Long-term and seasonal trends of water parameters in the karst riverine catchment and general literature overview based on CiteSpace

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ABSTRACT

Although Europe is the continent with the highest proportion of karst areas, where hydrological systems are essential but extremely sensitive, data on the ecological status of karst riverine catchments are scarce. The aim of the present study was to assess the spatial and temporal (long-term and seasonal) variability of the physico-chemical and organic water parameters in the headwaters of the Krka River and its tributaries, as representatives of a typical karst ecosystem, situated in one of the largest karst areas in Europe, Dinarides in Croatia. It is affected in its upper reaches by improperly treated wastewaters, so anthropogenic influences and ecological status were estimated with the aim to present consequences of pollution exposure and importance of strict monitoring of such sensitive karst ecosystems worldwide. Results indicated degraded water quality, poor ecological status, and disturbed seasonal fluctuations at wastewater-influenced sites, primarily due to high levels of nutrients and organic matter. However, improvement was observed downstream in the Krka National Park, confirming the self-purification as important processes in dynamic karst rivers. Natural seasonality, observed at sites without wastewater influence, was mainly driven by fluctuations in water levels and primary production during the year. Literature analysis by CiteSpace pointed to scarce data on this topic worldwide (China and the USA account for 49% of all publications) and in Europe (34%). Therefore, such study is a valuable contribution in presenting the long-term and seasonal variability of ecological water parameters and in providing a more comprehensive understanding of the health of catchment under influence of multiple stressors.

Keywords: physico-chemical parameters, organic parameters, wastewaters, water quality, Krka River, scientometric analysis, CiteSpace

1. INTRODUCTION

Karst areas are one of the most diverse landscapes in the world, with outstanding natural, cultural, and hydrogeological values. Highly important components of the karst areas are hydrological systems, since they are a key factor in the karstification process, which acts as a natural sink for atmospheric CO_2, but also water resources for human consumption, aquatic ecosystems, soil formation, and agricultural irrigation (Goldscheider 2019). Their importance is also reflected in the fact that many karst terrains have been declared protected areas. In fact, 23% of all national parks in Europe are partially or mostly karstic, which corresponds to the percentage of karst in the land area of Europe (21.6%) (Chen et al. 2017; Goldscheider 2019; Goldscheider et al. 2020; Telbisz and Mari 2020).

Accordingly, many of the unique karst phenomena and surface and subsurface biodiversity depend on the good quality of karst water systems (Goldscheider 2019). The main factors affecting water quality in karst are diffuse pollution from agricultural lands and point source pollution from landfills and improperly treated wastewater. In karst areas, pollutants can move rapidly and unfiltered from the surface to groundwater through sinkholes and fracture networks in the bedrock (Ford and Williams 2007; Yue et al. 2019). Due to the unique hydrologic characteristics and dynamic interactions with groundwater, karst hydrologic systems can exhibit large variations in water levels and water quality parameters and therefore be particularly difficult to predict and manage. However, it is critical to study temporal trends since current changes in climate and human activities significantly affect water quality (Alamdari et al. 2022). Monitoring both long-term and seasonal trends in physico-chemical and organic parameters contributes to a better understanding of natural variability and enables a timely response to observed deviations that could be harmful to the ecosystem or local population.

Typical example of the karst river catchment, protected as a natural park, but also anthropogenically impacted by wastewater and agricultural runoff, is the Krka River in Dinaric karst region in Croatia. Based on the intercalibration river typology, it belongs to the IC type R-M2 Mediterranean rivers with catchment area of 100-1000 km^2, mixed geology (except non-siliceous) and high seasonality (Schöll et al. 2012). The Krka River springs at the base of Dinara Mountain near the Town of Knin (8300 inhabitants), after which it flows downstream through a series of valleys (poljes) and canyon formations until reaching the Adriatic Sea near the Town of Šibenik (42600 inhabitants). Along the course of the Krka River there are seven prominent tufa deposits forming barrages and cascades which cause the water to change flow and velocity with alternating lotic and lentic microhabitats. Since 1985, part of the Krka River watercourse has been protected as National Park (GRC 1985). Although known for its exceptional beauty, species richness and sensitivity, and therefore need to monitor and estimate its water quality, there are only few papers indicating physico-chemical parameters of the upper course of the Krka River (Cukrov et al. 2008; Filipović Marijić et al. 2018; Sertić Perić et al. 2018).

General review of the literature data showed that research on water quality of European karst waters is scarce and mostly focused on groundwater and springs (Hoaghia et al. 2021; Puig et al. 2017) and lake systems (Barešić et al.

2011; Sertić-Petić et al. 2011; Sironić et al. 2017; Vurnek et al. 2021), while physico-chemical and organic water parameters in surface karst rivers are less frequently studied. In order to obtain a systematic and objective overview of a research domain, scientometric analysis software CiteSpace is increasingly used (Li et al. 2022; Yang et al. 2023; Zhong et al. 2022). CiteSpace can map a set of bibliographic records as a several types of networks, such as co-cited documents, collaborating countries, or co-occurring keywords, where the nodes represent the objects of analysis (e.g., cited references, countries, keywords, etc.), and the links describe the relationship between these nodes. Citation burst of a node, i.e., a keyword, reflects an increase in its citation frequency in a short period of time related to a particular topic within a research area (Chen 2006; Chen 2017). Although there are two studies that have used CiteSpace to analyze the current state of research on karst in general (Zhao et al. 2021) and karst groundwater pollution (Zhou et al. 2020), to our knowledge, no attempt was made to use CiteSpace to visualize the literature data related to water quality parameters and quality status of karst rivers.

Accordingly, the main aim of the present paper was to assess long-term trends of the physico-chemical (turbidity, temperature, conductivity, total dissolved solids (TDS), pH, dissolved oxygen, saturated oxygen, dissolved CO_2, chemical oxygen demand (COD), ammonium, total nitrogen, nitrate, nitrite, total phosphorus) and organic (total organic carbon (TOC), dissolved organic carbon (DOC), mineral oils, phenols) water parameters in the Krka River, and get general conclusions on theirs seasonal and spatial variability in the karst ecosystem. Specifically, the impact of wastewater discharges on ecological status and seasonality in the dynamic karst area was evaluated, as well as the physico-chemical properties of the industrial and municipal wastewaters, with the aim to give insights for further monitoring and protection of this sensitive karst area. As a general overview, scientometric data of the current research situation, the main topic categories and developing trends in this field worldwide and in Europe were presented based on CiteSpace analysis.

2. MATERIALS AND METHODS

2.1. Study area

To maintain the water quality of a river, monitoring and management at the catchment level is recommended, as tributaries can significantly influence the spatial and temporal dynamics of the river water quality (Calmuc et al. 2020). Therefore, this study included sampling sites of the whole upper catchment of the Krka River and presented for the first time its water quality since previous included only a few sampling sites in the upper reaches and omitted the influence of the tributaries (Fig. S1). A total of eight sampling sites, differing by anthropogenic influences, were investigated: A) sites without direct anthropogenic influence: KRS (1) - the source of the Krka River (a reference site), TKR (4) - the Krčić Stream (flows into the Krka River near its source); B) anthropogenically influenced sites: TKO (5) – the Kosovčica River (flows near the Knauf gypsum factory, which has caused several ecological incidents), TOR (6) – the Orašnica River (passes by the screw factory and its basins with technological wastewater), KRK-MWW (2) - Krka watercourse influenced by the municipal wastewater outlets from the Town of Knin, TBU (7) - the Butišnica

River (flows through the area influenced by agricultural runoff and numerous septic tanks from the surrounding settlements near the Town of Knin, but also from Bosnia and Herzegovina), KBL-NP (3) - Brljan lake (located in the Krka National Park, downstream from the other sites and providing insight into the ecological status of the park); C) wastewater sampled directly from basin: IWW (8) - industrial wastewater from the screw factory.

As seen, the main point sources of pollution in the Krka River are industrial and municipal wastewaters discharged into the river without adequate purification treatment (Filipović Marijić et al. 2018). The industrial wastewaters come from the artificial basins near the screw factory, located 3.3 km west of the Krka National Park. It has been active since 1956 and is known for numerous ecological incidents (DLS 2018; Kisić et al. 2019), especially due to the karst nature of the soil, allowing industrial wastewaters to reach the groundwater and enter the nearby Orašnica and Krka rivers through the underground fracture networks. Previous analyses of this water confirmed a high concentration of oil, volatile organic compounds, trace metals and metalloids, chlorides, and aromatic hydrocarbons such as toluene, ethene, benzene, and xylene (DLS 2018; Filipović Marijić et al. 2018; Kisić et al. 2019). However, there are no previous data for organic pollutants in the Krka River and its tributaries, so concentrations of total phenols and mineral oils were presented for the first time in this study. Municipal wastewaters from the Town of Knin are also regularly discharged into the Krka River without appropriate treatment. The municipal outlet is located downstream of the factory and about 2 km upstream from the border of the National Park. Previous studies reported poor water quality at this location, and parameters such as pH, COD, nutrient and trace metal concentrations, as well as microbiological parameters reflected the impact of sewage effluents (Filipović Marijić et al. 2018; Sertić Perić et al. 2018).

