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Hydrochemical characterization of a Dinaric karst catchment in relation to emerging organic contaminants

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Abstract

The main findings of a hydrochemical investigation conducted within a typical Dinaric karst catchment located in Southern Croatia are outlined. The studied aquifer is drained by the Jadro and Žrnovnica springs, which are important for the regional and local water supplies, respectively. Presumably, there is intercatchment groundwater flow coming from the neighbouring Cetina River catchment. Various factors governing aquifer hydrochemistry and their interplay with emerging organic contaminants (EOCs) that were detected at different water resources in ng/L concentrations was assessed. A total of 26 sampling campaigns (October 2019 – October 2022) were conducted at two springs, in a river and at a deep borehole, all representative of this complex hydrogeological system. Assessment of major ion constituents and saturation indices calculated with PHREEQC revealed the sampled water resources are of a Ca-HCO_3 type due to the predominant weathering of the carbonate mineral calcite. Sharp spikes observed in chemographs indicated a highly karstified system with an effective conduit network allowing rapid spring responses to precipitation events. Water resources are of good chemical status, as affirmed by anthropogenic contamination indicators, with nitrates, chlorides and sulphates all below maximum threshold values. Strong positive correlations were found between EOCs concentration, number of detected compounds, and nitrates in the Cetina River, indicating a common origin, most likely wastewater. Identification of persistent EOCs including widely used repellent N,N-diethyl-meta-toluamide (DEET) during base flow conditions and its strong positive correlation with the Ca^{2+} content in both the Cetina and Jadro samples, suggests potential storage in the epikarst and aquifer matrix. This coupling of conventional hydrochemical indicators and novel markers of anthropogenic impacts, including EOCs, in vulnerable karst water resources is a crucial advancement in the assessment and management of emerging environmental and potential human health risks. Such an approach is pivotal for the sustainable protection of hydrogeologically intricate sites.

Keywords: karst hydrogeology, major ions, isotopes, time series analysis, emerging organic contaminants, Jadro and Žrnovnica springs

1. INTRODUCTION

Karst aquifers are intricate, highly dynamic and heterogeneous systems with enlarged fractures, an often well-developed conduit network, direct surface-subsurface connection via ponors, and high hydraulic conductivity, leading to preferential flow pathways and significant drinking water resources susceptible to anthropogenic contamination (PADILLA & VESPER, 2018; ŽIVANOVIĆ et al., 2022). Interpreting hydrochemical spring responses and identifying the origins of chemical compounds in karst water, some of which as natural traces allow the understanding of system functioning and structure (PERRIN, 2003; MUDARRA et al., 2011; SHEIKHY NARANY et al., 2019), can help to pinpoint contamination sources and pathways (HILLEBRAND et al., 2014). The hydrochemical research of the karst aquifer in question is fundamental in characterising the behaviour and origin of emerging organic contaminants (EOCs). In 26 sampling campaigns within the Jadro and Žrnovnica Dinaric karst catchment (Croatia), water samples were collected for ion and stable isotope analysis. Notably, in seven of these campaigns, samples were specifically taken for EOC analysis. EOCs are typically encountered in karst water resources at concentrations ranging from ng/L to µg/L, encompassing a myriad of anthropogenic organic compounds (LUKAČ REBERSKI et al., 2023). Some EOCs exert adverse effects on aquatic ecosystems and human health (CIZMAS et al., 2015; SCHRIKS et al., 2010).

Numerous uncertainties persist regarding the presence and behaviour of EOCs within large hydrogeological domains (LLAMAS et al., 2022). Due to diverse physico-chemical properties and sources, coupled with the intricacy of Dinaric karst structures and (ground)water pathways, datasets and analyses necessary to comprehend EOCs behaviour can be extensive. Multivariate statistical analyses have a broad application in simplifying large datasets, facilitating characterization of interrelationships among numerous hydrogeological variables, uncovering main hydrogeological processes, and providing insights into temporal and spatial variations (MATIATOS et al., 2014; JEBREEN et al., 2018). These invaluable analytical tools were employed in this study for the reliable interpretation of intricate karst dynamics and hydrochemical fluctuations (CAETANO BICALHO, 2012; VASIĆ et al., 2020; ĆUK ĐUROVIĆ et al., 2022).

The hydrological and hydrogeological features of the Jadro and Žrnovnica aquifer have been extensively documented in prior studies by JUKIĆ & DENIĆ-JUKIĆ (2008), KAPELJ et al. (2012), BONACCI & ANDRIĆ (2015), KADIĆ et al., (2019), and SELAK et al. (2024). Additionally, the (eco)toxicological aspects related to EOCs occurrence in this karst aquifer were previously explored by SELAK et al. (2022, 2024). This study seeks to enhance our understanding of karst aquifer behaviour under varying hydrological conditions by utilizing major ion and stable water isotopes data. The analysis of stable isotopes of oxygen δ^{18}O and hydrogen δ^{2}H has been effective in discerning groundwater provenance and karst aquifer recharge processes (CLARK & FRITZ, 1997). We posited that certain identified EOCs could correlate with physico-chemical parameters of water resources within the studied system. These relationships may facilitate the identification of potential contamination sources, behaviour, and transport. We pursued the objective of elucidating factors that govern the hydrochemistry of the Jadro and Žrnovnica springs catchment. This involved monthly sampling at two aforementioned karst springs, a deep borehole, and the adjacent Cetina River from which presumably groundwater inflows into the studied catchment (FRITZ, 1979; JUKIĆ & DENIĆ-JUKIĆ, 2015).

2. MATERIALS AND METHODS

2.1. Study area

The immediate catchment of the Jadro and Žrnovnica springs in Southern Dalmatia (Croatia) extends to an area of around 500 km^2 of heterogeneous relief defined by interchanging mountains and karst poljes. Both Jadro (35 m a.s.l.) and Žrnovnica (spring zone 78 to 90 m a.s.l.) emerge at the foot of Mosor Mountain where an impermeable coastal flysch belt meets with the permeable carbonate rocks of the hinterland (for detailed hydrogeological map readers are referred to SELAK et al., 2024). Typical karst, well-expressed geomorphology has a predominant NW-SE Dinaric orientation. The catchment mainly consists of karstified carbonate rocks of Mesozoic and partly Eocene age, characterized by their high permeability, lack of soil cover and consequently absence of surface watercourses (KAPELJ et al., 2012). Jadro with a mean discharge of 9.4 m^3/s (data period 2011-2022) is used for the regional water supply of Split and its wider area. Žrnovnica with mean discharge of 1.7 m^3/s (data period 2011-2022) supplies the nearby settlement and local agricultural areas. Previous studies denote overlap of the springs' catchments and groundwater exchange between them (JUKIĆ & DENIĆ-JUKIĆ, 2008; BONACCI & ROJE-BONACCI, 1997; BONACCI & ANDRIĆ, 2015; KADIĆ et al., 2017). Moreover, a tracer test undertaken at the Grabov mlin *ponor* proved the presence of intercatchment groundwater flows coming from the adjacent Cetina River catchment (Fig. 1) (GEOTEHNIKA, 1975; FRITZ, 1979), thereby expanding the overall catchment area.

The diverse relief affects the local climate, with a prevalence of temperate humid Köppen climate type *Cfa*, while the mountainous areas of Kozjak and Mosor exhibit a temperate humid climate type *Cfb* (ŠEGOTA & FILIPČIĆ, 2003). The mean daily air temperature, recorded at Split Marjan meteorological station at 122 m a.s.l. (data period 2009-2022), is 17.4°C. Annual precipitation averages 1304 mm (data period 2009-2022) with non-uniform spatial distribution within the catchment.

