinka, 2007; Meaški, 2011**), and interpreted in conjunction with the wind's motion. It was concluded that 80% of the precipitation in the Plitvice Lakes region originates from the continent, and 20% is of Mediterranean origin. In the study conducted by **Krajacar Bronić et al. (2020)**, they analysed the same data set and concluded that the Plitvice region is predominantly impacted by precipitation that originates from the Mediterranean and influences of attitude effect (but regarding the precipitation in the Zagreb area). This finding is consistent with the conclusions derived from the investigation within this thesis **(Boljat et al., 2024b)**.

The origin of the air masses and their impact on the groundwater were determined using the deuterium excess parameter. The d-excess parameter is a valuable tool in hydrogeology and climatology for understanding the origins and history of water masses and the climatic conditions under which precipitation is formed. In simple terms, the parameter indicates the specific location where the air mass originated **(Dansgaard, 1964)**. The d-excess parameter was calculated for all water samples of precipitation and springs. The three-year data set reveals d-excess values ranging between 8.75 to 18.56 in precipitation and 11.96 and 15.86 in aquifers of the first springing zone.

Conversely, in the second spring zone, the d-excess values range from 12.84 to 15.36 (Fig. 9, Table 3 in Boljat et al. 2024b). The calculated d-excess values show similarities in the groundwater samples, providing compelling evidence that Mediterranean air masses largely supply the aquifers in the northern Dinaric karst in Croatia. Anticipated average values in the second spring zone were slightly lower because of its proximity to the northeastern edge of Kapela Mountain. The mountain impedes the passage of air masses with a lower d-excess originating from the north, causing them to be depleted before crossing the mountain range.

The depletion of stable isotopes in spring water, subsequently in the precipitation that replenishes them, is observed from north to south of the study area or from Gorski Kotar to Lička Jesenica (Figure 10, Chapter 3, Boljat et al., 2024b). The interpretation of this validity arises from the impact of rugged terrain on the air masses or attitude effect.

In the south, the Mediterranean air masses must cross several climbs of the Velebit Mtn., with a peak of 1754 m a.s.l, before reaching the Kapela Mtn., or ~ 60 km to the catchment areas of Dretulja and Veliko Vrelo. Conversely, in the north, the Kapela Mtn. is the first significant barrier for Mediterranean air masses, affecting the catchment areas of Vitunj and Zagorska Mrežnica, with an aerial distance to the Adriatic coast of ~20 km **(Boljat et al., 2024b)**.
Due to the depletion of stable isotope content caused by the terrain, it is not possible to apply the principle used to calculate the mean recharge altitude based on the stable isotope content in spring waters on the regional level. If we take the calculated $\delta^{18}O$ gradient of -0.25 ‰/100 m, established as an average in the wider observed area (**Hunjak et al. 2013**), the Slunjčica and Mrežnica catchment areas would be over 800 m at a higher altitude than the Vitunj catchment area, which is hydraulically impossible.

4. CONCLUSION

The primary focus of this doctoral dissertation was to provide a new insight into the hydrogeological relationships of the northern Dinaric karst region in Croatia. The general of surface and groundwater flow direction in this area is towards the northeast and east, placing the area within the Black Sea basin. There are two types of karst, deep karst, and shallow karst (or fluviokarst). The main difference between them is in the depth of karstification and water flow in the aquifers. The research began with the collection of available literature and spatial data. The first step was to identify areas with the greatest vulnerability and man-made hazards. The results were summarised and mapped in water quality index maps and hazard maps created for the entire Kupa River catchment area spread in Croatia and Slovenia. The hydrogeological research was conducted in the central part of the Kupa River basin, focusing on the Kapela massif and its foothills. Hydrologically, this area includes the catchments of the Dobra, Mrežnica, and Slunjčica rivers in two levels of sinking and springing. The study area is characterised by hydrochemical and isotopic research, defined dissolution and precipitation processes of carbonate rocks, groundwater retention times, recharge area elevation, and anthropogenic influence. Groundwater dynamics was defined as a null state that is the basis for monitoring of new hydrotechnical interventions. The hydrogeological complex was investigated with an emphasis on defining the transition zone between deep karst and shallow or fluviokarst, which significantly differs from other Dinaric karst areas, and in the study area, the conceptual grouping model of springs sharing catchment areas according to dynamics and hydrochemical properties was outlined. The following conclusions were derived from the findings of this investigation:

- The karst part of the Kupa River catchment area is classified into five classes of WQIgw values. Very high and high WQIgw covers 3.8% of the total area (agricultural activities on land consist mainly of carbonate rocks with good permeability and traffic networks laid over karstified carbon rocks). Medium values cover 1.4% (built-up areas - settlements, industrial and commercial areas, construction sites, agricultural land with significant natural vegetation areas that extend over carbonate rocks with good permeability, vineyards and non-irrigated arable land on carbonate rocks with medium to low permeability). Low and very low values cover ~95% (forest areas on carbonate rocks with medium to low permeability, areas without aquifers and anthropogenic activities)

- The types of hazards are mapped and classified within the karst part of the Kupa River catchment area. There are no hazards classified at a very high level. High hazard levels include direct wastewater treatment outflows into karst and waste illegally disposed in karst features and caves. Moderate hazards include active landfills with remediation processes, wastewater effluent from various industrial activities discharged into the watercourses, and settlement areas without a sewerage system. Low hazard levels include agricultural activities such as arable land, vineyards, orchards, settlements with potentially leaking sewer networks, and the railway and road network in the 5 m impact zone. Very low levels include pastures and the railway and road network in the 5-25 m impact zone.
- The karst in northern Dinaric karst differs from the rest of the karst in Croatia by the depth of karstification and depth of water circulation: in deep karst zone (so-called accumulated karst), karstification extending over several hundred meters, while in shallow karst zone (or fluviokarst) it rarely reaches 200 m. The shallow or fluviokarst zone has a limited depth of water circulation due to the thinner, more highly permeable carbonate deposits than the deep karst zone. The conducted time series analyses established a significant difference between the deep and shallow karst areas, suggesting a more developed karst network, faster water exchange, and shorter groundwater retention in the shallow karst zone, classified it as one of the most karstified regions of the Dinaric karst.
- Determined by tracing tests, temperature dynamics and time series analysis, the velocity of the groundwater is up to 10 times faster in the shallow karst zone than in the mountain area of the deep karst zone.
- The study region consists of a deep karst zone extending across the mountain area of Kapela Mtn. and a shallow karst zone in its foothills and further toward the north. This research suggests relocating the boundary between deep and shallow karst westward, locating it immediately below Kapela Mtn.
- The conceptual hydrogeological model, which addresses historical discrepancies in groundwater tracing results, accurately represents the underground water system and zonal groundwater divides. The challenges encompass tracer dilution during high water conditions, challenging detection of tracer, and changes in the groundwater flow direction depending on the aquifer saturation.