Despite the decades long influence of wastewaters in the upper reaches of the Krka River and vicinity of the Krka National Park, long-term trends in water quality parameters in this area are still unknown. As there have been some ecological incidents in this area in the past, and some industrial pollutants remain in the sediment of water bodies even after the pollution sources are no longer present, it is important to assess the long-term changes in water quality parameters (Dragun et al. 2022). Other factors such as changes in climate, surrounding land cover and land use may also affect water quality and potentialy be reflected in long-term trends (Alamdari et al. 2022). Maintaining good ecological status of the water at the tufa barriers downstream is a top priority task and a long-term objective of Krka National Park, as the biotic communities at the barriers and the process of tufa deposition depend on it (Gulin et al. 2021).

2.2. Sampling procedure

Water sampling was conducted in each season of 2021: Winter (January 28), Spring (April 25–27), Summer (July 20), and Autumn (October 18–20). The only exception of this seasonal sampling dynamic was the Krčić Stream (TKR), which went dry in summer and autumn and measurement of organic parameters. After the first sample analysis in January, there was a need to monitor other organic parameters besides TOC and DOC, at anthropogenically impacted sites. Therefore, concentration of total phenols, and mineral oils (total hydrocarbons) were also measured during the next three sampling campaigns at the reference (KRS) and pollution impacted sites (KRK-MWW, TOR, TBU, and IWW) in the same water samples as TOC and DOC. For chemical laboratory analysis of physico-chemical parameters, river water samples were collected manually in polyethylene plastic bottles, while for organic parameters in glass bottles, and stored in the dark at temperatures up to 8 °C until analysis. The schematic framework of the methodological procedure can be seen in Fig. S2.

2.3. Analyses of physico-chemical and organic water parameters

A total of 18 physicochemical parameters were analyzed, among them temperature, pH, conductivity, dissolved oxygen concentration and saturation, and TDS were measured in situ at 0.1 m depth using portable field probes (Mettler Toledo, precision of ± 0.2; ± 0.01; ± 0.5%; ± 1,5%; ± 0.5%, respectively). In situ measurements were not performed only for industrial wastewater, because immersion of probes in the water of such poor quality could damage them, so only pH, conductivity and TDS were measured subsequently in filtered samples. Concentrations of nutrients (ammonium, nitrite, nitrate, total nitrogen, and phosphorus), turbidity, COD, and dissolved CO_2 were determined in the laboratory using the respective standardized methods (Hach 2013, APHA 2018). The concentration of total nitrogen was determined by UV spectrophotometric method with alkaline potassium persulfate digestion. Total phosphorus was analyzed colorimetrically, by ascorbic acid method. COD was measured with potassium permanganate and sulfuric acid following standard procedure HRN EN ISO 8467:2001. Total dissolved CO_2 was analyzed by standard titration procedure using Na_2CO_3 and phenolphthalein. Declared uncertainties of spectrophotometer used for the listed measurements (Hach Lange) are < 1% for 0.50-2.0 Abs at 546 nm. Among organic water parameters, TOC and DOC were measured according to the method HRN EN 1484:2002 (± 4.40%) using TOC analyzer TOC-VCSH + ASI–V + SSM-5000A (Shimadzu), while qualitative analysis and concentration measurements of phenols and mineral oils were performed according to ASTM D 4763-06 (2020) using the Fluo-Imager MB53 (Skalar Analytical B.V.).

The overall assessment of the water quality was performed according to the Directive on water quality status of the Government of the Republic of Croatia, which defines the limit values for “very good”, “good” and “bellow good“ ecological status of the main types of water bodies present in Croatia (GRC 2019). According to ecological and physicochemical characteristics, majority of investigated Krka River watercourse fits to a national type HR-R_12: medium and large upland river, as a 73 km long karst river flowing in the Dinaric Western Balkan ecoregion (ER5; sensu Illies 1978; GRC 2019). Industrial wastewater parameters were compared with the emission limit values defined by the Regulation on limit values for waste water emissions (GRC 2020).

2.4. Literature collection and scientometric visualization by CiteSpace

Prior to CiteSpace analysis, literature datasets on water quality of karst rivers worldwide and on European karst rivers were collected separately. For both datasets, the Web of Science (WoS) Core Collection was used as the data collection platform. In creating both datasets papers on marine environments were filtered out. Therefore, the topics "karst" AND "water quality" AND "river" NOT "marine" NOT "ocean" were used for global scientometric dataset, and a total of 237 publications from 1995-2022 were found. For the second dataset, containing research papers on karst rivers in Europe, the topics "Europe" AND "karst" AND "river" were chosen and 61 publications from 1999-2022 were found. For both datasets, literature data were stored as complete records and cited references.

A scientometric analysis was then performed using CiteSpace 6.1.R6 (Basic). To analyze the collaborative network and identify the most important countries in the karst river water quality research worldwide, the network was constructed by setting the node type to "country" and the node rendering mode to "tree ring history", so that each node represents a country and the concentric citation rings represent the number of citations for the country in the corresponding years. The size of the node indicates the number of papers published in that country, and the links between nodes indicate the collaboration between co-authors from different countries (Chen 2006; Chen 2017). A cluster analysis was conducted to analyze the main themes and developing trends in the research on karst river water quality worldwide and on European karst rivers. For this purpose, the node type was set to "reference and keyword", combining document co-citation network and keyword co-occurrence network. In the co-citation network, each node represents a research paper, and the link between them represents that they were co-cited in the later literature. In the keyword co-occurrence network, each node represents a keyword, and the linked nodes co-occur in the same paper (Chen 2006; Chen 2017). The network nodes were then clustered. For the first dataset, "title words" were chosen as the source to label clusters and for the second dataset, "keywords" were chosen.

3. RESULTS AND DISCUSSION

3.1. Spatial differences and long-term trends in the Krka River

3.1.1. Physico-chemical water parameters

At all sampling sites along the karst Krka River and its tributaries, water temperature, pH, and dissolved oxygen saturation were within the range typical for karst rivers (Table S1), while their spatial distribution followed the trends previously recorded in the Dinaric karst watercourses (Cukrov et al. 2008; Filipović Marijić et al. 2018; Sertić Perić et al. 2018; Terzić et al. 2014; Žutinić et al. 2020). Specifically, average pH increased in the downstream direction of the main Krka River flow (7.48–8.02), while dissolved CO_2 concentration showed the opposite trend, decreasing 4.9–3.3 mg L^{-1} (Table S1). Both trends could be explained by CO_2 degassing, as previously noted by Srdoč et al. (1986), Cukrov et al. (2008), Sironić et al. (2017) and Žutinić et al. (2020). The temperature increase was evident in the downstream direction of the Krka River and in the four tributaries in summer (10.5–20.4 °C), while it was mostly comparable and uniform between all sites in other seasons (Table S1). Turbidity trend pointed to low levels at the river source and in the national park as expected (0-1 FAU), with increasing levels at the tributaries (1–9 FAU), especially showing the influence of industrial discharge to clearness of water at nearby TOR. The highest turbidity value was found at KRK-MWW (4–10 FAU) and IWW (15–2355), clearly reflecting impact of municipal and industrial wastewaters, respectively (Table S1).

Anthropogenic influences were also reflected in the increase of dissolved ion content downstream, as evidenced by conductivity and TDS, which levels were much higher at IWW than any other freshwater sampling site. If IWW is excluded, the highest TDS and conductivity values were measured in the tributaries TKO, TBU and TOR (Table S1), probably originating from agricultural runoff at TBU and industrial wastewater at TOR. Both of these influences are present in the catchment of TKO, but, since the Kosovčica River flows through an area composed of gypsum and anhydrite rock mass, it is also enriched by sulfates from the underlying bedrock, which might explain maximum TDS values at this site (Mihaljević et al. 2011; Terzić et al. 2014). In addition, increased nitrate, total nitrogen and total phosphorus concentrations at the IWW and KRK-MWW compared to the other sites confirmed industrial and municipal wastewaters as an important source of these nutrients (Table S1). Our results on COD, total phosphorus, total nitrogen and nitrate concentrations were higher compared to the karst Mrežnica River, which has been historically contaminated with industrial waste (Dragun et al. 2022). However, nutrient concentrations were still lower than in the agriculture impacted Karašica River and the Vučica River, non-karstic Croatian rivers with the same catchment size as the Krka River, indicating the importance and positive effect of the groundwater sources and water turbulence for the water quality of the karst catchment (Amić and Tadić 2018).