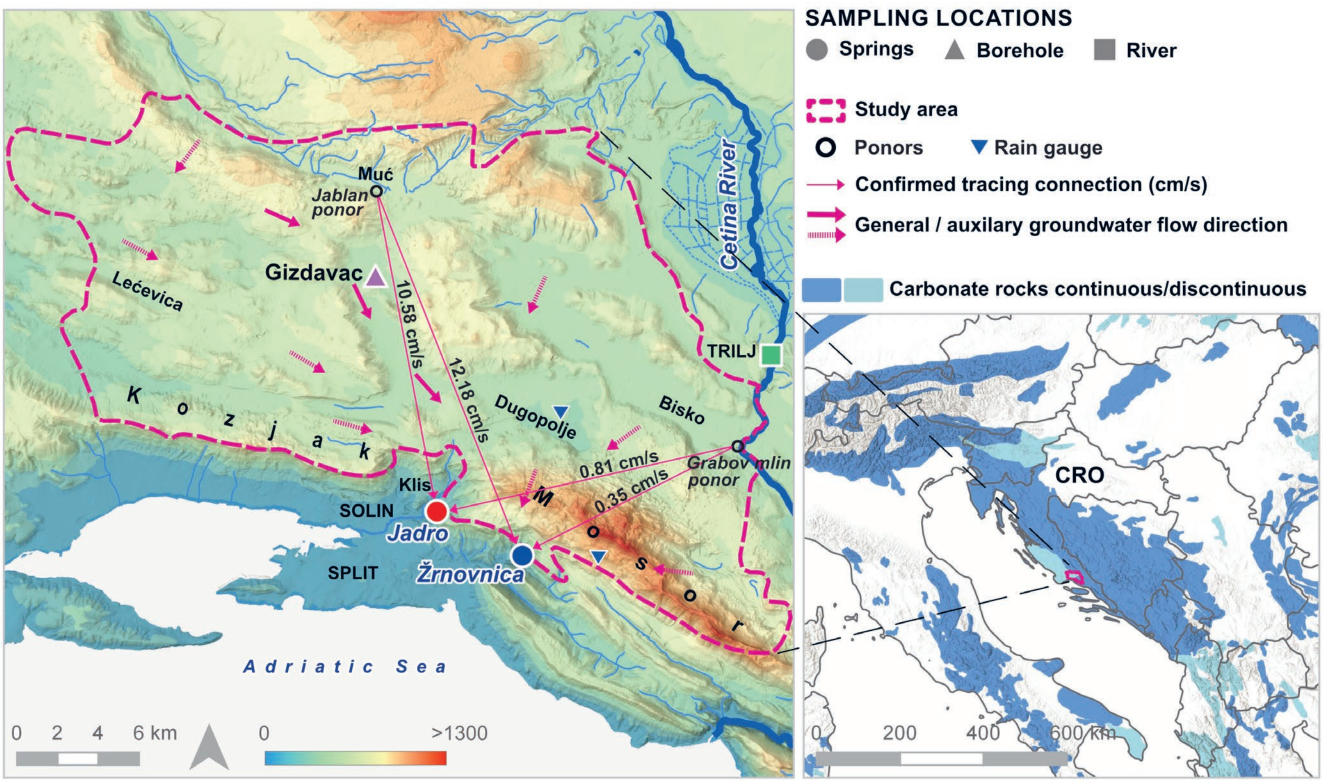

Figure 1. Location of the study area (World Karst Aquifer Map by BGR et al. (2017)).

Both springs respond rapidly (within 24 hours) to rainfall, indicating the presence of a substantial rapid flow component (KADIĆ et al., 2019) primarily generated by rainfall from the Dugopolje area (JUKIĆ et al., 2022). Consequently, rapid alterations in spring hydrochemistry, accompanied by prompt arrival of potential anthropogenic inputs can be anticipated.

2.2. Sampling and analysis of physico-chemical and hydrochemical parameters

In 26 sampling campaigns between October 2019 and October 2022, physico-chemical parameters were measured *in situ* using a WTW multi-parameter probe at the Jadro and Žrnovnica springs, Cetina River and Gizdavac borehole. Only Jadro was monitored in March 2019. The Covid-19 pandemic disrupted regular monthly surveys in 2019 and 2020. Measurements and sampling were undertaken directly at the springs, while a bucket of water was collected from the midstream of the Cetina River. Before conducting sampling and measurements in the bucket, three volumes of groundwater were pumped from the borehole Gizdavac to ensure a representative sample of the aquifer. During our research, among the three deep boreholes used for groundwater monitoring, only the Gizdavac borehole featured a functional pump (installed at the depth of 266 metres).

Alkalinity was determined by volumetric titration using 1.6N H_2SO_4 until reaching a pH 4.5, employing HACH digital titrator Model 16900 with bromocresol green-methyl red as an indicator. The water temperature and electrical conductivity data in the Jadro and Žrnovnica springs, as well as the Cetina River (upstream of Trilj City at Vedrine hydrological station), were recorded using HOBO data loggers U24 from Onset Computer Corporation (Bourne, MA, USA). The data was captured with hourly readings, commencing on 10th March 2021 for the Jadro and Žrnovnica springs, and on 11th March 2021 for the Cetina River.

A total of 84 water samples were collected, including 26 from each of the Cetina River, Jadro and Žrnovnica springs, and an additional 6 samples from the Gizdavac borehole. Samples were collected in 200 ml and 100 ml polyethylene bottles for analysis of major anions, cations, and stable water isotopes. For conservation purposes, samples were transported to the laboratory at 4°C and were analysed within 48h at the Hydrochemical laboratory of the Croatian Geological Survey. Principal ion composition was determined using ion chromatography on a DIONEX ICS-6000 DP. Water quality analyses were assessed for cation-anion balance by calculating the relative deviation from charge balance ($\Delta meq = 100 \times (\Sigma meq+ - \Sigma meq-)/(\Sigma meq+ + \Sigma meq-) < \pm 5\%$) (DOMENICO & SCHWARTZ, 1990). Stable water isotopes $\delta^{18}O$ and $\delta^{2}H$ were measured using isotope-ratio mass spectrometry with a Picarro L2130i (Santa Clara, USA) employing Cavity Ring-Down Spectroscopy (CRDS) technology. Isotope measurements were crosschecked against Picarro's standards, which are periodically verified against International Atomic Energy Agency (IAEA) standards: Vienna Standard Mean Ocean Water 2 (VSMOW2) and Standard Light Antarctic Precipitation 2 (SLAP2). Measurement precision was ± 0.3 ‰ for δ18O and ± 1 ‰ for δ2H. Deuterium excess (d-excess), defined as $d = \delta^2H - 8 \times \delta^{18}O$ (DANSGAARD, 1964), was used as an indicator of precipitation air mass origin and non-equilibrium conditions during evaporation. In order to take into account the infiltration of precipitation into the system, mean isotopic precipitation values were weighted with the amount of precipitation using the following equation (YURTSEVER & GAT, 1981):

$$\delta_w = \sum_{i=1}^{n} \frac{P_i \times \delta_i}{\Sigma P_i} \qquad (1)$$

where P_i is the monthly precipitation amount (mm), δ_i is the isotopic composition (‰), and n is the number of months.

The Croatian Meteorological and Hydrological Service provided discharge data for the Jadro and Žrnovnica springs for the period 2011-2022 and precipitation data for 2009-2022. Groundwater temperature and electrical conductivity data from the Gizdavac borehole logger (period 2010-2022) were provided by Croatian Waters. They also provided discharge data for the Cetina River, measured at the Trilj žičara station.

A Piper plot was used for classifying the predominant water types for the springs, groundwater, and surface water. This plot characterizes water based on major cation and anion content in meq/L, enabling analysis of the chemical composition for each water source (PIPER, 1944; APPELO & POSTMA, 2005).

Saturation indices (SI) were calculated to determine the chemical equilibrium between minerals and groundwater using PHREEQC v. 3.7.3.15968 (PARKHURST & APPELO, 1999; USGS, 2021). When SI values are negative, minerals will be dissolved, since the water is undersaturated with respect to them. Conversely, positive SI values indicate oversaturation and mineral precipitation.