- In the deep karst area, newly infiltrated water and potential contaminants from a hazardous event reached the spring within 3 to 18 days. This process occurred within half a day to 1.5 days in the shallow karst zone. Additionally, the water waves caused by heavy rainfall and potential flooding appear within one day at the first spring level and a few hours later at the second spring level.
- In the unsaturated karst system, new infiltrated precipitation appears in the spring water within the first discharge impulse. In the saturated aquifer, infiltrated water appears with a lag of a few days, depending on the degree of saturation.
- Hydrochemical analyses of spring water identified that the aquifers across Kapela Mtn. and its foothill drain mainly carbonates. The eight main springs exhibit calcium–hydrogen carbonate (Ca–HCO_3) to calcium-magnesium hydrogen carbonate (Ca–Mg–HCO_3) hydrochemical facies, indicating the dissolution and weathering of limestone and dolomite, with the absence of evaporites and other noncarbonate rocks. A slightly higher proportion of dolomitic component is observed in the waters of Vitunj, Gojak, Veliko Vrelo and Mrežnica springs. In contrast, the aquifer of Zagorska Mrežnica, Dretulja, Tounjčica and Slunjčica springs are predominantly developed in limestones. Groundwater mineralisation generally increases from the north to the south of the area.
- The drinking water supply springs, Zagorska Mrežnica and Dretulja, have extremely high groundwater quality, similar to all bountiful springs that drain the Kapela Mtn. The slight human impact was observed in the Gojak and Tounjčica springs which take place downstream in the urban area and cultivated Ogulin polje. Although the observed impact is not alarming, it is crucial to consider the aquifers' high vulnerability when planning the spatial development of the region.
- Based on a three-year dataset (June 2018 – May 2021), the new LMWL was calculated for Kapela Mtn. It is observed that predominant precipitation originates from the Mediterranean air mass regardless of the season. The isotopic composition of spring water indicates the meteoric origin of groundwater. The spatial distribution of monitored springs and calculated d-excess values indicate a dominant reach from the Mediterranean air masses and a significant continental (altitude) effect on the isotopic composition of spring waters in the southern area due to the strong influence of Velebit Mtn. on the isotopic composition. The spatial distribution of stable isotope across aquifers in the northern Dinaric karst in Croatia is generally depleted from north to south.

- The MRT was estimated using the stable isotopes oxygen ($\delta^{18}O$) and deuterium ($\delta^{2}H$) as environmental tracers, and in the observed aquifers is up to 1.5 years. The MRT of aquifers in the deep karst zone was ascertained over one year, and the established average water retention in aquifers developed in the shallow karst areas is for less than one year.
- The MRA was calculated based on the average spring water temperature as a reliable indicator. The MRA of the monitored springs ranges over 710 meters from the lowest positioned catchment area of Gojak with calculated MRA at ~ 400 m a.s.l. to the highest Veliko Vrelo situated at 1120 m a.s.l., similar to Vitunj at 1080 m a.s.l.

5. REFERENCES

1. Babinka, S. (2008): Environmental isotopes as a tool for hydrological characterisation of karsta aquifer , groundwater protection and estimation of groundwater reserves – case study: Plitvice lakes and Bihać area, In: Savjetovanje hidrološka mjerenja i obrada podataka, Nacionalni park Plitvička jezera (Consultation on Hydrological Measurements and Data Processing, Plitvice Lakes National Park), 232–255

2. Babinka, S. (2007): Multi-Tracer Study of Karst Waters and Lake Sediments in Croatia and Bosnia and Herzegovina: Plitvice Lakes National Park and Bihać Area.– Doctoral Thesis, Universität Bonn, 168 p., Bonn.

3. Bahun, S. (1968): Geološka osnova hidrogeoloških odnosa krškog područja između Slunja i Vrbovskog (Geological basis of the hydrogeological relations in the karst area between Slunj and Vrbovsko), Geološki vjesnik, 21, 19–82

4. Bahun, S. (1970): Geološka osnova hidrogeoloških odnosa krške zavale Ogulin – Plaški (Geological basis of hydrogeological relations in the karst basin of Ogulin – Plaški), Krš Jugoslavije (Karst of Yugoslavia), JAZU 7/1, Zagreb, 1-20

5. Bakula M.; Harambašić, T.; Anić, I.; Kiš, K.; Hriberšek, T.; Klaić Jančijev, D.; Juratek, I. (2023) Elaborat zaštite okoliša za provedbu postupka ocjene o potrebi procjene utjecaja na okoliš za zahvat: Izgradnja dobavnog vodoopskrbnog sustava "Lička Jasenica – Rakovica – NP Plitvička Jezera", Dvokut ecro d.o.o., Zagreb, 138 p

6. Biondić, R.; Marković, T.; Kapelj, S.; Žugaj, R. (2003): Hidrogeološka istraživanja za zaštitu izvorišta pitke vode na području Vrbovskog (Hydrogeological Investigations for the Protection of Drinking Water Sources in the Vrbovsko Area), Croatian Geological Survey, Zagreb

7. Biondić, B.; Biondić, R.; Kapelj, S. (2006): Karst groundwater protection in the Kupa River catchment area and sustainable development, Environmental Geology, 2006, 49/6, 828–839. doi: 10.1007/s00254-006-0178-4