Long-term trends of the physico-chemical water parameters could be evaluated for pH, temperature, conductivity and dissolved oxygen concentration at KRS, KRK-MWW and KBL-NP (Fig. 1), since the data for mentioned parameters were previously published for the same sampling locations along the Krka River (Cukrov et al. 2008; Filipović Marijić et al. 2018; Rovan et al. 2021; Sertić Perić et al. 2018; Terzić et al. 2014; Žutinić et al. 2020). All selected sampling campaigns were performed in autumn to omit seasonal influences and the results confirmed an increase in physico-chemical water parameters from KRS, as an unpolluted and most upstream location, downstream along the Krka River in each period, except dissolved oxygen concentrations which were mostly comparable among the sampling sites. Comparison over the years showed comparable levels of most of the parameters, with exception of few peaks downstream (mostly 2008, 2018, 2019, Fig. 1), probably reflecting influence of few ecological incidents (DLS 2018; Kisić et al. 2019).

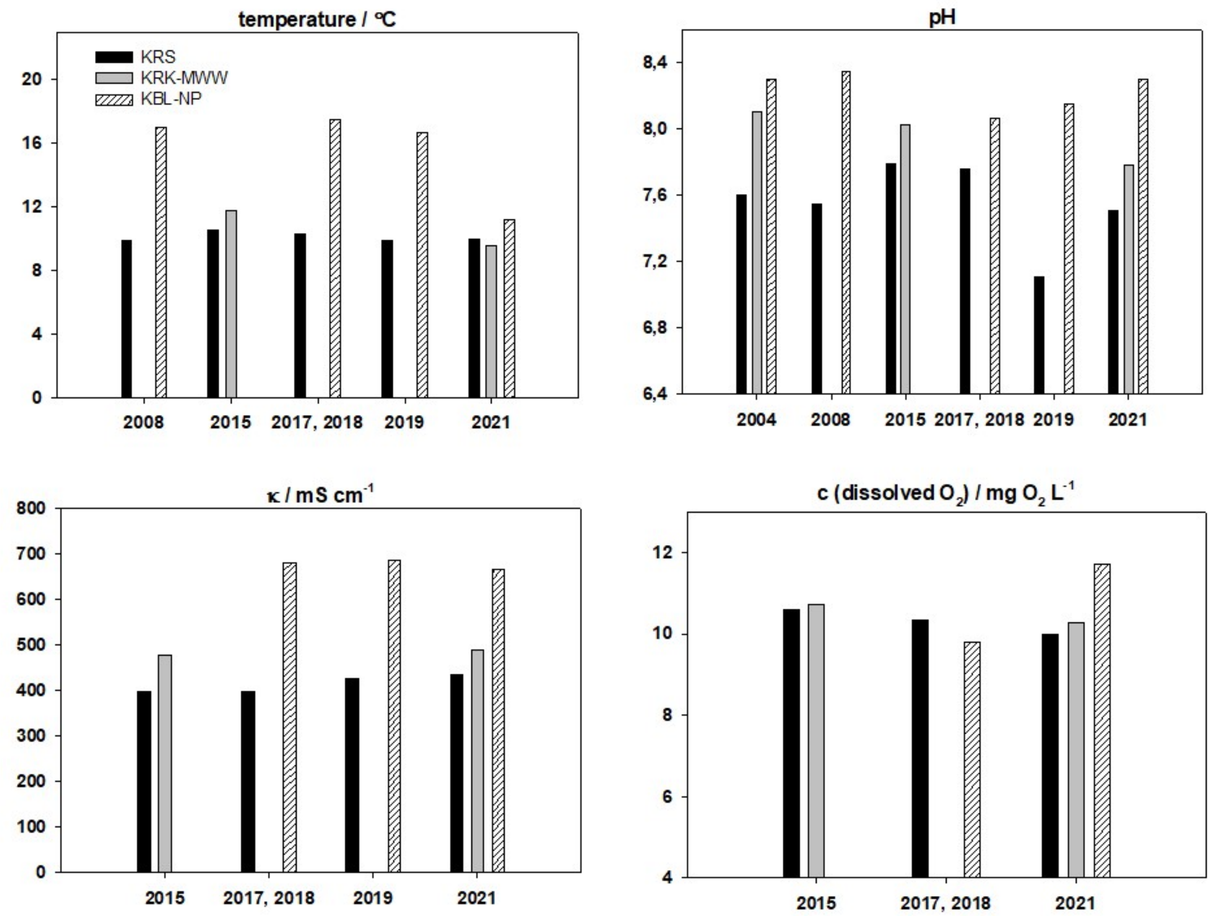

Fig. 1 Long-term trends of the average water pH value, temperature, conductivity (κ) and dissolved oxygen concentration along the sampling sites 1, 2 and 3 in the Krka River watercourse in autumn season. Data are related to the following publications: 2004 - Cukrov et al. (2008); 2008 - Terzić et al. (2014); 2015 - Filipović Marijić et al. (2018) and Sertić Perić et al. (2018); 2017 and 2018 - Žutinić et al. (2020); 2019 - Rovan et al. (2021); 2021 - from this study.

When considering IWW and Regulation on limit values for waste water emissions (GRC 2020), water quality of samples taken in 2021 was worse compared to samples taken in 2015 (Filipović Marijić et al. 2018) due to much higher conductivity, TDS, dissolved CO_2, ammonium and total nitrogen concentrations, and especially turbidity (55 times higher average levels) and COD (46 times higher average levels) in 2021. But for these data possible coincidence of the the moment of sampling with the wastewater discharge should be considered. On the contrary, lower values of the same parameters at nearby TOR in our study than 2018 could possibly be due to the gradual purification since 2014, when the dam between industrial wastewaters and the Orašnica River was built and mitigated the overflow of the wastewater during high water levels.

3.1.2. Organic water parameters

Spatial differences in TOC and DOC values in the natural karst system pointed to the lowest organic matter values at KRS and TBU (Table S2) and showed comparable values to the TOC results obtained previously in the Krka River (Žutinić et al. 2020) and other karst sources in the Dinaric mountain range (Matić et al. 2013), and also to the DOC values reported for the Krka River (Cukrov et al. 2012; Strmečki et al. 2018; Žutinić et al. 2020). As expected, the highest TOC and DOC levels were recorded at IWW, as a site impacted by industrial effluent. Besides IWW, maximum TOC and DOC concentrations were obtained in TOR and KRK in all seasons, reflecting the impact of industrial and municipal wastewaters on these locations, respectively (Table S2). Although presented results on organic content pointed to some impact of wastewaters on the karst ecosystem, the average DOC concentrations in the Krka River were still lower than in the other European rivers such as Douro (2.4 mg L^{-1}) and Loire (3.9 mg L^{-1}) (Abril et al., 2002).

The impact of wastewaters on the river water quality was also reflected in content of mineral oils and total phenols. Mineral oil concentrations in our study area ranged from below 0.005 to 56.811 mg L^{-1} (Table S2). Values over 0.005 mg L^{-1} were found at TOR and IWW in all three seasons in which they were measured, but also at KRK-MWW in summer and autumn (Table S2). For total phenols, IWW was the only site where concentrations over 0.005 mg L^{-1} were observed (0.047 mg L^{-1} in summer and 0.182 mg L^{-1} in autumn) (Table S2). Such results suggested that the main sources of organic carbon, mineral oils, and phenols in the Krka River and its tributaries are industrial, but also municipal wastewaters discharged into the watercourse without adequate treatment (Filipović Marijić et al. 2018).

Our results represent one of the first data reported for organic water parameters in the upper reaches of the Krka River. Long-term trends could therefore not be presented, except the comparison with TOC and DOC values reported for KRS and KBL-NP by Strmečki et al. (2018) and Žutinić et al. (2020). In these studies, TOC concentration was 1.44 mg L^{-1} at KRS and 1.56 mg L^{-1} at KBL-NP, while DOC levels were mostly below 1.00 mg L^{-1}, therefore confirming comparable values with our data, except much higher levels in our study at KRK-MWW, TOR, and especially IWW, as a result of direct impact of wastewater discharges (Table S2). In addition, results for mineral oils and total phenols in the Krka River were recorded only between 1969 and 1978 (Munjko 1979), being much higher (0.7–5.4 mg L^{-1} for mineral oils and 0.0–7.0 mg L^{-1} for total phenols) compared to 2021, but here differences in analytical methodology should be considered.