2.3. Multivariate statistical analysis

Statistical analyses were performed in R (v. 1.4.1717; R CORE TEAM, 2021) using packages stats (R CORE TEAM, 2023), dunn.test (DINNO, 2017), corrplot (WEI & SIMKO, 2021), vegan (OKSANEN et al., 2022), and Hmisc (HARELL, 2023). The Shapiro-Wilk test was performed to investigate whether the hydrogeochemical data is normally distributed (p-value > 0.05). A nonparametric Kruskal-Wallis test with a post hoc Dunn test with Bonferroni correction (HOLLANDER & WOLFE, 1973; OGLE et al., 2023) was used to test for a statistically significant difference between the hydrochemical parameters from different sampling locations.

To gain insights into the relationships between the hydrochemical parameters in each sample, a correlation matrix was performed using Spearman's rank correlation coefficient (SPEARMAN, 1904) on a normalized dataset. Furthermore, the total sum of EOCs and their detection rate (number of detected compounds per sampling location) were correlated with major cations and anions.

4. RESULTS AND DISCUSSION

4.1. Hydrochemical composition of the springs, river and groundwater

Temporal variability in water quality inherent to the karstic system of Jadro and Žrnovnica springs was comprehensively monitored for three years. This facilitated the inclusion of the

Table 1. Main statistical descriptors of the physico-chemical parameters and discharge (m^3/s) observed within the study area. Water temperature (°C) and electrical conductivity (EC, µS/cm) data encompass the period from October 2019 to October 2022 for the Jadro, and Žrnovnica springs, and the Cetina river, and from 9.11.2010.-31.10.2022 for the Gizdavac borehole. Commencing in March 2021, logger data for both springs and the river were incorporated into the statistical analysis. pH data is given for the period from October 2019 to October 2022, while discharge data is from January 2011- December 2022 for the Jadro and Žrnovnica springs and from January 2019 – December 2022 for the Cetina river (Trilj žičara hydrological station). Major ion data (mg/L) is shown for the period October 2019 – October 2022.

Site	Statistics	T	EC	pH	Q	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-
Jadro spring	Min	12.47	259.62	7.25	3.73	2.38	0.15	2.21	70.71	3.69	1.50	3.17	204.50
	Max	13.99	433.24	8.02	56.62	21.44	0.95	8.03	79.50	40.89	4.32	22.70	274.50
	Mean	13.12	355.36	7.47	9.42	9.43	0.52	5.56	75.55	14.84	2.31	12.47	236.07
	Median	13.09	351.45	7.46	6.62	6.39	0.50	5.75	75.62	9.47	2.27	11.61	236.07
	Variance	0.18	1573.60	0.03	49.9	36.17	0.03	2.60	4.01	120.00	0.36	31.48	171.41
Žrnovnica spring	Min	12.32	263.50	7.35	0.27	2.96	0.22	1.49	66.52	4.10	0.88	2.87	192.76
	Max	13.38	399.84	8.52	17.00	20.47	1.97	6.77	73.10	39.31	3.89	15.99	256.20
	Mean	12.84	320.01	7.79	1.73	8.99	0.72	4.44	70.50	14.29	1.66	9.00	222.36
	Median	12.88	312.20	7.76	0.87	6.88	0.57	4.59	71.08	10.49	1.50	8.20	224.48
	Variance	0.08	1311.65	0.05	4.96	30.57	0.18	2.34	4.51	104.19	0.45	12.23	176.59
Cetina River	Min	6.89	263.10	7.80	11.10	1.71	0.32	3.32	55.55	2.53	0.52	9.36	176.90
	Max	16.90	562.00	8.57	305.00	52.76	2.25	7.37	73.07	85.92	3.26	28.49	267.18
	Mean	11.98	362.64	8.25	86.76	20.02	0.83	5.26	65.13	30.11	1.24	15.99	202.40
	Median	11.85	334.10	8.29	70.90	12.06	0.80	5.15	64.93	18.80	1.05	14.43	198.86
	Variance	8.26	5359.92	0.03	2771.38	304.56	0.19	0.91	10.57	713.30	0.43	23.10	316.55
Gizdavac borehole	Min	12.00	329.60	7.26	/	2.36	0.19	2.30	91.92	3.83	2.47	2.59	296.46
	Max	12.80	501.60	7.58	/	3.38	0.78	6.43	108.89	9.93	4.22	5.65	318.42
	Mean	12.44	399.82	7.38	/	2.89	0.61	5.43	97.96	5.59	3.02	3.73	306.73
	Median	12.40	396.17	7.36	/	2.94	0.68	6.24	96.39	4.98	2.72	3.54	307.44
	Variance	0.005	0.0003	0.01	/	0.20	0.05	2.64	40.79	5.07	0.42	1.06	65.85

entire spectrum of hydrological conditions and detailed hydrochemical characterization of the Dinaric karst aquifer during both dry and wet seasons. Table 1 summarizes the descriptive statistics of eleven physico-chemical parameters (T, pH, EC, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^-) ascertained across 26 distinct sampling campaigns and different hydrological conditions.

Consistent with findings for sizable karst aquifers (PULIDO-BOSCH, 2021), water temperature in both the springs and groundwater exhibited limited variability over the observed period. As expected, the Cetina River displayed a broader temperature range with pronounced daily oscillations due to direct contact with the atmosphere (Table 1). All water constituents in the investigated catchment exhibited a slightly alkaline pH typical of carbonate aquifers (MATIĆ et al., 2012; PATEKAR et al., 2022; MALDINI et al., 2023). Given the relatively low anthropogenic interference in the studied catchment (LOBOREC et al., 2015), we postulate that the electrical conductivity oscillations are predominantly governed by the dissolution of karst aquifer rocks. Comparatively, groundwater exhibited somewhat higher mean EC values, reflecting prolonged residence periods.

The Piper plot (Fig. 2) revealed a $Ca\text{-}HCO_3$ hydrogeochemical facies present in all the examined samples. This facies is indicative of prevailing carbonate weathering processes, aligning with the characteristic hydrochemical profile of Dinaric karst water resources, as substantiated in prior studies (MATIĆ et al., 2012; TERZIĆ et al., 2014; FILIPOVIĆ et al., 2023; MALDINI et al., 2023). In contrast to Ca^{2+}, Mg^{2+} exhibits relatively low abundance (Table 1, Fig. 1), suggesting the predominance of limestone deposits over dolomite. This observation aligns with the lithological analysis of the

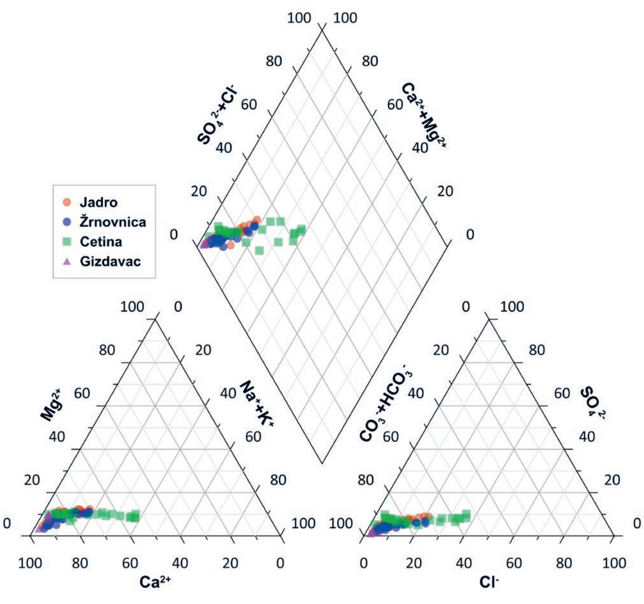

Figure 2. Piper plot presentation of the hydrochemical composition of the springs, river, and groundwater samples within the study area.

Gizdavac borehole, which identified limestone as the sole aquifer rock constituent in that area (KAPELJ et al., 2006).