8. Biondić, B.; Biondić, R.; Meaški, H. (2010): The conceptual hydrogeological model of the Plitvice Lakes, Geologia Croatica, 63/2, 195 – 206. doi: 10.4154/gc.2010.17

9. Biondić, R. (2014): Zone sanitarne zaštite izvorišta na području grada Ogulina (Sanitary Protection Zones of Drinking Water in the area of Ogulin City), The Faculty of Geotechnical Engineering, University of Zagreb, Varaždin

10. Biondić, R.; Meaški, H.; Biondić, B.; Loborec, J. (2021): Karst Aquifer Vulnerability Assessment (KAVA) Method – A Novel GIS-Based Method for Deep Karst Aquifers, Sustainability, 13/6, 3325, 20. doi: 10.3390/su13063325

11. Bogunović, M.; Bensa, A. (2005): Tla krša-temeljni čimbenik biljne proizvodnje (Karst Soils-Fundamental Factor of Agriculture Production), Biondić, B., Božičević, J., Eds.; Centar za Krš (Karst Center): Gospić/Zagreb, Croatia; 41–50

12. Bonacci, O.; Andrić, I. (2010): Impact of an inter-basin water transfer and reservoir operation on a karst open streamflow hydrological regime: An example from the Dinaric karst (Croatia), Hydrological Processes, 24, 3852–3863

13. Bojanić, L. (1972). Regionalna hidrogeološka istraživanja područja sliva Kupe (Regional Hydrogeological Investigations of the Kupa River Basin), Croatian Geological Survey, Zagreb

14. Bojanić, L., Ivičić, D. (1981): Hidrogeološka istraživanja područja Drežnice, Krakara, Jasenka, Vitunjčice, Ribnjaka i Gojačke Dobre (Hydrogeological investigations of the areas of Drežnica, Krakar, Jasenak, Vitunjčica, Ribnjak, and Gojačka Dobra), Croatian Geological Survey , Zagreb

15. Boljat, l.; Terzić, J.; Duić, Ž.; Lukač Reberski, J.; Selak, A. (2024a) Conceptual Model Based on Groundwater Dynamics in the Northern Croatian Dinaric Region at the Transition from the Deep Karst and Fluviokarst, Water 2024, 16, 1630, https://doi.org/10.3390/w16111630

16. Boljat, l.; Terzić, J.; Duić, Ž.; Lukač Reberski, J.; Selak, A.; Briški, M. (2024b) Tracing hydrological processes: insights from hydrochemical and isotopic investigations in the northern part of Croatian Dinaric karst, Geologia Croatica, 77/2, 127-144, doi: 10.4154/gc.2024.09

17. Buljan, R.; Gulam, V.; Frangen, T.; Terzić, J.; Bostjančić, I.; Blagus, Z. (2013): Retencija Drežničko polje - prva faza istražnih radova za Glavni projekt, Inženjerskogeološka i hidrogeološka istraživanja (Drežničko Polje Retention – First Phase of Investigative

for the Main Project, Engineering Geological and Hydrogeological Investigations), Croatian Geological Survey, Zagreb

18. Buljan, R.; Pavlić, K.; Terzić, J.; Perković, D. (2019): A Conceptual Model of Groundwater Dynamics in the Catchment Area of the Zagorska Mrežnica Spring, the Karst Massif of Kapela Mountain, Water, 11/10. doi: 10.3390/w11101983

19. Buljan R.; Bočoć, N.; Pavlić, K.; Boljat, I.; (2020) Analiza uzroka povećanja otjecanja i mutnoće vode na sljevovima rijeka Mrežnice i Korane (Analysis of the causes of increased runoff and water turbidity in the watersheds of the Mrežnica and Korana Rivers), Croatian Geological Survey and Univerity of Zagreb, Zagreb

20. Bura, D. (1958): Statistika Krša Jugoslavije (Statistical Analysis of Jugoslavian Karst); Savezno savjetovanje o kršu (Federal Conference on Karst), Split, Croatia, 67–98

21. Celle-Jeanton. H.; Travi. Y.; Blavoux. B. (2001): Isotopic typology of the precipitation in the Western Mediterranean region at three different time scales, Geophysical Research Letters, 28, 1215–1218. doi:10.1029/2000GL012407

22. Clark, I.; Fritz, P. (1997): Environmental Isotopes in Hydrogeology, Lewis, 328 p

23. COST Action 620 (2004): Vulnerability and Risk Mapping for the Protection of Carbonate (Karst) Aquifers; Final Report; Zwahlen, F. (Ed.) European Commission, Directorate-General for Research: Luxembourg

24. Croatian Meteorological and Hydrological Service (DHMZ) (2020) Available online: https://meteo.hr/podaci.php?section=podaci_vrijeme&param=oborina (accessed on 19 November 2020)

25. Croatian Parliament (2008): Water Management Strategy – Official Gazette of Croatia, Zagreb, 91 p.

26. Croatian waters (2021): Plan upravljanja vodnim područjima 2022.-2027. (River Basin Management Plan 2022.–2027.) https://www.voda.hr/sites/default/files/2023-07/PLAN%20UPRAVLJANJA%20VODNIM%20PODRUCJIMA%20DO%202027..pdf (accessed on 16 January 2023)

27. Čanjevac, I.; Martinić, I.; Radišić, M.; Rubinić, J.; Meaški, H. (2023): Hydrology, Hydrogeology and Hydromorphology of the Plitvice Lakes Area, Plitvice Lakes.– In:

Miliša, M. & Ivković, M. (eds): Plitvice Lakes, Springer Water, Springer, Cham., 17–64. doi: 10.1007/978-3-031-20378-7_2

28. Čenčur Curk, B.; Cheval, S.; Vrhovnik, P.; Verbovšek, T.; Herrnegger, M.; Nachtnebel, H.; Marjanović, P.; Siegel, H.; Gerhardt, E.; Hochbichler, E.; et al. (2014) CC-WARE -Mitigating Vulnerability of Water Resources under Climate Change. WP3 - Vulnerability of Water Resources in SEE; Report Version 5; Available online: https://www.researchgate.net/publication/301889158_CC-WARE_Mitigating_Vulnerability_of_Water_Resources_under_Climate_Change_WP3_-_Vulnerability_of_Water_Resources_in_SEE (accessed on 29 January 2020)

29. Dansgaard, W. (1964): Stable isotopes in precipitation, Tellus, 16, 436–468. doi: 10.1111/j.2153-3490.1964.tb00181.x

30. European Environment Agency & Copernicus Land Service. Corine Land Cover CLC (2018) Available online: https://land.copernicus.eu/pan-european/corine-land-cover/clc2018 (accessed on 26 November 2019).