3.2. Seasonal differences in the Krka River

3.2.1. Physico-chemical water parameters

Seasonality of specific physico-chemical water parameters in the karst catchment was estimated in the Krka River for the first time. The water level of this karst watercourse followed common trend for temperate climate zone, with the highest levels in winter and spring (219 cm in January; 117 cm in April) and decreased in summer and autumn (77 cm in July; 80 cm in October), being in accordance with the precipitation regime (Croatian Meteorological and Hydrological Service). Water temperature also followed the trend specific for temperate climate zone with the highest levels in April and July at downstream locations, while stable values were confirmed at karst river source (10–11 °C) (Table S1).

Seasonal variations of the most physico-chemical water parameters were not specific, especially at the wastewater impacted sites IWW and KRK-MWW, since temporal variations at these sites mostly depend on the moment of the wastewater discharge. Regarding other sites, variations in the dissolved nutrient and total solid levels pointed to the influence of the rainfall and water level regime. Generally, elevated nitrite concentrations were recorded during the wet season (winter and spring) at all locations except TOR in autumn, probably reflecting the impact of nearby IWW where the highest nitrite levels were recorded in autumn (Fig. 2a, Table S1). An increase in nitrite or nitrate levels during a rainy period was commonly observed in rivers and groundwater (Huebsch et al. 2014; Yue et al. 2018), especially in regions with a Mediterranean climate, characterized by large differences in precipitation between seasons, when nitrate peaks are often observed after the summer drought (Bernal et al. 2005). In our study, nitrate concentrations peaked in autumn, which coincided with the end of the summer drought and low water levels (77 cm in July) and the beginning of the rainy periods (Fig. S3) that cause surface runoff. Although point sources of pollution (such as industrial wastewaters and sewage effluents) have a big impact on nitrogen levels in aquatic environments, typically the main sources of nitrogen are the chemical fertilizers from the soil in the river catchment (Huebsch et al. 2014; Malá et al. 2022; Schliemann et al. 2021; Wang et al. 2020). During low flows in the dry summer season, nitrogen from organic matter and fertilizers cannot be transported into receiving water so they are stored in farmland or infiltrated into groundwater. Then, in the wet season precipitation accelerates surface runoff and subsurface flow, flushing the accumulated nitrogen from soils into rivers, what can also be related to our study (Glavan and Pintar 2010; Huebsch et al. 2014; Wang et al. 2020; Xu et al. 2019).

On the other hand, average values of TDS and electrical conductivity were higher during the dry season (summer and autumn) (Fig. 2a), being in accordance with the results of Jebreen et al. (2018) and might be the result of the lower water levels and less effective purification processes in the river and its tributaries (Filipović Marijić et al. 2018). In addition, generally higher levels of COD, ammonium, total nitrogen were recorded in April and of total phosphorus in July, but mostly due to their increased levels at TOR and TKO (Table S1). These are locations under the impact of nearby industry, TOR of screw factory and TKO gypsum facilities and probably reflect specific impact of pollution related to discharge peaks and as such, cannot be related to natural seasonality.

3.2.2. Organic water parameters

Measured organic water parameters had the highest values at the wastewater impacted locations, KRK-MWW and IWW, but without common seasonal trends since these values probably reflect discharge peaks. Still, the highest values of TOC and DOC at IWW were especially evident in spring (Table S2), coinciding with the higher values of physico-chemical parameters at the nearby site TOR, which may reflect the timing of wastewater discharge in this season (Table S1). If wastewater impacted sites are excluded, mineral oils showed a tendency to increase in dry periods, after agricultural activities and during low water levels in summer (77 cm) and autumn (80 cm) (Table S2; Fig. S3). Strmečki et al. (2018) reported the highest TOC values at KBL-NP in spring and explained it as the result of autochthonous phytoplankton production. The DOC concentrations measured by Marcinek et al. (2020) in the Krka River estuary (approximately 33 km downstream of the sampling sites in this study) were also higher in summer than in winter. In our study, the highest TOC and DOC concentrations in the river watercourse were recorded in spring and summer (Fig. 2b), especially at TOR as the location directly impacted by the wastewater effluents. Therefore, our results may reflect increased biomass of primary producers in the river system and increased agricultural activities in the catchment area (Cukrov et al. 2012; Stanley et al. 2012), but again were additionally influenced by wastewater discharge from the nearby screw factory and cannot only be presented as natural seasonal variations of organic matter in the river.

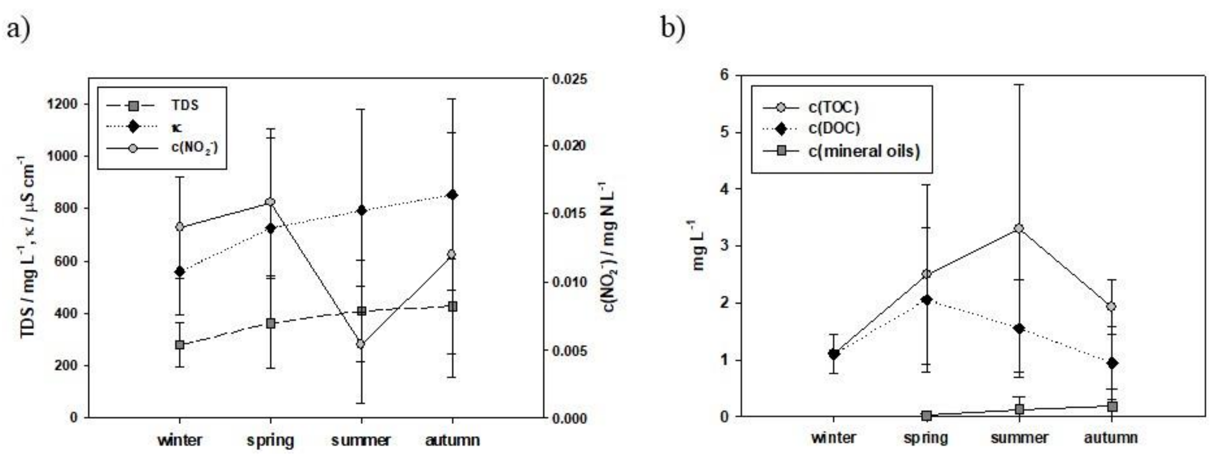

Fig. 2 Seasonal dynamics of **a)** the average values of TDS, electrical conductivity (*κ)* and nitrites measured at six sampling sites in the Krka River catchment (locations 1, 3–7); **b)** the average TOC, DOC and mineral oil concentrations measured at three sampling sites in the Krka River catchment (locations 1, 6, 7)

3.3. Ecological status of the Krka River

3.3.1. Physico-chemical water parameters

According to the Directive on water quality status of the Government of the Republic of Croatia (GRC 2019), the ecological status of a water body can be classified as "very good", "good" or "bellow good" based on the limit values for pH, COD, and concentration of ammonium, nitrate, total nitrogen and total phosphorus. In our study, the ecological status of water from the reference site was very good considering all parameters except ammonium concentrations in spring and autumn (0.02 mg N L^{-1}) and pH value in winter (7.29) (Fig. 3). Ecological status of water at KRS was previously classified as very good by Hrvatske vode (2016), Filipović Marijić et al. (2018) and Sertić Perić et al.

(2018), including also ammonium concentrations (below 0.01 mg N L^{-1}) and pH value (7.4–8.5). As there are not some specific sources of pollution here, such data can be classified as occasional disturbances due to the complex subsurface hydrological systems in karstified regions and big catchment area of the river source (Bonacci et al. 2006; Ravbar and Kovačič 2014). Moreover, the Krčić Stream flows into the Krka River near its source so TKR might have a direct impact on KRS water quality. Most parameters at TKR were within the range for very good ecological status (Fig. 3) and values typical for karst streams, comparable to Kolda et al. (2019), who confirmed pristine oligotrophic conditions in the Krčić Stream.

However, physico-chemical parameters measured in the other downstream tributaries pointed to ecological status below good in all seasons at KRK-MWW, TOR and TKO, mainly due to high concentrations of nutrients and COD (Fig. 3), confirming long-term influence of municipal and industrial wastewaters from the Town of Knin (8300 inhabitants), screw factory and gypsum factory, respectively (Filipović Marijić et al. 2018; Magdaleno et al. 2001; Mihaljević et al. 2011; Sertić Perić et al. 2018). Considering the other parameters, which were not defined in the Directive (GRC 2019), the highest water turbidity, TDS, conductivity, and total nitrogen concentrations were recorded at KRK-MWW, TOR and TKO, indicating anthropogenic degradation of water quality compared to the reference site (Table S1). Higher turbidity at KRK-MWW might be the result of microbial activity, typical for municipal wastewater outlets as already confirmed by Kapetanović et al. (2009) and Filipović Marijić et al. (2018), while extremely high turbidity at IWW is the result of high content of mineral and fuel oils in these wastewaters.