SI values calculated using PHREEQC (Table S3) indicate that most water samples are oversaturated with respect to calcite (Fig. 4). $SI_{calcite}$ values ranged between -0.02 and 1.2 in the springs, ranged from 0.2 to 0.5 in groundwater, and varied between 0.4 and 1 in the Cetina River. According to WHITE (1997), a $SI_{calcite}$ of -0.3 marks the kinetic threshold for slowdown in dissolution processes, while a $SI_{calcite}$ value of +0.5 indicates the onset of precipitation. In contrast to the Jadro spring and groundwater samples, the Cetina River exhibited oversaturation with respect to dolomite, while over half of the Žrnovnica spring samples showed dolomite undersaturation. These carbonate minerals are the prominent constituents of the host rocks within the studied aquifer. Accordingly, river and spring samples exhibited Ca^{2+} prevalence for cations, with an abundance order generally observed as $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$. Groundwater samples demonstrated a distinctive abundance order of cations, with Ca^{2+} being the most prevalent, followed by $Mg^{2+} > Na^{+} > K^{+}$. In groundwater and springs, a robust positive correlation (0.69 and 0.67, respectively) between Ca^{2+} and HCO_3^- suggests their common origin from calcite dissolution. Most water samples were enriched with Ca^{2+} and Mg^{2+} relative to HCO_3^- (Fig. 3a) which confirms how the dissolution of calcite and dolomite by carbonic acid is not the only source of alkaline earths. Excess Ca^{2+} and Mg^{2+} charges must be balanced by other major anions through dissolution or ion exchange processes. Figure 3b shows samples aligning with the 1:1 line, suggesting gypsum and anhydrite dissolution alongside calcite and dolomite dissolution. This observation is further supported by gypsum saturation indices averaging around -2.5 for the springs, -2.9 for groundwater, and -2.4 for the Cetina River, along with anhydrite saturation indices averaging around -3 for the springs, -3.3 for groundwater, and -2.8 for the Cetina River (Table S3). According to FRITZ'S hydrogeological study (1979), gypsum and anhydrite are expected near the surface in the northern part of the catchment along a fault delineating contact with Triassic deposits and subsequent strata, north of Muć *polje*.

The average $[Mg^{2+}]/[Ca^{2+}]$ molar ratios observed in all water samples approximated 0.1, as expected in aquifers draining predominantly limestone rocks. Such ratios imply dolomite dissolution and calcite precipitation processes (APPELO & POSTMA, 2005). We noted a conspicuous decline in $[Mg^{2+}]/[Ca^{2+}]$ during the hydrograph peaks and higher values in the recession periods. The highest values occurred at the later stages of recessions, consistent with the prevailing interpretation of increased mean residence time of karst groundwater during recession periods. Elevated $[Mg^{2+}]/[Ca^{2+}]$ ratios can be indicative of matrix water or diffuse recharge through the epikarst, whereas lower $[Mg^{2+}]/[Ca^{2+}]$ values observed in spring water are associated with conduit recharge (TORAN & REISCH, 2013). The observed lower $[Mg^{2+}]/[Ca^{2+}]$ values, distinct positive and negative fluctuations in chemographs (Fig. 4), and rapid hydrodynamic responses corroborate a highly karstified system with effective conduit network that transmits infiltration to springs under high flow conditions and the absence or presence of only thin overlying layers that fail to dampen the springs' response to rainfall events. Mobile compounds including Cl^- and SO_4^{2-}, which tend to accumulate in soil solution due to elevated evapotranspiration processes during the summer months (GOLDSCHEIDER & DREW, 2007), display a concentration peak with the first significant autumn rainfall events (Fig. 4). The measured levels of Cl^-, SO_4^{2-} and NO_3^- at all sampling sites remained appreciably below the maximum allowed concentrations (250 mg/L, 250 mg/L, and 50 mg/L, respectively) specified in the Drinking Water Directive (2020/2184).

In contrast to the springs and groundwater, the Cetina River displayed a greater degree of variability in chemical composition, particularly with respect to concentrations of Cl^-, Na^+, HCO_3^-, and K^+ ions (Table 1, Fig. 4). The strongest positive correlation of R=0.99 was observed between Na^+ and Cl^-

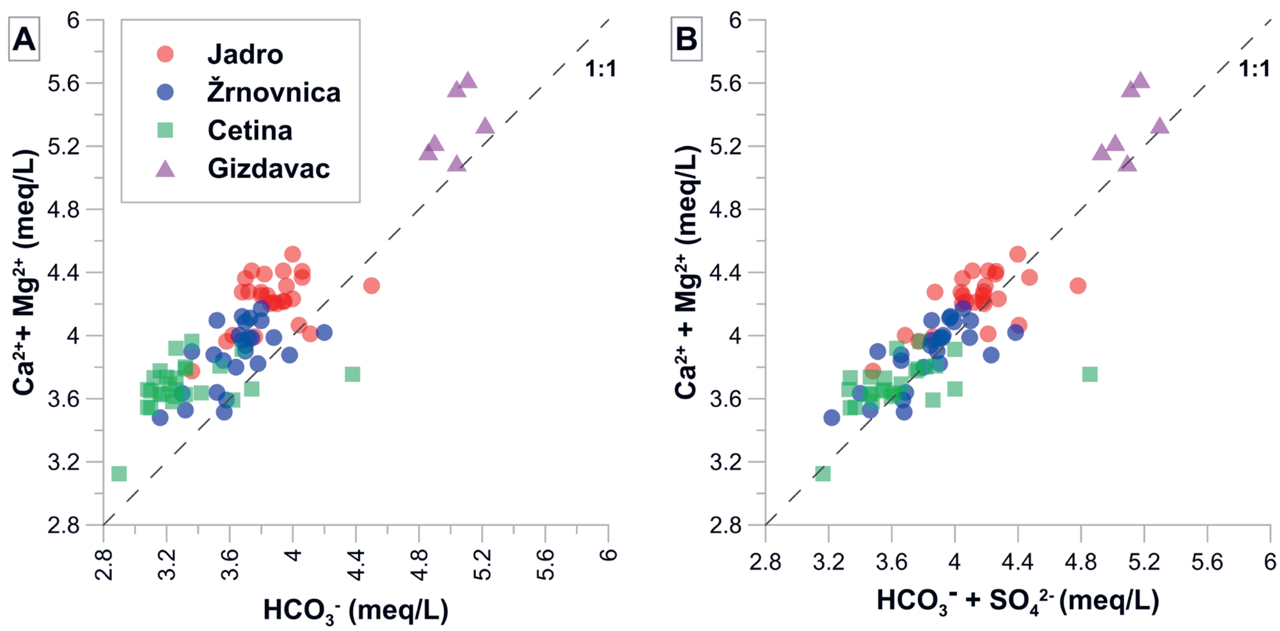

Figure 3. A) Biplots of ($Ca^{2+}+Mg^{2+}$) versus (HCO_3^-). B) ($Ca^{2+}+Mg^{2+}$) versus ($HCO_3^-+SO_4^{2-}$).