31. EU Directive 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (recast) (Text with EEA relevance)

32. Franciśković-Bilinski, S.; Bhattacharya, A.K.; Bilinski, H.; Bhaskar, D.B.; Mitra, A.; Sarkar, S.K. Fluvial (2012): Geomorphology of the Kupa River Drainage Basin, Croatia: A Perspective of Its Application in River Management and Pollution Studies, Z. Fur Geomorphology, 56, 93–119

33. Frančišković-Bilinski, S.; Cuculić, V.; Bilinski, H.; Häusler, H.; Stadler, P. (2013): Geochemical and stable isotopic variability within two rivers rising under the same mountain, but belonging to two distant watersheds. Chemie Der Erde, Geochemistry, 73(3), 293–308. doi:10.1016/j.chemer.2013.02.004

34. Gorjanović-Kramberger (1912) Plitki krš okolice Generalskog stola u Hrvatskoj. Predjel oko Lešća (Shallow karst landscape around Generalski Stol in Croatia), Glasnik Srpskog geografskog društva, 1

35. Gorjanović-Kramberger (1914) Nekadašnji otvoreni tok Dobre i Krških ravnjaka u Ogulinu, (The former open course of the Dobra River and the karst plateaus in Ogulin), Vijesti geološke povijesti, 3

36. Habič, P.; Kogovšek, J.; Bricelj, M.; Zupan, M. (1990): Izviri Dobličice in njihovo širše kraško zaledje (Springs of Dobličica and Their Broader Karst Hinterland), Acta Carsologica, 19, 5–100

37. Habič, P.; Kogovšek, J. (1992): Sledenje voda v kraškem zaledju Krupe v JV Sloveniji (Tracking Water in the Karst Hinterland of Krupa in Southeastern Slovenia), Acta Carsologica, 21, 35–76.

38. Herak, M. (1953): HE Gojak, O trasi tunela i smještaj građevinskih objekata, (HPP Gojak, On the tunnel route and the placement of construction structures) Croatian Geological Survey, Zagreb

39. Herak, M. (1954) Geološki prikaz ponornih zona Ogulinske Dobre (Geological representation of the sinking zones of the Ogulinska Dobra River) Croatian Geological Survey, Zagreb

40. Herak, M. (1956) O nekim hidrogeološkim problemima Male Kapele (s hidrogeološkom i geološkom kartom) (On some hydrogeological problems of Mala Kapela (with a hydrogeological and geological map)) Geološki vjesnik, 8, 19-37

41. Herak, M. (1972): Karst of Yugoslavia. In Karst: Important Karst Regions of the Northern Hemisphere; Herak, M., Stringfield, V.T., Eds.; Elsevier: Amsterdam, The Netherlands, 25–83

42. Hunjak T.; Lutz H.O.; Roller-Lutz Z. (2013): Stable isotope composition of the meteoric precipitation in Croatia, Isotopes in Environmental and Health Studies, 49:3, 336-345, doi: 10.1080/10256016.2013.816697

43. Hunjak, T. (2015): Spatial Distribution of Oxygen and Hydrogen Stable Isotopes from Precipitation in Croatia.– Unpubl. PhD Thesis, University of Zagreb, 75 p.

44. Ivičić, D. (1985): Hidrogeološka istraživanja za idejni projekt akumulacije HE Lešće na Dobri (Hydrogeological Investigations for the Conceptual Design of the Lešće HPP Reservoir on the Dobra River), Croatian Geological Survey, Zagreb

45. Ivičić, D. (1987): Izvještaj o bojanju ponora na Jasenačkom polju (Trecer test in the Jasenak Polje), Croatian Geological Survey, Zagreb

46. Ivičić, D.; Biondić, B.; Viljevac, Ž. (1988): Hidrogeološka istraživanja za glavni projekt akumulacije HE Lešće (Hydrogeological Investigations for the Main Design of the HPP Lešće Reservoir), Croatian Geological Survey, Zagreb.

47. Ivičić, D.; Viljevac, Ž.; Goatti, V.; Biondić, B.; Crnogaj, S. (1990): Hidrogeološka istraživanja u visokom području sliva Zagorske Mrežnice. Druga faza radova (Hydrogeological Investigations in the Upper Basin of the Zagorska Mrežnica: Second Phase), Croatian Geological Survey, Zagreb

48. Ivičić, D.; Kuhta, M.; Marković, T. (2001): Hidrogeološka istraživanja u visokom području sliva Zagorske Mrežnice. Trasiranje ponora u Jezeranama i speleološki radovi u jami Rokina Bezdana (Hydrogeological Investigations in the Upper Basin of the Zagorska Mrežnica: Tracing of Sinkholes in Jezerane and Speleological Research in Rokina Bezdana Cave), Croatian Geological Survey, Zagreb

49. Ivičić, D. (1994): Odvodnja otpadnih voda grada Ogulina (Wastewater Drainage of the Ogulin City), Croatian Geological Survey, Zagreb

50. Ivičić, D. (2003): Istraživanje podzemnih veza u zaleđu izvorišta Slunjčica sjeverno od Rakovice, trasiranje ponora Švica (Investigation of Groundwatrer Connections in the Catchment area of the Slunjčica Spring North of Rakovica: Tracing of the Švica Sinkhole), Croatian Geological Survey, Zagreb

51. Jurak, V. (1983): Kompararivna analiza hidroloških režima rijeka Gline, Korane i D. Mrežnice s aspekta hidrogeoloških značajki porječja (Comparative analysis of the hydrological regimes of the rivers Glina, Korana, and Lower Mrežnica from the perspective of the hydrogeological characteristics of the watershed), Disertacija, Rudarsko-geološki fakultet Univerziteta u Beogradu, 181, Beograd