The water parameters at TBU were within the limits for very good or good ecological status, depending on the season, except COD, which exceeded the limit of 4 mg O_2 L^{-1} in all seasons except autumn. Higher nutrient concentrations, TDS and conductivity than at the reference site were also observed, possibly indicating the impact of agricultural activities on the quality of the Butišnica River (Divya and Belagali 2012) (Fig. 3).

Water from KBL-NP, the only sampling site situated in the Krka National Park, had mostly very good quality compared to the other sampling sites. The only parameters that exceeded the limit values for good ecological status according to GRC (2019) were COD and ammonium concentrations in spring and summer (Fig. 3). Good water quality of the Brljan Lake may be the result of limited anthropogenic activities within the borders of the Krka National Park, sedimentation due to the lower water velocity in the lake, positive effect of aquatic macrophytes, and mixing with new freshwater originating from the Zrmanja River which enters into the Krka by underground springs (Cukrov et al. 2008; Srivastava et al. 2008). Self-purification of surface karst rivers downstream of the pollution source has also been previously reported by Cukrov et al. (2008) and Malá et al. (2022).

Compared to the other sites, much higher concentrations of ammonium, total nitrogen, nitrates, nitrites, total phosphorus, and COD were determined at KRK-MWW, indicating deteriorated water quality due to urban wastewater effluents (Filipović Marijić et al. 2018; Schliemann et al. 2021; Xu et al. 2019). However, dissolved oxygen saturation at KRK-MWW was quite high (91.6–97.9%), contrary to the most sites near the municipal wastewater outlets (Magdaleno et al. 2001; Olatunde et al. 2015). These results are in accordance with the results from 2017 (104.0%, 114.3%) and 2018 (99.8%) and might be explained by the oxygen production by submerged aquatic macrophytes, abundant at the KRK–MWW sampling site, which compensates oxygen loss due to biodegradation of organic matter

(Filipović Marijić et al. 2018; Malá et al. 2022; Sertić Perić et al. 2018). Based on the results of the present study, it is important to connect the Town of Knin to a wastewater treatment plant. According to Malá et al. (2022), this is a factor that influences the quality of surface waters in karst areas more than the population size of a municipality and that could significantly reduce the concentrations of ammonium and total phosphorus.

The quality of industrial wastewater (sampling site IWW) was poor throughout the whole year, especially in summer when all parameters, except pH, exceeded the limits set by the Regulation on limit values for waste water emissions (GRC 2020) (Fig. 3). Moreover, the highest concentrations of some nutrients were also measured in autumn, when they were about 5 times (total nitrogen) and even 9 times (nitrites) above the emission limit values for pollutants in wastewater prior to their discharge into the surface waters.

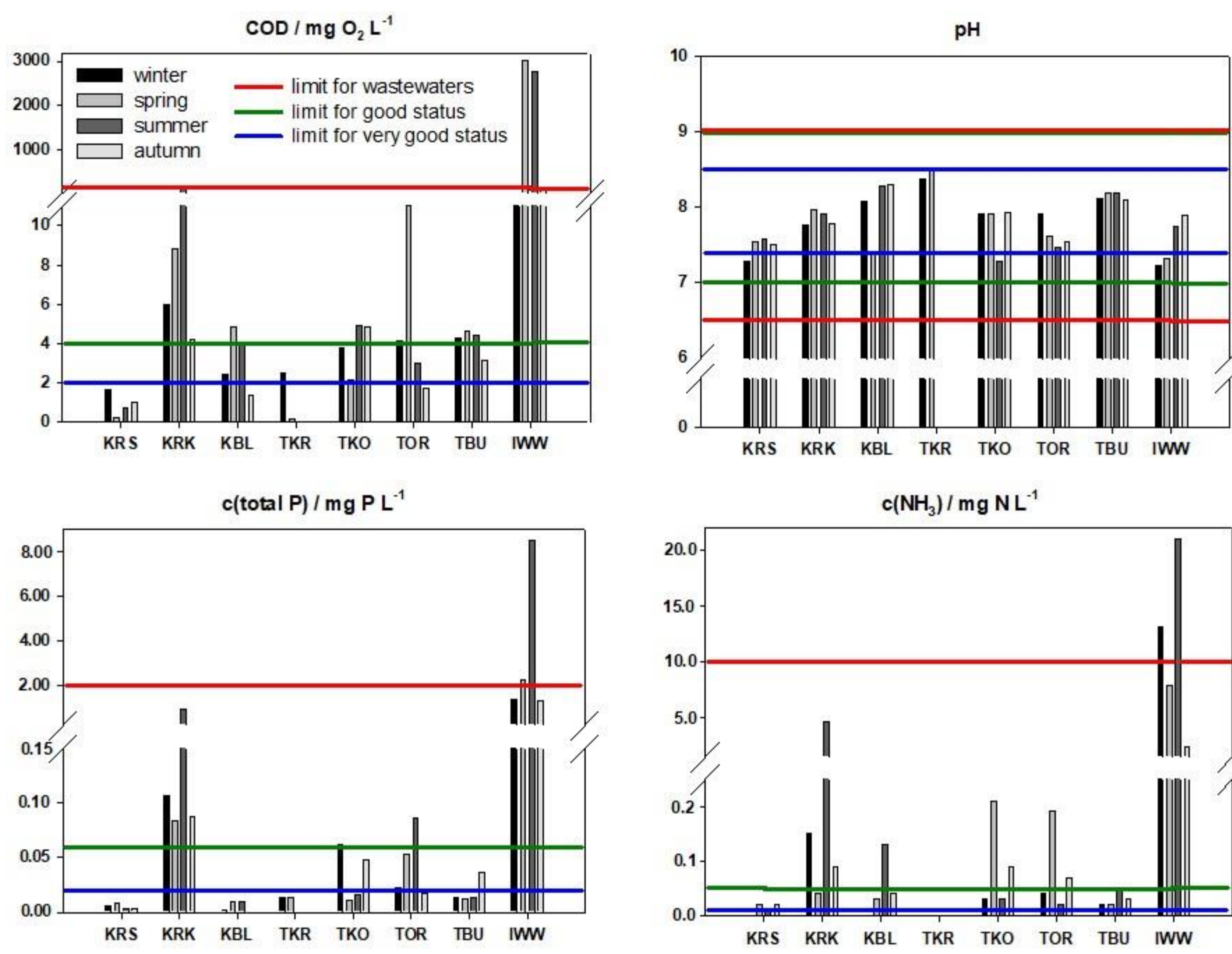

Fig. 3 Comparison of physico-chemical water parameters in the Krka River catchment with limit values for "very good" and "good" ecological status (locations 1-7) according to the Directive on water quality status (2019) and limit values for "good" quality of wastewaters (location 8) according to Regulation on limit values for waste water emissions (2020). As defined, upper and lower limits are presented for the pH value and the upper limit for all other parameters.

3.3.2. Organic water parameters

There are not defined limits for organic water parameters (TOC, DOC, mineral oils, total phenols) in natural freshwater systems related to specific ecological status, but only for wastewater emissions (GRC 2020), and are defined as 10 mg L^{-1} mineral oils, 0.10 mg L^{-1} total phenols and 30 mg L^{-1} TOC. In industrial wastewater near the Krka River (IWW) these regulatory limits were exceeded for mineral oil concentrations in all investigated seasons (24.902–56.811 mg L^{-1}), phenols in autumn (0.181 µg L^{-1}) and TOC in spring (100 mg L^{-1}) (Fig. 4) with around three times higher levels than the permissible limit (GRC 2020).

The Regulation does not specify a limit value for the concentration of DOC, but they were also the highest at IWW, followed by KRK-MWW, in accordance with all other organic parameters and therefore, confirming elevated levels of organic matter at municipal and industrial wastewater impacted sites (Table S2). The lack of adequate treatment process resulting in such high hydrocarbon concentration in the wastewater discharged into the environment poses a threat to the Krka National Park (Filipović Marijić et al. 2018). Therefore, immediate remediation of the basins with industrial wastewater from the screw factory is necessary.

Our study provided the first data on organic water parameters in the upper reaches of the Krka River and confirmed the impact of wastewater discharges on the concentration of mineral oils in this ecosystem, so further assessment of organic pollutant exposure is recommended. Integrated approach of water quality assessment and maintenance of good water quality in the lower part of the Krka River is also recommendable for nature conservation, but also for the drinking water supply of the Town of Šibenik (Ravbar and Kovačič 2014).