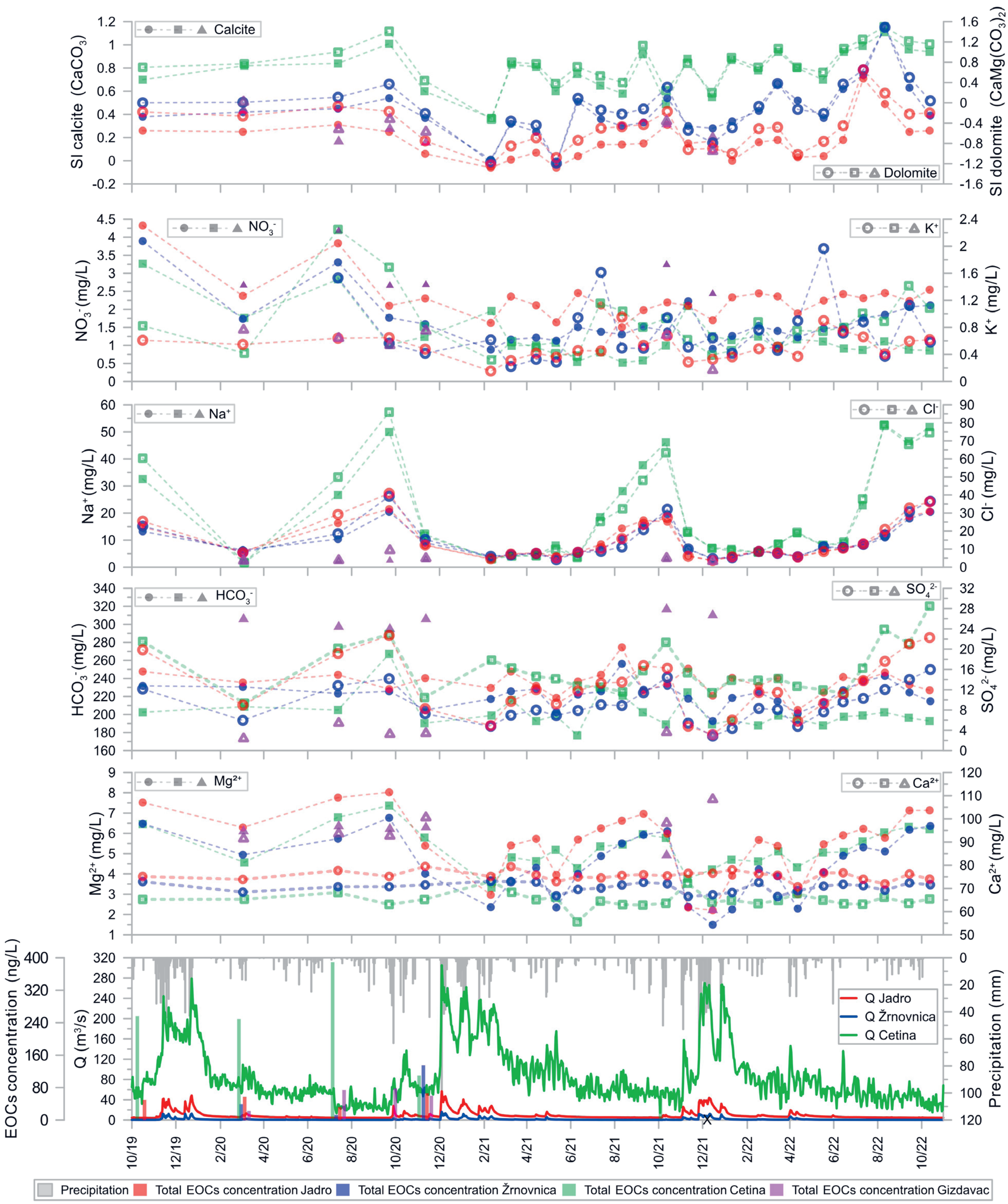

Figure 4. Multivariate chemographs showing the temporal variation in major ion and saturation indices for calcite and dolomite observed at the Jadro and Žrnovnica springs, Cetina River and in groundwater from the Gizdavac borehole. Total EOCs concentration per location (bar graph) were reported in SELAK et al. (2022a). X on the x-axis marks the sampling campaign with no EOCs detected above limits of detection.

ions for the Jadro, Žrnovnica, springs and the Cetina River (Fig. S1). Kruskal-Wallis post hoc Dunn test revealed no statistically significant distinction in terms of Cl^- ion content among the observed locations (except for Cetina vs. Gizdavac) (Table S2). This lends support to the presence of intercatchment groundwater flow, whereby groundwater from the Cetina catchment traverses towards the Jadro and Žrnovnica springs. Elevated Na^+ and Cl^- concentrations are usually anticipated within coastal aquifers affected by seawater intrusion or input of airborne salts (LUKAČ REBERSKI et al., 2020; PLAN-

TAK et al., 2021; PATEKAR et al., 2022; FILIPOVIĆ et al., 2023). In our case, the impermeable Eocene flysch coastal belt hinders Adriatic Sea intrusion into the land, as observed by FRITZ (1979). However, strong positive correlations between SO_4^{2-}, Mg^{2+}, Na^+, and Cl^- in all water samples, and between those ions and K^+ in the Jadro spring and Cetina River may indicate sea spray influence (Fig. S1). Furthermore, the presence of chloride may stem from evaporite dissolution (SCHMIDT et al., 2013) or anthropogenic sources including wastewater and fertilizers (DOGDEN et al., 2017), warranting additional research for comprehensive elucidation.

Elevated nitrate concentrations are typically associated with agricultural practices, encompassing the application of synthetic fertilizers (e.g. N/P/K and ammonium sulphate), the utilization of manure in cultivated fields, and septic systems discharges (DOGDEN et al., 2017). The mean NO_3^- concentrations observed within the research area remained below the recorded average in Croatian Dinaric karst groundwater, which stands at approx. 5 mg/L (ONDRASEK et al., 2021). Over the course of six sampling campaigns at the deep borehole site, groundwater exhibited NO_3^- concentrations somewhat higher than those observed at other sampling locations, with mean values of 3.02 mg/L compared to 2.31 mg/L for the Jadro, and 1.66 mg/L for the Žrnovnica springs, and 1.24 mg/L for the Cetina River (Table 1, Fig. 4). LOBOREC et al. (2015) observed the trajectory of increasing nitrate concentrations in the Jadro spring over nearly four decades (1975-2014), substantiating the growing anthropogenic pressures exerted upon the catchment area. The presence of nitrates in groundwater may suggest rapid infiltration processes (CELLE-JEANTON et al., 2003), which is also indicated by the occurrence of biodegradable EOCs gabapentin identified in groundwater from the Gizdavac borehole (Selak et al., 2024). NO_3^- displayed a strong positive correlation with SO_4^{2-} in the Žrnovnica spring (R=0.77) and groundwater from the Gizdavac well (R=0.81) (Fig. S1), as well as with K^+ in groundwater (R=0.75). These ions could have similar anthropogenic sources in fertilizers and wastewater (HAN et al., 2016; MASS et al., 2019; TORRES-MARTÍNEZ et al., 2020). As previously mentioned SO_4^{2-} may originate from the dissolution of gypsum deposits north of Muć, highlighting the intricate interplay between inherent hydrogeological processes and potential site-specific pollution sources. Given the absence of concurrent stable nitrogen isotope analysis alongside nitrate measurement, a definite attribution of nitrate concentrations in groundwater to wastewater or agriculture pollution sources cannot be conclusively established. The strategically situated borehole along the regional Muć-Gizdavac-Klis fault, delineates a prevailing groundwater flow direction from the NW to the SE towards the Jadro and Žrnovnica springs (identified through a tracer test from the Jablan ponor with high apparent groundwater flow velocities of 10.58 cm/s and 12.18 cm/s, respectively) (FRITZ, 1979). According to this, there is the potential conveyance of agricultural pollutants including fertilizers and pesticides from Muć *polje* towards the sampled groundwater and spring locations within a relatively short time. It should be noted how recent research questions the reliability of the tracer tests conducted, as the electrical conductivity of the Jadro spring does not display the rainfall effect from Muć despite the highest apparent groundwater velocity (JUKIĆ et al., 2022). Further investigation is necessary to deepen our understanding of the sources and pathways of anthropogenic contaminants within the studied catchment.

4.2. Stable water isotopes

Table 2 provides a descriptive statistical overview of the stable water isotopes $\delta^{18}O$ and δ^2H, including deuterium excess, for springs, river, groundwater, and precipitation. Cetina River $\delta^{18}O$ data deviated from a normal distribution (Table S1). The results for the Jadro and Žrnovnica springs corroborates earlier research by KAPELJ (2001; published in BRKIĆ et al., 2020) and POLJAK (2014), aligning with the average stable water isotopic values observed in Dalmatian karst springs, which typically vary between -6.7‰ and -8.7‰ for $\delta^{18}O$ and -39.7‰ and -58‰ for δ^2H (BRKIĆ et al., 2020). The isotopic content of precipitation is slightly depleted compared to the data presented by HUNJAK et al. (2013) for the Split station, (located outside of catchment), that had an average of -5.5‰ for $\delta^{18}O$, -34.7‰ for δ^2H and d-excess of 9.2 (for period 2007-2010). This is to be expected as our rain gauges were positioned in the hinterland and at higher altitudes than the Split station (located near the coast at 40 m a.s.l.; Fig. 1). The average d-excess values of karst groundwater, (springs and borehole) and surface water, correspond to the d-excess values of West Mediterranean precipitation (GAT & CARMI, 1970; CELLE-JEANTON et al., 2001). Precipitation at the Dugopolje rain

Table 2. Elementary statistics of isotopic signatures for all sampling points (data period October 2019 – October 2022 for springs, river, and groundwater, and data period March 2021 – October 2022 for precipitation).