52. Krajcar Bronić, I.; Barešić J.; Sironić, A.; Lovrenčić Mikelić, I.; Borković, D.; Horvatinčić, N.; Kovač, Z. (2020): Isotope Composition of Precipitation, Groundwater, and Surface and Lake Waters from the Plitvice Lakes, Croatia, Water 12, no. 9: 2414. https://doi.org/10.3390/w12092414

53. Kazemi, G.A., Lehr, J.H., Perrochet, P. (2006): Groundwater Age: Hoboken, New Jersey, John Wiley & Sons, 325 p

54. Kovačević, A. (2005): Hidrogeološke značajke Karlovačke županije (Hydrogeological features of Karlovac County), Unpubl. Master Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Croatia, 126 p.

55. Lauber, U.; Goldscheider, N. (2014): Use of artificial and natural tracers to assess groundwater transit-time distribution and flow systems in a high-alpine karts system (Wetterstein Mountains, Germany). Hydrogeology Journal, 22, 1807–1824.

56. Magdalenić, A. (1956): HE Gojak, Geološki profil dovodnog tunela dionica Drenovac-Gojak (HPP Gojak: Geological Profile of the Intake Tunnel Section Drenovac-Gojak), Croatian Geological Survey, Zagreb

57. Magdalenić, A. (1957): HE Gojak, Geološki profil dovodnog tunela dionica Sabljaci-Drenovac (HPP Gojak: Geological Profile of the Intake Tunnel Section Sabljaci-Drenovac) Croatian Geological Survey, Zagreb

58. Maloszewski, P.; Stichler, W.; Zuber, A.; Rank, D. (2002): Identifying the flow systems in a karst-fissured-porous aquifer, the Schneealpe, Austria, by modelling of environmental 18O and 2H isotopes. Journal of Hydrology, 256, 48–59.

59. Maloszewski, P.; Zuber, A. (1982): Determining the turnover time of groundwater systems with the aid of environmental tracers: 1. Models and their applicability. Journal of Hydrology, 57, 207–231

60. Mandić M.; Mihevc A.; Leis A.; Krajcar Bronić I. (2013): Concentration and stable carbon isotopic composition of CO2 in cave air of Postojnska jama, Slovenia. International Journal of Speleology, 42 (3), 279-287. Tampa, FL (USA) ISSN 0392-6672 http://dx.doi.org/10.5038/1827-806X.42.3.11

61. Meaški, H. (2011): Model zaštite krških vodnih resursa na primjeru nacionalnog parka „Plitvička jezera“ (Model of the karst water resources protection on the example of the Plitvice Lakes national park), Unpubl. PhD Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, 211 p

62. Meaški, H.; Marciuš, M.; Ptiček Siročić, A. (2016): Hidrogeološke značajke vodotoka Plitvica na području Plitvičkih jezera, Hrvatska (Hydrogeological Characteristics of

the Plitvica Stream in the Plitvice Lakes Area, Croatia), Inženjerstvo okoliša, 3, 21–32.

63. Michelsen, N.; Geldern, V.R.; Roßmann, Y.; Bauer, I.; Schulz, S.; Barth, J.A.C.; Schüth, C. (2018): Comparison of precipitation collectors used in isotope hydrology, Chemical Geology, 488, 171–179. doi:10.1016/j.chemgeo.2018.04.032

64. Pahernik, M. (2012): Prostorna gustoća ponikava na području Republike Hrvatske (Spatial Density of Sinkholes in the Republic of Croatia), Hrvatski Geografski Glasnik, 74, 5–26.

65. Pavičić, D.; Terzić,J.; Marković, T.; Dukarić, F. (2008): Elaborat za uspostavu regionalnog vodocrpilišta Lička Jesenica (Report on the Establishment of the Lička Jesenica Regional Water Supply System), Croatian Geological Survey, Zagreb

66. Pavlić, K. (2016): Regionalna hidrološka analiza krškog porječja Kupe (Regional hydrological analysis of the Kupa karstic basin), Unpubl. PhD Thesis, Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, 143 p

67. Pavlić, K.; Parlov, J. (2019): Crosscorrelation and Cross-Spectral Analysis of the Hydrographs in the Northern Part of the Dinaric Karst of Croatia, Geosciences; 9/2, 86 p. doi: 10.3390/geosciences9020086

68. Piper, A. M. (1944): A graphic procedure in the geochemical interpretation of water-analyses.– Transactions of the American Geophysical Union, 25, 914-928. doi: 10.1029/TR025i006p00914

69. Poljak (1922): Periodičko jezero Blato (Periodic Lake Blato), Glasnik, naučni časopis za prirodne nauke, 34/1, str 71-78, Hrvatsko prirodoslovno društvo (Croatian Natural History Society)

70. Poljak (1925): Geomorfologija i hidrografija okoliša Ogulina i ogulinskog Zagorja (Geomorphology and Hydrography of the Ogulin and Zagorje), Glasnik Hrvatskog prirodoslovnog društva (Croatian Natural History Society), 37-38, 111-137, Zagreb

71. Poljak, J. (1948) Geološko mišljenje o visini akumulacije u Istočnoj Mrežnici (Geological assessment of the reservoir height in the Eastern Mrežnica River, Croatian Geological Survey

72. Posavec, K.; Bačani, A.; Nakić, Z. (2006) A visual basic spreadsheet macro for recession curve analysis. Groundwater, 44, 764–767, https://doi.org/10.1111/j.1745-6584.2006.00226.x

73. Posavec, K.; Parlov, J.; Nakic, Z. (2010) Fully Automated Objective-Based Method for Master Recession Curve Separation. Groundwater, 48, 598–603, https://doi.org/10.1111/j.1745-6584.2009.00669.x

74. Posavec, K.; Giacopetti, M.; Materazzi, M.; Birk, S. (2017) Method and Excel VBA Algorithm for Modeling Master Recession Curve Using Trigonometry Approach. Groundwater, 55, 891–898, https://doi.org/10.1111/gwat.12549

75. Prelogović, E.; Aljinović, B.; Bahun, S. (1995): New data on structural relationships in the Northern Dalmatian Dinaride Area, Geologia Croatica, 48, 167-176

76. Prelogović, E.; Dragičević, I.; Mayer, D.; Buljan, R. (2005): Retencija Drežničko polje, Podloge i novelacije idejnog rješenja - geološki i hidrogeološki dio (Drežničko Polje Retention: Background and Updates to the Conceptual Design - Geological and Hydrogeological Components), Elektroprojekt, Zagreb.