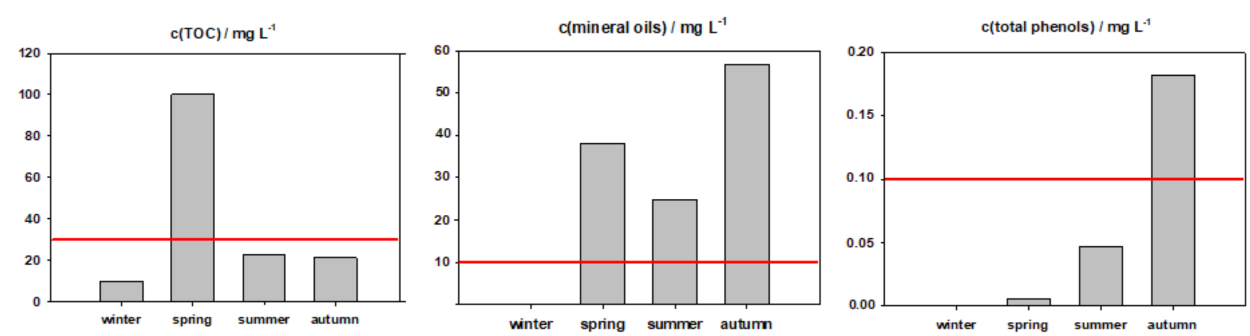

Fig. 4 Comparison of organic water parameters of industrial wastewaters (location 8) with defined emission limit values for pollutants in wastewater (red line) prior to their discharge into the surface waters, according to the Regulation on limit values for waste water emissions (2020)

3.4. Scientometric literature analysis using CiteSpace

According to the CiteSpace literature analysis, most research on these topics was conducted in Asia (38%), Europe (34%), and North America (22%). This distribution differs somewhat from the proportion of karst areas on these continents (Europe 21.8%, North America 19.6%, Asia 18.6%), likely due to factors such as the availability of research funding or the number of research institutions (Goldscheider et al. 2020). The most productive countries were China with 85 papers and the United States with 57 papers, accounting for 49% of all publications (Fig. S4). According to their betweenness centrality, China (0.56), Germany (0.42), the United States (0.17), the Czech Republic (0.15), and Switzerland (0.13) played a central role in establishing collaborations with other countries. The leading European countries by number of publications were Germany (16 papers), Croatia (15 papers), and Spain (9 papers). According to Chen et al. (2017), carbonate rocks cover 50.5% of Croatia, 29.2% of Spain, and only 21.4% of Germany.

3.4.1. Worldwide literature dataset

Literature set after combining the topics "karst", "water quality" and "river" and not including the "marine environment", resulted in 237 papers worldwide, suggesting that water quality parameters in karst rivers are not commonly studied overall. A total of 18 clusters were identified from the co-citation network of references and keywords and labeled using the log-likelihood ratio (LLR) algorithm (Fig. 5). Based on the input dataset, four major research areas on water quality of karst waters were identified for the period 1995-2022: first ranked was cluster #0, labeled "Southwest China" (size = 69 nodes, mean silhouette value = 0.808), and contained mainly literature on hydro(geo)chemical variations in groundwater and rivers in subtropical karst areas in southwest China characterized by monsoon climate. The second was cluster #1, labeled "karst water quality protection" (size = 54, mean silhouette value = 0.722), which focused on the pollution of karst waters by nitrates from fertilizers and the prevention of pollution from agricultural land. Third ranked was cluster #2, labeled "mantled karst spring" (size = 49, mean silhouette value = 0.770) and literature in this cluster mainly measured bacterial pathogens and heavy metals in karst waters to assess the health risk when using these waters as a drinking water source. The fourth cluster was cluster #3, labeled "geochemical response" (size = 49, mean silhouette value = 0.940), and it was focused on monitoring the hydrochemical and hydrodynamic behavior of karst springs and rivers (Fig. 5).

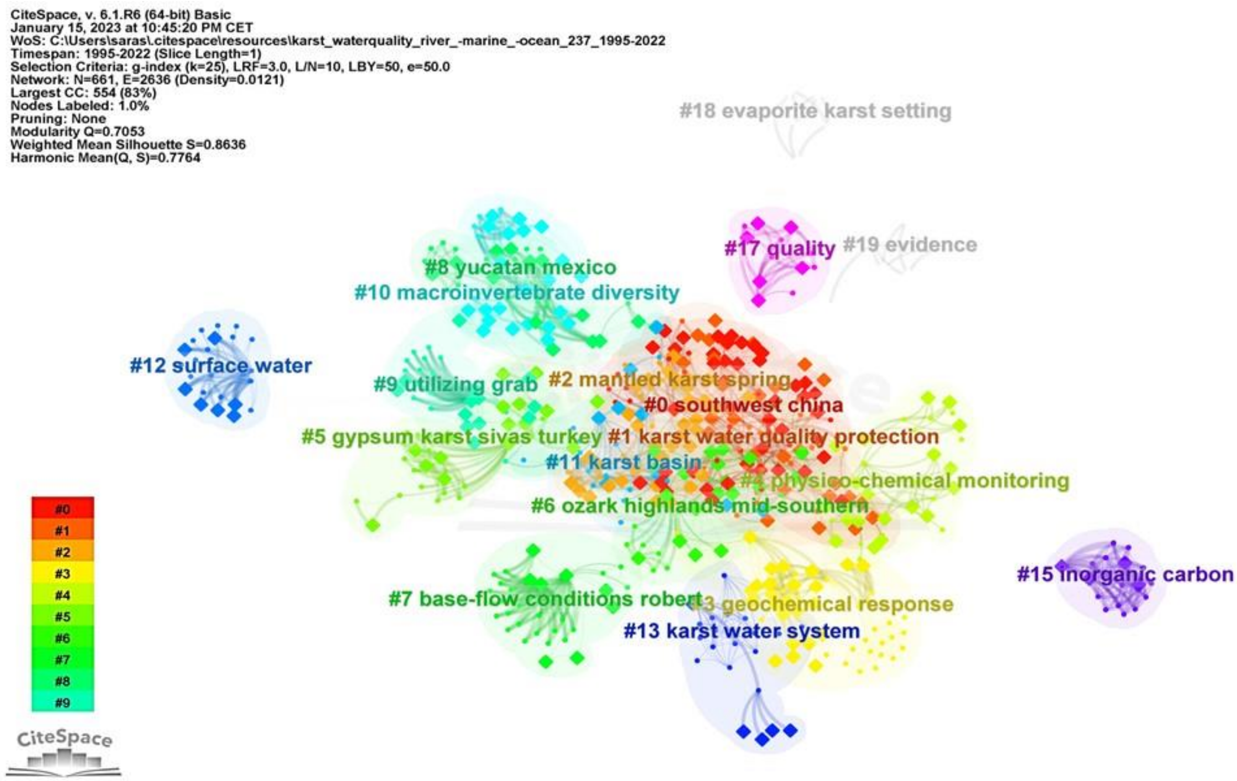

Fig. 5 Clustered network of co-cited references (dots) and co-occurring keywords (diamonds) created from literature connecting topics "karst", "water quality", and "river". Cluster labels were determined from title words using the log-likelihood algorithm.

Based on the mean year of publications of each cluster (Fig. 6), it can be concluded that the focus of karst water quality research has shifted from case studies of hydrologic connections and water quality in specific karst systems (1993-1999, clusters #7, 12, 17, 18, 19) to developing sampling strategies, studying the influence of land use on water quality and biota, monitoring hydrochemical and hydrodynamic changes, and using macroinvertebrate diversity as a bioindicator of karst water quality (2001-2008, clusters #0, 3, 5, 8, 9, 10, 15). The most active topics during the most recent period (2009-2014, clusters #1, 2, 4, 6, 11, 13) involved human impact on karst groundwater quality, monitoring of physico-chemical parameters, environmental isotopes, heavy metals, and bacterial pathogens at the catchment scale, and identifying sources of these pollutants. Therefore, the main topic of our study fits into the current framework of the global research and complement the sparse database on long-term and seasonal trends of water quality parameters in surface karst rivers. These results are not only relevant for the Dinaric karst, but also for other geologically similar karst landscapes distributed worldwide (Ford and Williams 2007; Goldscheider et al 2020).