Sampling location	Altitude (m.a.s.l.)	$\delta^{18}O$ (‰)				δ^2H (‰)				d-excess (‰)
		min	max	mean	sd	min	max	mean	sd	mean
Jadro	35	−7.82	−7.05	−7.47	0.17	−47.31	−41.44	−44.76	1.43	15
Žrnovnica	90	−8.05	−7.09	−7.56	0.22	−47.58	−40.79	−44.97	1.94	15.53
Cetina	~294	−8.46	−7.20	−8.13	0.3	−52.93	−44.06	−50.1	2.02	14.96
Gizdavac	~356	−7.09	−6.66	−6.94	0.17	−41.85	−39.31	−40.89	0.96	14.62
Rain gauge Dugopolje*	497	−9.09	−1.59	−6.42***	1.94	−58.45	−6.33	−39.72***	14.16	11.66***
Rain gauge Mosor**	869	−10.25	−3.43	−7.45***	1.85	−62.53	−13.69	−43.33***	13.47	16.28***

Due to insufficient rain amounts collected in the rain gauge, the following data is missing: *no data for July 2021 and 2022; **no data from July to November 2021, and for July 2022. *** amount-weighted mean values.

gauge displayed a weighted-mean d-excess of 11.66‰, which is close to the global mean d-excess of 10‰ associated with Atlantic air masses, but indicates a slight Mediterranean influence. The Mosor rain gauge recorded predominantly higher weighted-mean d-excess values (16.28‰), signifying a stronger Mediterranean influence, but also the altitude effect (the rain gauge is located at 869 m a.s.l. in a mountainous area).

Water isotopic content is affected by meteoric processes and orographic effects (BRKIĆ et al., 2020). KAPELJ et al. (2012) determined an altitude gradient variation in $\delta^{18}O$, ranging from -0.2‰ to -0.4‰/100 m. Slightly more negative $\delta^{18}O$ and $\delta^{2}H$ values for Žrnovnica than Jadro can be attributed to the altitude effect, i.e. recharge with precipitation from higher altitudes. The Cetina River had an even lower average $\delta^{18}O$ and $\delta^{2}H$ values, which is attributed to a recharge area of higher altitudes and a stronger continental influence. In June 2021, there were notable similarities in the stable isotopic composition, particularly for $\delta^{18}O$ and Cl^- content (Fig. 4), between both springs and the Cetina River. This observation hints at inter-catchment groundwater flow coming from the Cetina River to the Jadro and Žrnovnica springs. Such inflows from the adjacent Cetina River catchment were identified by JUKIĆ & DENIĆ-JUKIĆ (2015) in the partial auto-correlation function of the discharge signal. This phenomenon is likely more pronounced during dry periods, as indicated by the increase in the minimum flow rates at both springs (KADIĆ et al., 2017).

4.3. Correlation between hydrochemical parameters and emerging organic contaminants

Exploring relationships between emerging organic contaminants and other chemical indicators helps to understand the

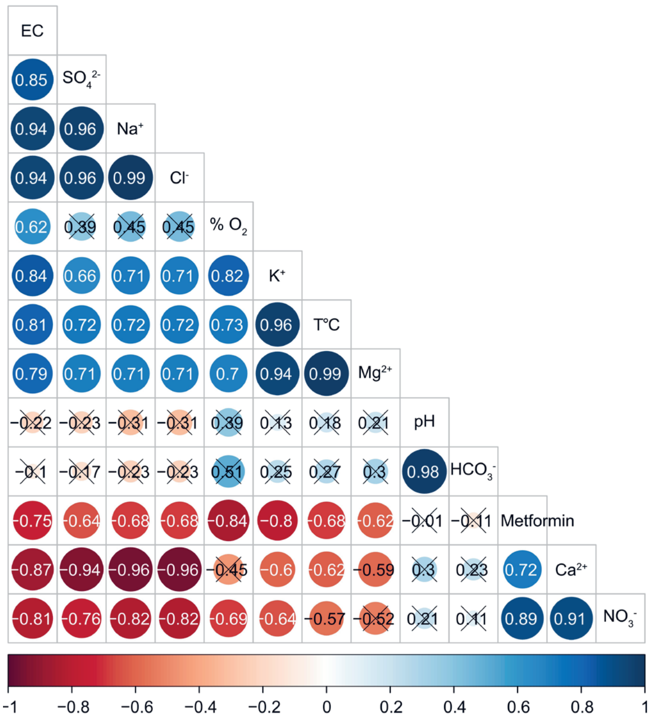

Figure 5. Correlation matrix of hydrochemical parameters for Cetina (correlation coefficients order with AOE algorithm - the angular order of the eigenvectors) and EOC metformin. Values marked with X are not significant.

sources, occurrence, and transport of emerging contaminants in karst aquifers (KATZ & GRIFFIN, 2008; HILLEBRAND et al., 2014; ZEMANN et al., 2015). Owing to a limited quantity of samples, the correlation between the hydrochemical parameters and concentrations of a particular EOC was solely feasible for the Cetina River. Readers are referred to the work by Selak et al. (2022b) for a comprehensive inventory of analysed and identified EOCs along with their limits of detection and physico-chemical properties. A very mobile pharmaceutical compound metformin ($C_4H_{11}N_5$) was the only EOC detected more than twice at a single location (recorded in 4 out of 7 campaigns). Metformin exhibited a statistically significant and strong positive correlation with Ca^{2+} and NO_3^- ions in the Cetina River, with correlation coefficients of R=0.72 and R=0.89, respectively (Fig. 5).

Additionally, a strong positive correlation (R=0.87) was observed between the total concentration of EOCs and NO_3^- ion in samples collected from the Cetina River (Fig. 6). Nitrates, often indicative of anthropogenic contamination from wastewater or agriculture, were previously associated with particular EOCs, including herbicides (HILLEBRAND et al., 2014), X-ray contrast media (ZEMANN et al., 2015), and carbamazepine (DOUMMAR et al., 2014). Nitrates showed a positive correlation with increasing EOCs detection number (ZEMANN et al., 2015; RICHARDS et al., 2023) and total EOC sum (SCHAIDER et al., 2014). Similar to findings of ZEMANN et al. (2015) and RICHARDS et al. (2023), this research identified a statistically significant correlation (R=0.90) between the EOCs number and NO_3^- concentrations in the Cetina River (Fig. 6). These positive correlations validate the EOCs sources map and conceptual model presented by SELAK et al. (2024).