77. Roglić, J. (1969): Geografski aspekt Dinarskog krša (Geographical aspect of Dinaric karst). In Krš Jugoslavije 1; Petrik, M., Ed.; JAZU: Zagreb, Croatia, 19–39.

78. Schmid, S.M., Bernoulli, D., Fügenschuh, B., Matenco, L., Schefer, S., Schuster, R., Tischler, M. & Ustaszewski, K. (2008): The Alpine-Carpathian-Dinaridic orogenic system: Correlation and evolution of tectonic units, Journal of Geosciences, 101, 139–183. doi: 10.1007/s00015-008-1247-3

79. Selak, A.; Boljat, I.; Lukač Reberski, J.; Terzić, J., Čenčur Curk, B. (2020) Impact of Land Use on Karst Water Resources—A Case Study of the Kupa (Kolpa) Transboundary River Catchment, Water, 12, 3226; doi:10.3390/w12113226

80. Tari, V. (2002): Evolution of the northern and western Dinarides: a tectono-stratigraphic approach, Stephan Mueller Spec. Publ. 1, European Geosciences Union, 1, 223–236

81. Terzić, J.; Stroj, A.; Frangen, T. (2012) Hydrogeological investigation of karst system properties by common use of diverse methods: a case study of Lička Jesenica springs in Dinaric karst of Croatia, Hydrological Processes, Vol 26, 3302-3311

82. Viljevac, Ž., Ivičić, D. (1990): HE Lešće. Istražni radovi za glavni project (HPP Lešće - Exploratory work for the main project), Croatian Geological Survey , Zagreb

83. Zaninović, K., Gajić-Capka, M., Perčec Tadić, M. & Vučetić, M. (2008): Klimatski Atlas Hrvatske (Climate Atlas of Croatia) 1961–1990., Državni hidrometeorološki zavod: Zagreb

84. Zwahlen, F. (2004) COST Action 620 Vulnerability and Risk Mapping for the Protection of Carbonate (Karst) Aquifers; Final Report; European Commission, Directorate - General for Research: Luxembourg, 2004.

6. BIOGRAPHY

Ivana Boljat (née Vincetić) was born on January 14, 1983, in Zagreb, where she completed gymnasium in 2001. In 2009, she graduated in Geology at the Faculty of Science, University of Zagreb. She began her professional career during her studies at the private companies Estavela in Solin and Sinjal in Civljane, performing hydrogeological and geophysical work. Before joining the Croatian Geological Survey in 2013, she worked as an external collaborator for companies unrelated to geology, engaging in cartography, administration, and marketing. In 2013, she was employed as the secretary of the Department of Mineral Resources at the Croatian Geological Survey. In 2014, she transitioned to the Department of Hydrogeology and Engineering Geology as a project assistant for European Union projects. In 2017, she became an expert associate at the same department, and in 2023, she advanced to the position of expert advisor. Her scientific interest and skills in karst hydrogeology are field investigation (hydrogeological mapping, discharge measuring, monitoring and sampling of natural waters, collecting of logger data), hydrochemistry of groundwater, stable isotopes in groundwater and precipitation, dynamics of karst aquifers (time series analysis: cross-correlation, autocorrelation, recession analysis). In addition to her scientific work in karst hydrogeology, she has specialised in the application and implementation of projects co-financed by the European Union.

BIBLIOGRAPHY

Boljat, Ivana; Terzić, Josip; Duić, Željko; Lukač Reberski, Jasmina; Selak, Ana (2024) Conceptual Model Based on Groundwater Dynamics in the Northern Croatian Dinaric Region at the Transition from the Deep Karst and Fluviokarst // Water, *16*(11), 1630, *https://doi.org/10.3390/w16111630*

Boljat, Ivana; Terzić, Josip; Duić, Željko; Lukač Reberski, Jasmina; Selak, Ana; Briški, Maja (2024) Tracing Hydrological Processes: Insights from Hydrochemical and Isotopic Investigations in the Northern Part of Croatian Dinaric Karst // Geologia Croatica, *in press*

Amadio; Jessica; Kanakoudis, Vasilis; Dimkic, Dejan; Matić, Branislava; Banovec, Primož; **Boljat, Ivana**; Campione, Emanuela; Čenčur Curk, Barbara; Duro, Andrea; Kovač, Darko; Papadopoulou, Anastasia; Papakonstantinou, Argiris; Lukač Reberski, Jasmina; Srša, Matjaž; Tsitsifli, Stavroula; Romano, Emanuele (2024). Natural hazard risk analysis in the framework of water safety plans, Journal of Water and Health, 22 (3): 451–466, 10.2166/wh.2024.124.