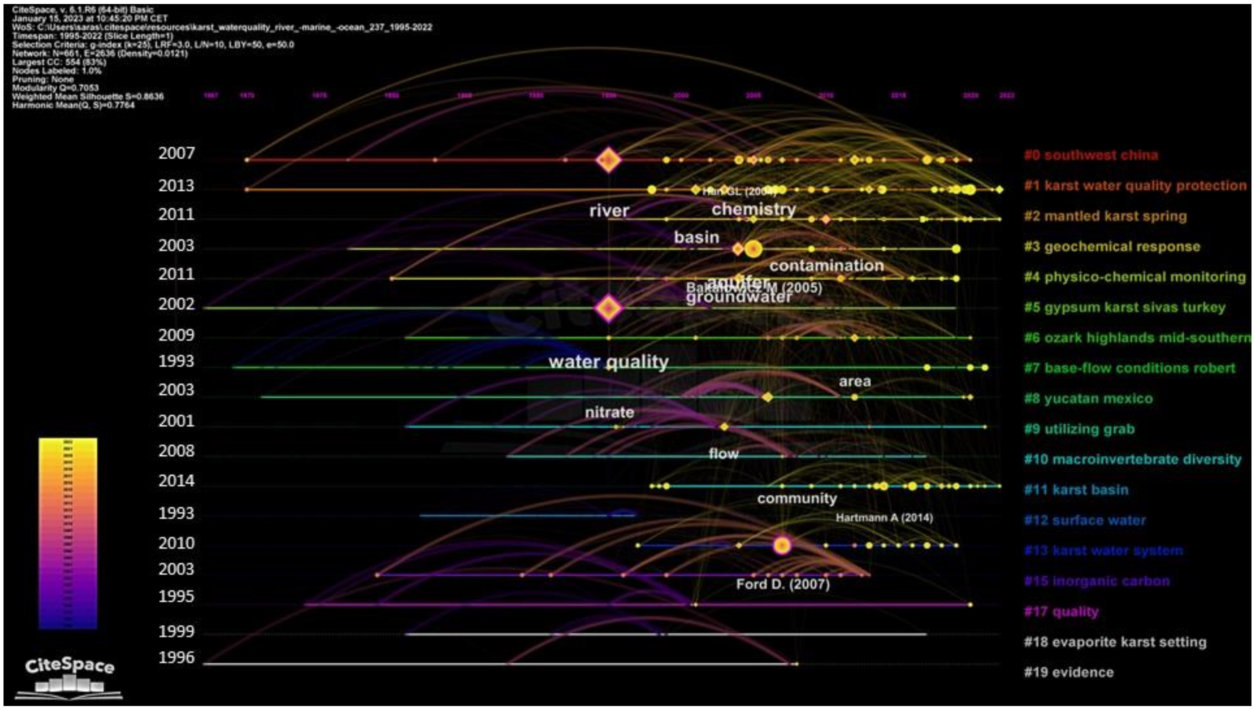

Fig. 6 Timeline view of clustered network of co-cited references (dots) and co-occurring keywords (diamonds) created from literature connecting topics "karst", "water quality", and "river". The numbers on the left are the mean years of each cluster's publications. The color of the links indicates when citations were made.

3.4.2. European literature dataset

Scientometric analyses of the 1999-2022 literature connecting the topics "Europe," "karst," and "river" identified a total of 12 clusters, labeled using the latent semantic indexing (LSI) algorithm (Fig. 7). After examining the characteristic keywords for each cluster, resulting main research areas are those focused on organisms dependent on karst waters, especially macroinvertebrates and plants: cluster #0 "dinaric karst" (aquatic beetles and macrophytes), cluster #4 "genetic diversity" (phylogeny and population dynamics), cluster #7 "regression trees" (endemic crustaceans), cluster #12 "macroinvertebrates", cluster #17 “alpine” (changes in plant communities in Europe). The second group of research areas focused on geology and geomorphology: cluster #1 "multilevel caves" (radiocarbon dating and travertine deposits), cluster #3 "paleoweathering" (paleogeomorphology), cluster #5 "central Europe" (reconstruction of hydro-geomorphic processes), cluster #6 "recent tectonic activity" (geological mapping and modelling), cluster #16 “geomorphology” (Holocene tufa changes in response to human impacts and climate change). The third, smallest group focused on water quality parameters: cluster #2 "camaro-d project" (hydrochemical characteristics of the karst river basin and impact of land use on water quality), cluster #11 "busko blato reservoir" (trophic index, eutrophication, nutrients) (Fig. 7). Since CiteSpace analysis confirmed that there are only few data on physico-chemical and organic water parameters for the European karst rivers, the present field study results are important for understanding hydrological systems similar to the Krka River, in the Dinaric karst region in Croatia (e.g. Plitvice Lakes), but also other south-eastern European countries such as Slovenia (e.g. the Reka River), Bosnia and

Herzegovina (e.g. the Pliva River), Montenegro (e.g. the Tara River), Albania (e.g. the Osum River) and Italy (e.g. the Sorgue River) (Stevanović et al. 2016; Stevanović and Milanović 2023).

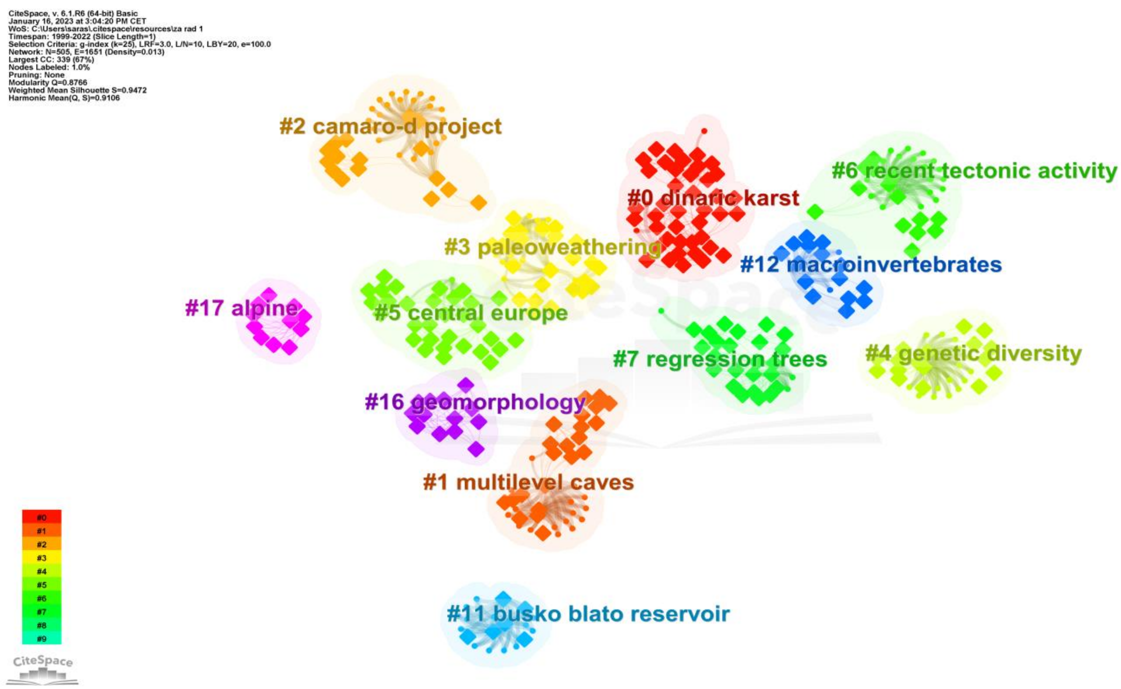

Fig. 7 Clustered network of co-cited references (dots) and co-occurring keywords (diamonds) created from literature connecting topics "Europe", "karst", and "river". Cluster labels were determined from keywords using the latent semantic indexing algorithm.

Timeline report by average year of publications in each cluster from the Fig. 7 revealed the following current research areas related to European karst rivers: a) aquatic macroinvertebrate distribution and population history using DNA barcoding and species distribution modeling ("regression trees", 2016); b) the reconstruction of hydro-geomorphic processes based on tree-ring data to identify hydro-meteorological triggers ("central Europe", 2016); c) the study of Holocene tufa changes in response to human impacts and climate change ("geomorphology", 2019). The focus of this research domain on global issues such as biodiversity loss and climate change was also confirmed by citation burst analysis, which identified climate change, Europe, and diversity as keywords with the strongest citation burst (with citation burst strengths 3.01, 2.54 and 2.39 respectively). Although these issues are important, human-induced degradation of water quality is also a major environmental problem in the modern world and requires attention.