In groundwater samples, EOCs detection number and total concentration were strongly negatively correlated with HCO_3^- and Ca^{2+} ions, while a strong positive correlation was observed between the EOCs detection number, the total concentration and Mg^{2+} ion (Fig. 6). The prevalence of calcium and bicarbonate ions in groundwater, attributed to the predominance of limestone in the aquifer rocks, suggests that in this tectonically disturbed and highly permeable part of the aquifer with low matrix porosity typical of Dinaric karst aquifers, the detected EOCs undergo swift infiltration. This explains the presence of rapidly biodegradable gabapentin in the sample extracted from the Gizdavac borehole. In the Cetina River, we observed strong negative correlations (in descending order of correlation coefficient strength) between the number of EOCs detections, the total concentration sum of EOCs, and SO_4^{2-}, Cl^-, and Na^+, as well as between EOCs detection rate and Mg^{2+} and K^+ ions, as depicted in Fig. 6. Similar patterns were noted in Jadro samples, where the total EOCs concentration and detection number displayed strong negative correlations with K^+, Na^+, Cl^-, SO_4^{2-}, and Mg^{2+} (Fig. 6). Moreover, Žrnovnica spring samples exhibited strong negative correlations between EOCs detection rate and Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, and K^+ ions. Since Cl^-, Na^+, K^+, SO_4^{2-}, and Mg^{2+} ions can partly originate from sea spray, the negative correlation discerned with the EOCs number and total concentration may suggest the absence of atmospheric input of EOCs in the study

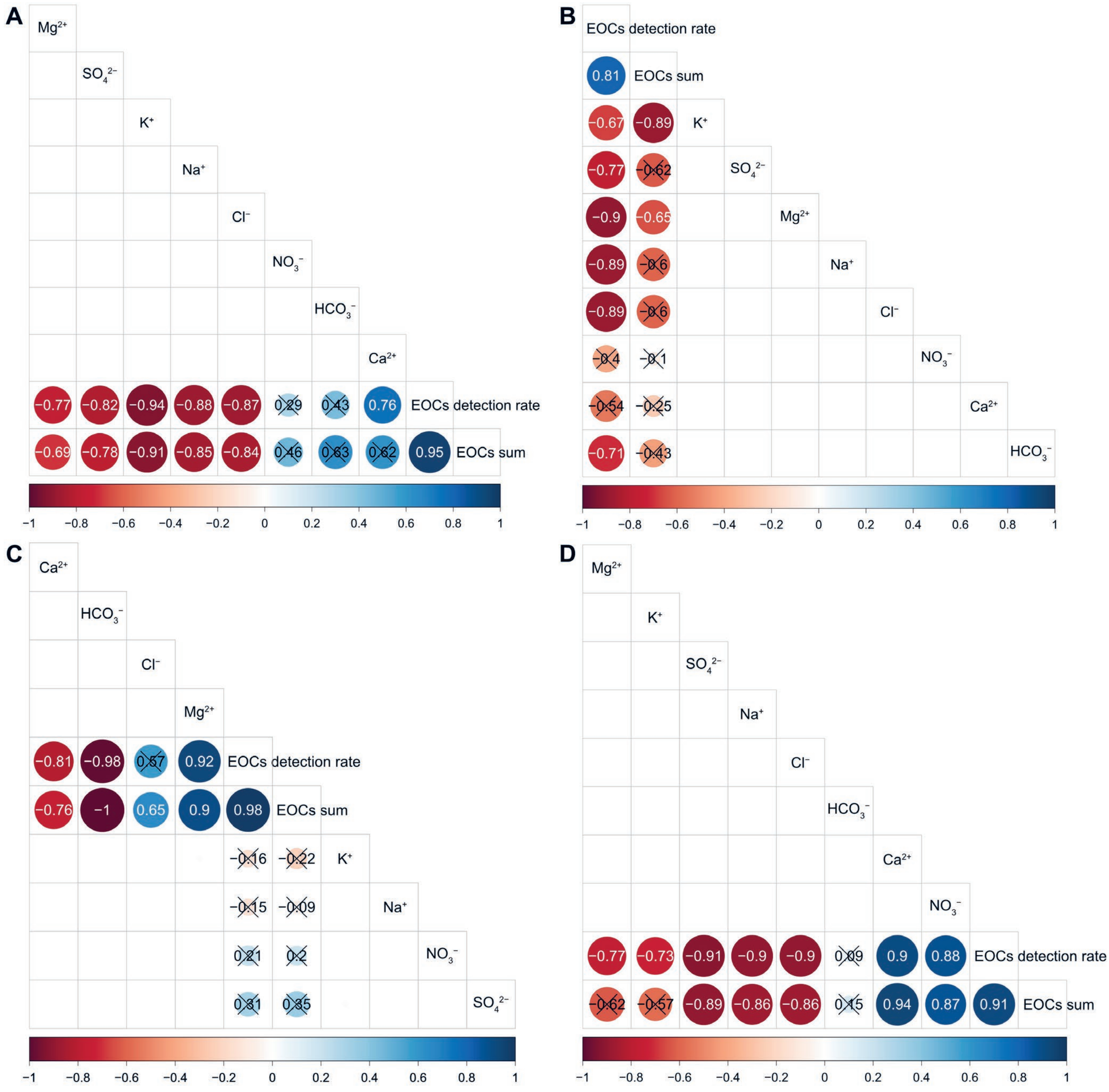

Figure 6. Correlation matrix of hydrochemical parameters for the Jadro (A), Žrnovnica (B), Gizdavac (C), and Cetina (D) (correlation coefficients order with AOE algorithm - the angular order of the eigenvectors), EOCs detection number and total concentration sum. Values marked with X are not significant.

area. Conversely, a strong positive correlation was observed between the EOCs detection number and total concentration sum with respect to Ca^{2+} content in the Cetina River and EOCs detection number and Ca^{2+} in the Jadro spring samples. HILLEBRAND et al. (2014) established a robust correlation between calcium ions and the herbicide atrazine, which they attributed to the gradual release of atrazine from the karst rock matrix into the groundwater. Persistent and mobile compounds including DEET detected in the Cetina River and Jadro spring, showed limited attenuation within the studied karst aquifer (SELAK et al., 2024). This compound showed elevated concentrations during autumn runoff and persisted even during base flow conditions, suggesting potential storage within the epikarst and matrix.

5. CONCLUSIONS

This hydrochemical characterization study has provided a comprehensive examination of the Jadro and Žrnovnica karst aquifer in both spatial and temporal dimensions, while analyzing factors influencing the quality of its water resources. The hydrochemical fingerprint of this aquifer is typical for coastal Dinaric aquifers characterised by highly karstified structures, a prevalence of limestone, as indicated by the Ca-HCO_3 hydrogeochemical facies, and clear evidence of seaspray influence. Stable isotope signatures confirmed a common catchment area shared by the Jadro and Žrnovnica springs while also revealing intercatchment groundwater flow originating from the Cetina River.

Alongside the hydrodynamics, hydrochemical characterization has a pivotal role in comprehending the complexity of karst systems and assessing their susceptibility to EOCs. Sharp spikes in chemographs, alongside rapid hydrodynamic responses are evidence of a highly karstified and inherently vulnerable system. Its well-developed conduit network can swiftly transport EOCs via infiltrated water to springs under high flow conditions, as the absence of or thin overlying "protective" layers fail in their attenuation. While conventional indicators of anthropogenic pollution including NO_3^-, Cl^-, and SO_4^{2-} remain below their respective maximum allowable concentrations in drinking water, detections of EOCs reflect the anthropogenic impact on water resources within the studied catchment. Significant strong positive correlation between metformin and NO_3^- concentration in the Cetina River, as well as significant strong positive correlation between total EOCs concentration, number and NO_3^- ion, indicates potential contamination stemming from wastewater or agriculture. Robust significant positive correlation between EOCs detection rate and Ca^{2+} content observed in the Jadro spring samples suggests the persistence of certain EOCs including DEET within the epikarst and aquifer matrix. To enhance the reliability of multivariate analyses of hydrochemical parameters and EOCs, we recommend that future research should involve a larger sample number and focus on monitoring prioritized EOCs. In the context of this Dinaric karst catchment, we propose directing research efforts towards persistent and mobile EOCs, for example; DEET, 1-H benzotriazole, and metformin. The future long-term monitoring and concurrent utilization of hydrochemical markers and novel tracers including EOCs will offer enhanced clarity in discerning the intricate interplay of dominant factors shaping hydrochemical patterns within karst aquifers subject to various anthropogenic pressures.