Selak, Ana; Lukač Reberski, Jasmina; **Boljat, Ivana**; Terzić, Josip (2024) Characterising occurrence of emerging organic contaminants in Dinaric karst catchment of Jadro and Žrnovnica springs, Croatia // Emerging contaminants, 10, 3; 100327, 12. doi: 10.1016/j.emcon.2024.100327

Barbetta, Silvia; Bonaccorsi, Bianca; Tsitsifli, Stavroula; **Boljat, Ivana**; Argiris, Papakonstantinou; Lukač Reberski, Jasmina; Massari, Christian; Romano, Emanuele (2022) Assessment of Flooding Impact on Water Supply Systems: A Comprehensive Approach Based on DSS // Water resources management, 36, 5443-5459. doi: 10.1007/s11269-022-03306-x

Terzić, Josip; Filipović, Marina; **Boljat, Ivana**; Selak, Ana; Lukač Reberski, Jasmina (2021) Groundwater level and electrical conductivity datasets acquired within pumping tests on Ilovik Island in Croatia // Data in brief, 37, 107180, 5. doi: 10.1016/j.dib.2021.107180

Patekar, Matko; Baniček, Ivona; Rubinić, Josip; Lukač Reberski, Jasmina; **Boljat, Ivana;** Selak, Ana; Filipović, Marina; Terzić, Josip (2021) Assessing Climate Change and Land-Use Impacts on Drinking Water Resources in Karstic Catchments (Southern Croatia) // Sustainability, 13, 9; 5239, 20. doi: 10.3390/su13095239

Terzić, Josip; Grgec, Damir; Lukač Reberski, Jasmina; Selak, Ana; **Boljat, Ivana**; Filipović, Marina (2021) Hydrogeological estimation of brackish groundwater lens on a small Dinaric karst island: Case study of Ilovik, Croatia // Catena (Cremlingen), 204, 105379, 0. doi: 10.1016/j.catena.2021.105379

Selak, Ana; **Boljat, Ivana**; Lukač Reberski, Jasmina; Terzić, Josip; Čenčur Curk, Barbara (2020) Impact of Land Use on Karst Water Resources—A Case Study of the Kupa (Kolpa) Transboundary River Catchment // Water, 12, 11; 3226, 21. doi: 10.3390/w12113226

Expert papers:

Selak, Ana; Lukač Reberski, Jasmina; **Boljat, Ivana**; Novosel, Tomislav; Terzić, Josip (2022) Projekt „Board for Detection and Assessment of Pharmaceutical Drug Residues in Drinking Water - Capacity Building for Water Management in Central Europe“ boDEREC-CE // Hrvatske Vode, 30, 120; 147-151

Lukač Reberski, Jasmina; Terzić, Josip; **Boljat, Ivana**; Rubinić, Josip; Radišić, Maja; Hasan, Ozren; Šparica Miko, Martina; Selak, Ana (2022) Utjecaj klimatskih promjena na vodonosnik Blatskog polja u zapadnom dijelu otoka Korčule // XXVI. znanstveno-stručni skup "Voda i javna vodoopskrba" - zbornik radova / Ujević Bošnjak, Magdalena (ur.). Zagreb: Hrvatski zavod za javno zdravstvo (HZJZ) str. 57-65

Lukač Reberski, Jasmina; Terzić, Josip; Selak, Ana; **Boljat, Ivana** (2019)"Novi onečišćivači" u podzemnim vodama Hrvatske - primjer projekata GeoTwinn i boDEREC-CE // Hrvatske vode u zaštiti okoliša i prirode - Croatian waters in environmental and nature protection / Biondić, D.; Holjević, D.; Vizner, M. (ur.). Zagreb: Hrvatske vode,. str. 513-521

Boljat, I.; Živković, P.; Lukač Reberski, J. (2021) Multihazardni okvir za upravljanje vodnim resursima // Hrvatska vodoprivreda, 235; 17-19

Congress paper:

Frangen, T.; Terzić, J.; **Boljat, I**.; Lukač Reberski, J.; Meaški, H.; Biondić, R.; Miculinić, K.; Markić, N.; Brožinčević, A.; Martinčić, M.; Selak, A.; Burić, H.; Stanić, N. (2023) Simultaneous Tracing Test with three Different Tracers in the Plitvice Lakes National Park, Croatia, // 7. HGK - Knjiga sažetaka (Book of Abstracts) / Fio Firi, Karmen (ur.). Zagreb: Hrvatski geološki institut, 57-58

Terzić, J.; Lukač Reberski, J.; **Boljat, I**.; Hasan, O.; Šparica Miko, M.; Selak, A. (2023) Hydrogeological, Geochemical, and Hydrogeochemical Characteristics of an Island's Karst Aquifer. Blatsko Polje on the Korčula Island // 7. HGK - Knjiga sažetaka (Book of Abstracts) / Fio Firi, Karmen (ur.). Zagreb: Hrvatski geološki institut, 187-188

Selak, A.; Lukač Reberski, J.; Klobučar, G.; Novosel, T.; Filipović, M.; **Boljat, I.;** Terzić, J. (2023) Occurrence of emerging organic contaminants in Dinaric karst catchment of Jadro and Žrnovnica springs, Croatia // 7. hrvatski geološki kongres s međunarodnim sudjelovanjem. Zagreb: Hrvatski geološki institut, 166-166

Bonaccorsi, B.; Barbetta, S.; Tsitsifli, S.; **Boljat, I**.; Papakonstantinou, A.; Lukač Reberski, J.; Massari, C. ; Romano, E. (2023) Assessment of flooding impact on water supply systems: a comprehensive approach based on DSS // Abstract EGU23-2811, doi: 10.5194/egusphere-egu23-2811

Terzić, J.; Briški, M. ; **Boljat, I.;** Padovan, B.; Lukač Reberski J.; Živković, P. (2022) Hydrogeological concept of the coastal karst spring Golubinka, a case study from the Dinaric karst, Croatia // Man and Karst 2022 in Sicily, International Scientific Conference, September 12th-17th Custonaci, Italy / Ruggieri, Rosario (ur.). Custonaci, 2022. str. 36-36

Živković, P.; Miklin, L.; Lukač Reberski, J.; **Boljat, I.**; Terzić, J.; Čohilj, M.; Kranjčić, D.; Romano, E (2022) The preparation of the drinking water systems for possible hazards – the MUHA project // 9th International Conference WATER FOR ALL 2022, Book of Abstracts, Osijek, Croatia, 34-35

Romano, E.; Banovec, P.; **Boljat, I**.; Campione, E.; Čenčur Curk, B.; Dimkić, D.; Duro, A.; Kanakoudis, V.; Kovač, D.; Lukač Reberski, J.et al.. (2022) The Adrion Project MUHA – Multihazard framework for water related risks management: linking water utilities and civil protection mechanisms through water safety plans // 5th EWaS International Conference, Naples, Italy, 756-760

Selak, A.; Lukač Reberski, J.; Terzić, J.; **Boljat, I**.; Čapalija, B.; Leontić, M.; Bulović, B.; Patekar, M.; Filipović, M. (2020) Emerging contaminants in water resources of Croatian karst - boDEREC-CE project // EGU General Assembly 2020, EGU2020: Sharing Geoscience Online, 2020. EGU2020-575, 2 doi:10.5194/egusphere-egu2020-575

Terzić, J.; Lukač Reberski, J.; **Boljat, I**.; Selak, A., Baniček, I.; Patekar, M.; Grgasević, T.; Buljan, R.; Novosel, T.; Burić, H.; Stanić, N. (2019) Protection of Drinking Water Resources Through Integrated Land-Use Management Approach // Abstracts Book / Horvat, Marija ; Matoš, Bojan; Wacha, Lara (ed.) Zagreb: Croatian Geological Survey, 2019., 201-202

Borović, S.; Terzić, J.; Lukač Reberski, J.; Biondić, R.; **Boljat, I**.; Urumović, K. (2019) Iskustva hidrogeologa u provedbi EU projekata tijekom triju desetljeća // Aktualna problematika u vodoopskrbi i odvodnji / Beslić, Mile; Ban, Dario (ed.). Bol: REVELIN d.o.o., 49-58

Lukač Reberski, J.; Terzić, J.; Selak, A.; **Boljat, I.** (2019) "Novi onečišćivači" u podzemnim vodama Hrvatske - primjer projekata GeoTwinn i boDEREC-CE // Hrvatske vode u zaštiti okoliša i prirode - Croatian waters in environmental and nature protection / Biondić, D.; Holjević, D.; Vizner, M. (ed.) Zagreb: Croatian Waters, 513-521

Lukač Reberski, J.; Terzić, J.; Selak, A.; **Boljat, I**.; Patekar, M.; Filipović, M.; Baniček I. (2019) Emerging contaminants in groundwater environment – boDEREC-CE project // Abstracts Book / Horvat, M.; Matoš, B.; Wacha, L. (ed.). Zagreb: Croatian Geological Survey, 119-119

Boljat, I.; Terzić, J.; Lukač Reberski, J.; Selak, A.; Patekar, M.; Baniček, I. (2019) Preliminary results of hydrochemical dynamic of TOC in a karst aquifer in the northern part of the Dinaric karst in Croatia // 6th Croatian Geological Congress/ Abstracts Book, Zagreb: Croatian Geological Survey, 33

Selak, A.; **Boljat, I**.; Terzić, J.; Baniček, I.; Patekar, M.; Lukač Reberski, J.; Rubinić J. (2019) Vulnerability assessment and mapping in relation to climate change - Kupa River catchment // Stevanović, Zoran; Živanović, Vladimir; Milanović, Petar (ed.).Beograd: International Association of Hydrogeologists (IAH) National Chapter (NC) of Serbia, The Serbian Geological Society (SGS), Karst Commission, 58-59

Patekar, M.; Lukač Reberski, J.; **Boljat, I**.; Baniček, I.; Selak, A.; Terzić, J.; Rubinić, J. (2019) Drinking water protection through efficient land use practices – South Dalmatia case study // Proceedings of 4th conference of the IAH CEG and guide of geotrip of the IAH karst commission / Stevanović, Z. ; Živanović, V. ; Milanović, P. (ur.). Beograd: IAH National Chapter Serbia, 64-65

Boljat, I.; Terzić, J.; Lukač Reberski, J.; Selak, A. (2019) Outlining the principles of carbonate rocks denudation rate – Kupa River catchment case study // Man and Karst 2019 in Sicily / Ruggieri, Rosario (ed.) Ragusa: CIRS-Hyblean Center of Speleo-Hydrogeological Research, Italy,. 20

Patekar, M.; Lukač Reberski, J.; **Boljat, I**.; Baniček, I.; Selak, A.; Terzić, J. (2018) Efficient land use practices as tools of drinking water protection in complex karst environment – Dalmatia case study // Zbornik povzetkov/book of abstracts / Novak, Matevž; Rman, Nina (ed.). Velenje, Slovenia: Geological Survey of Slovenia, 72

Selak, A.; **Boljat, I**.; Terzić, J.; Baniček, I.; Patekar, M.; Lukač Reberski, J. (2018) Vulnerability mapping criteria identification for karstic part of Kupa river catchment area within CAMARO-D project // Zbornik povzetkov/ Book of abstracts / Novak, Matevž ; Rman, Nina (ed.). Velenje: Geological Survey of Slovenia, 80-81

Boljat, I; Terzić, J; Lukač Reberski, J. (2018) Identification of the hydrogeological and hydrochemical characteristics – northern part of the Dinaric karst in Croatia //"Man and Karst" Book of abstracts / Mulaomerović, Jasminko (ed.) Sarajevo: Center for karst and speleology, 5-6

Terzić, J.; Frangen, T.; **Boljat, I**. (2017) Hidrogeološka istraživanja za zaštitu vodoopskrbnih izvorišta u slijevu Vranskog jezera // Upravljanje jezerima i akumulacijama u Hrvatskoj - procesi, zaštita i valorizacija i Okrugli stol o aktualnoj problematici Vranskog jezera kod Biograda na Moru / Rubinić, Josip (ed.). Rijeka: Croatian Water Pollution Control Socienty, 295-299

Filipović, M.; Lukač Reberski, J.; Marković, T.; Terzić, J.; Frangen, T.; **Boljat, I**. (2015) Land use impact on groundwater quality in Prud catchment area within project DRINKADRIA// International IAH Conference "Groundwater Risk Assessment in Urban Areas "Constanta, Book of abstracts/ 15-15

Terzić, J.; Lukač Reberski, J.; Frangen, T.; Rubinić, J.; **Boljat, I**.; Burić, H. (2015) Hidrogeološki odnosi dijela južne Dalmacije i Hercegovine// 5th Croatian Geological Congress – Book of abstracts // Horvat, Marija ; Wacha, Lara (ed.), Croatian Geological Survey, 262-263