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Supplement 1. – Figure S1

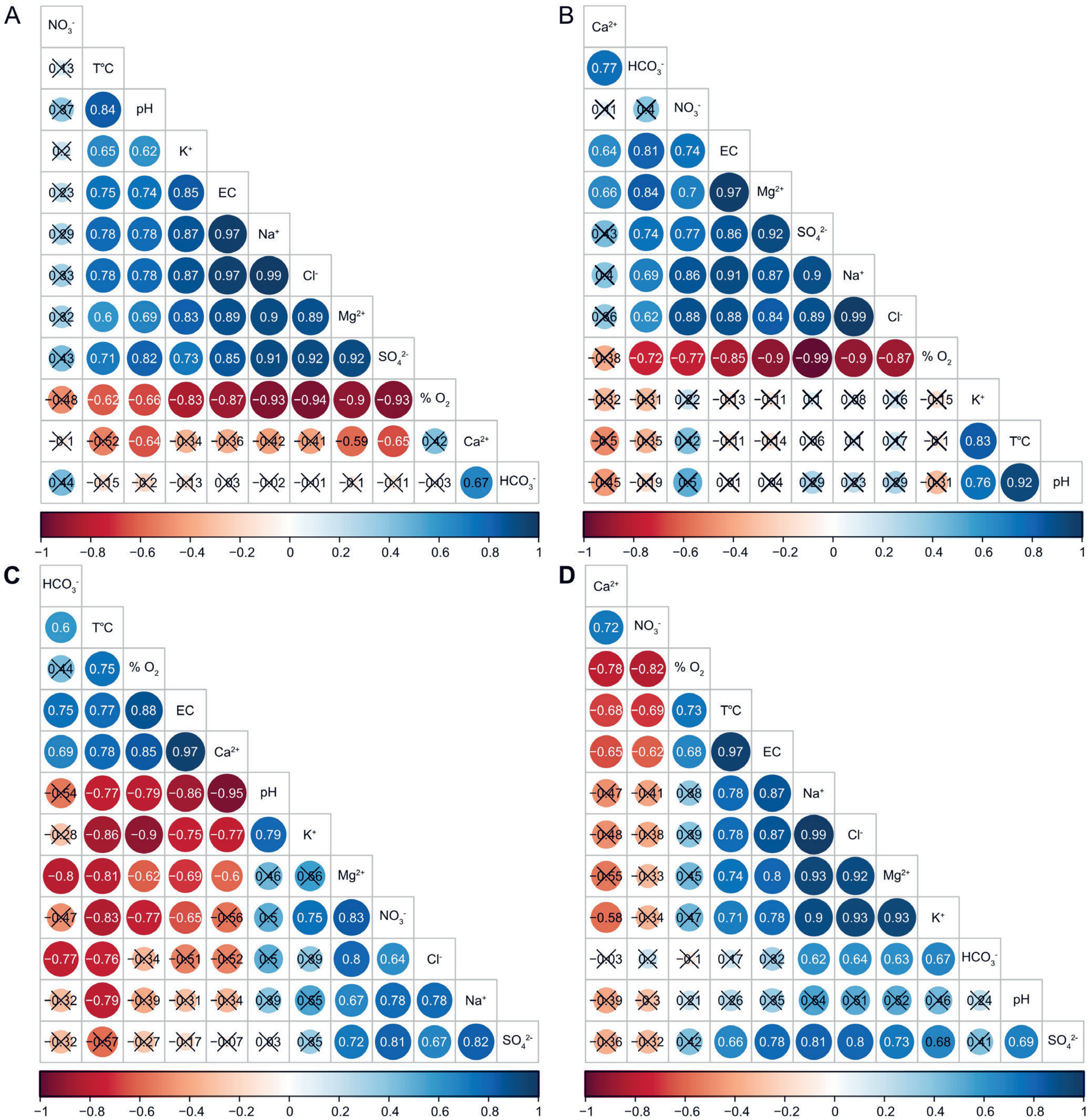

Figure S1. Correlation matrix of physicochemical parameters for Jadro (A), Žrnovnica (B), Gizdavac (C), and Cetina (D) (correlation coefficients order with AOE algorithm – the angular order of the eigenvectors). Values marked with X are not significant.

Supplement 2. – Tables S1, S2 and S3.

Table S1. Results of Shapiro-Wilk test (values in bold indicate normally distributed data i.e. p-value>0.05) (data October 2019 – October 2022).

	Jadro		Žrnovnica		Gizdavac		Cetina	
Parameter	W	p-value	W	p-value	W	p-value	W	p-value
Temperature	0.96	**0.35**	0.98	**0.76**	0.90	**0.40**	0.96	0.42
pH	0.89	0.01	0.92	0.04	0.89	**0.34**	0.96	0.49
Electrical conductivity	0.98	**0.83**	0.97	**0.52**	0.93	**0.61**	0.89	0.01
Na^+	0.86	2.36E-03	0.85	1.41E-03	0.89	**0.30**	0.84	8.02E-04
K^+	0.97	**0.73**	0.84	1.03E-03	0.80	**0.06**	0.87	2.93E-03
Mg^{2+}	0.92	4.75E-02	0.94	**0.14**	0.71	0.01	0.99	**1.00**
Ca^{2+}	0.97	**0.62**	0.90	0.02	0.90	**0.36**	0.87	3.01E-03
Cl^-	0.84	7.73E-04	0.82	4.68E-04	0.78	0.04	0.85	1.25E-03
HCO_3^-	0.95	**0.28**	0.97	0.50	0.95	**0.77**	0.81	2.28E-04
NO_3^-	0.76	3.74E-05	0.79	1.02E-04	0.79	**0.05**	0.78	7.93E-05
SO_4^{2-}	0.96	**0.40**	0.97	**0.54**	0.87	**0.23**	0.92	0.04
$\delta^{18}O$	0.96	**0.48**	0.96	**0.43**	0.83	**0.11**	0.86	2.40E-03
δ^2H	0.97	**0.71**	0.94	**0.16**	0.86	**0.18**	0.92	**0.05**
O_2 (%)	0.76	4.48E-05	0.93	**0.07**	0.95	**0.77**	0.91	0.02
	Jadro		**Žrnovnica**		**Gizdavac**		**Cetina**	

Table S2. Results of Kruskal-Wallis post hoc Dunn test (values in bold indicate significant difference i.e. p.adjusted<0.05) (data October 2019 – October 2022).

Comparison	P. adjusted						
	Ca^{2+}	Mg^{2+}	Na^+	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-
Cetina – Gizdavac	**1.72E-08**	1	**1.28E-04**	**1.94E-03**	**8.49E-08**	**5.06E-06**	**5.11E-06**
Cetina – Jadro	**5.14E-12**	1	0.34	0.34	**2.17E-08**	0.13	**1.44E-07**
Cetina – Žrnovnica	**5.40E-03**	0.73	0.3	0.37	**6.85E-03**	**4.60E-05**	0.8
Gizdavac – Jadro	0.71	1	**0.01**	0.09	0.24	**2.64E-03**	0.13
Gizdavac – Žrnovnica	**5.63E-04**	0.42	**0.01**	0.08	**1.40E-03**	0.17	**2.64E-03**
Jadro – Žrnovnica	**7.63E-04**	**0.04**	1	1	0.05	0.18	**6.21E-03**

Table S3. Main statistical descriptors of saturation indices (SI) calculated with PHREEQC for Jadro, Žrnovnica, Gizdavac, and Cetina samples (data October 2019 – October 2022).

Site	Statistics	Calcite ($CaCO_3$)	Dolomite ($CaMg(CO_3)_2$)	Anhydrite ($CaSO_4$)	Gypsum ($CaSO_4 \cdot 2H_2O$)
Jadro spring	Min	−0.06	−1.22	−3.41	−2.97
	Max	0.71	0.65	−2.60	−2.16
	Mean	0.17	−0.51	−2.89	−2.45
	Median	0.16	−0.49	−2.87	−2.43
Žrnovnica spring	Min	−0.02	−1.19	−3.49	−3.05
	Max	1.16	1.49	−2.76	−2.32
	Mean	0.43	−0.07	−3.04	−2.60
	Median	0.39	−0.10	−3.03	−2.59
Cetina River	Min	0.37	−0.32	−3.04	−2.55
	Max	1.11	1.50	−2.56	−2.13
	Mean	0.79	0.77	−2.82	−2.36
	Median	0.82	0.77	−2.84	−2.37
Gizdavac borehole	Min	0.17	−0.93	−3.47	−3.03
	Max	0.45	0.04	−3.13	−2.68
	Mean	0.27	−0.43	−3.31	−2.86
	Median	0.26	−0.42	−3.31	−2.86