4. CONCLUSIONS

Presented concentrations, seasonal and long-term changes in physico-chemical and organic water parameters are among the rare data for karst rivers in Europe and the first data for the upper reaches of the Krka River in Croatia. In this study, impact of anthropogenic activities on the sensitive karst ecosystem was also estimated, confirming that industrial and municipal wastewaters alter water quality and disturb natural seasonal variations. The impact of wastewater discharges as point sources of pollution to the river was found to be more severe than those of diffuse pollution from agricultural runoff. They were identified as the main source of nutrients and organic matter affecting the water quality and causing deteriorated ecological status of the surrounding area. Although the upper reaches of the river were affected by the wastewater discharges, our results indicated very good water quality downstream, in the national park, confirming the efficiency and importance of self-purification and underground flows in the complex hydrological karst systems. This self-regulation was also reflected in mostly stable long-term trends of water parameters along the river over the last 10-20 years. At sites with little or no wastewater influence, seasonal variations in dissolved nutrients and total solids reflected precipitation and water level regimes, while organic water parameters reflected changes in water levels, primary producer biomass and intensity of agricultural activities in the watershed. Presented data thus contribute to the understanding of the dynamics of karst ecological indicators and the effects of wastewater pollution in complex and valuable karst river ecosystems and indicate the need of strict monitoring and protection. According to CiteSpace visualization there are only few data on physico-chemical and organic water parameters for the karst rivers in Europe available, while keywords with the strongest citation burst are climate change (3.01), Europe (2.54), and diversity (2.39). Scientometric analysis of the global literature revealed that most research on these topics was conducted in Asia (38%), Europe (34%), and North America (22%), changing the focus from case studies of hydrologic connections and water quality to the recent studies on human impact on karst ecosystem and monitoring and identification of specific pollutants. Thus, CiteSpace analysis confirmed human-induced degradation of water quality as a major environmental problem in the modern world which requires significant attention.

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STATEMENTS AND DECLARATIONS

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Competing interests

The authors declare they have no competing financial or non-financial interests that could have appeared to influence the work reported in this paper.

Author contributions

The manuscript was written through contributions of all authors: Sara Šariri - Investigation, Resources, Data curation, Visualisation, Formal analysis, Writing - original draft, Writing - review and editing; Damir Valić - Investigation, Resources, Writing - review and editing; Tomislav Kralj - Investigation, Resources, Writing - review and editing; Želimira Cvetković – Investigation, Data curation, Formal analysis, Writing - review and editing; Tatjana Mijošek – Investigation, Resources, Data curation, Writing - review and editing; Zuzana Redžović - Investigation, Resources, Writing - review and editing; Ivana Karamatić - Investigation, Resources, Writing - review and editing; Vlatka Filipović Marijić - Conceptualization, Methodology, Funding acquisition, Resources, Supervision, Project administration, Investigation, Data curation, Formal analysis, Writing - original draft, Writing - review and editing. All authors read and agreed to publish the final manuscript.

Ethical Approval

Not applicable.

Consent to participate

Not applicable.

Consent for publication

Not applicable.

SUPPLEMENTARY MATERIAL

Table S1 Physico-chemical parameters of the Krka River water and its tributaries (locations 1–7) and of industrial wastewater (location 8) sampled in four sampling seasons (winter, spring, summer, autumn) in 2021 (* not measured *in situ* due to extremely low water quality and potential damage for measuring probes). The values in bold are those that exceed the limit value for "good" ecological status according to the Directive on water quality status of the Government of the Republic of Croatia (2019) or, in the case of IWW, the emission limit values according to the Regulation on limit values for waste water emissions (2020).

	Winter (28.1.2021)								Spring (25.-27.4.2021)								Summer (20.7.2021)							Autumn (18.-20.10.2021)						
	1 KRS	2 KRK-MWW	3 KBL-NP	4 TKR	5 TKO	6 TOR	7 TBU	8 IWW	1 KRS	2 KRK-MWW	3 KBL-NP	4 TKR	5 TKO	6 TOR	7 TBU	8 IWW	1 KRS	2 KRK-MWW	3 KBL-NP	5 TKO	6 TOR	7 TBU	8 IWW	1 KRS	2 KRK-MWW	3 KBL-NP	5 TKO	6 TOR	7 TBU	8 IWW
Turbidity / FAU	0	10	1	1	3	9	4	31	0	4	0	3	3	8	3	2355	0	4	1	2	3	4	35	0	5	0	3	2	1	15
Temperature / °C	11.0	10.6	8.0	9.0	11.0	9.0	7.0	-*	10.5	10.3	12.6	10.0	13.5	13.5	11.3	-*	10.5	14.9	17.0	20.4	18.6	15.0	-*	10.0	9.6	11.2	9.5	10.2	11.7	-*
κ / µS cm^{-1}	431	497	526	341	740	558	759	3670	388	430	533	351	1071	1127	881	3280	451	581	662	1426	540	881	5460	435	489	664	1407	806	955	10570
TDS / mg L^{-1}	215	248	263	170	370	279	379	1834	194	215	266	176	536	564	440	1642	226	291	331	731	320	440	2750	216	291	332	704	403	478	5290
pH	7.29	7.77	8.09	8.37	7.92	7.91	8.12	7.23	7.54	7.97	7.42	8.53	7.91	7.61	8.20	7.32	7.58	7.92	8.28	7.29	7.48	8.20	7.75	7.51	7.78	8.30	7.93	7.54	8.10	7.89
c (dissloved O_2)/ mg O_2 L^{-1}	10.07	10.63	12.59	11.91	10.49	10.44	11.40	-*	10.39	10.62	9.77	11.60	10.98	8.62	10.62	-*	10.50	9.26	10.60	7.28	8.29	10.62	-*	10.00	10.29	11.70	9.96	8.29	9.50	-*
Saturated oxygen / %	93.9	95.6	108.4	106.5	97.8	92.9	96.4	-*	96.1	97.9	93.4	106.6	108.9	85.2	100.1	-*	95.6	93.9	112.0	82.7	88.6	100.1	-*	103.8	91.6	108.0	88.5	88.6	88.7	-*
c (dissolved CO_2) / mg L^{-1}	5.2	1.6	2.7	3.8	2.8	2.5	2.3	20.3	4.7	31.0	4.3	2.1	2.1	2.7	1.1	14.0	4.0	4.1	2.5	2.0	1.7	1.6	8.8	5.7	3.6	3.8	2.4	2.0	4.9	9.1
COD / mg O_2 L^{-1}	1.6	**6.0**	2.4	2.5	3.8	**4.1**	**4.3**	12.0	0.2	**8.8**	**4.8**	0.2	2.11	**11.0**	**4.6**	**3030**	0.72	**165.5**	**4.0**	**4.9**	3.02	**4.4**	**2770**	1.0	**4.2**	1.4	**4.8**	1.7	3.1	101.7
c (NH_3) / mg N L^{-1}	<0.01	**0.15**	<0.01	<0.01	0.03	0.04	0.02	**13.15**	0.02	0.04	0.03	<0.01	**0.21**	**0.19**	0.02	7.88	0.01	**4.60**	**0.13**	0.03	0.02	0.05	**21.00**	0.02	**0.09**	0.04	**0.09**	**0.07**	0.03	2.40
c (total N) / mg N L^{-1}	0.2	**1.3**	0.3	0.2	0.6	1.0	0.9	**30.6**	0.1	0.8	0.2	0.6	**3.1**	**1.9**	0.6	**21.2**	0.2	**6.5**	0.9	0.3	0.5	0.8	**60.0**	0.3	**3.0**	0.7	**1.2**	**1.8**	0.8	**69.0**
c (NO_3^-) / mg N L^{-1}	0.03	0.14	0.02	0.05	0.09	0.10	0.10	**9.05**	0.08	0.15	0.09	0.05	0.07	0.22	0.11	**7.09**	0.04	0.41	0.07	0.02	0.02	0.10	**3.07**	0.11	0.21	0.23	0.05	0.25	0.03	**3.07**
c (NO_2^-) / mg N L^{-1}	0.010	0.027	0.017	0.009	0.018	0.014	0.016	**7.410**	0.014	0.017	0.019	0.006	0.016	0.021	0.019	0.405	<0.001	0.052	0.005	0.008	0.003	0.011	**1.230**	0.008	0.022	0.007	0.008	0.028	0.009	**9.090**
c (total P) / mg P L^{-1}	0.006	**0.107**	0.002	0.013	**0.062**	0.022	0.014	1.350	0.009	**0.084**	0.010	0.013	0.011	0.053	0.012	**2.210**	0.003	**0.890**	0.010	**0.016**	**0.086**	0.014	**8.540**	0.004	**0.087**	<0.001	**0.048**	0.017	0.037	1.300

Table S2 Organic parameters of the Krka River water and its tributaries (locations 1, 2, 6, 7) and of industrial wastewater (location 8) sampled in four sampling seasons (winter, spring, summer, autumn) in 2021 (* not measured). The values in bold are those that exceed the emission limit values according to the Regulation on limit values for waste water emissions (2020).

	Winter (28.1.2021.)					Spring (25.-27.4.2021)					Summer (20.7.2021)					Autumn (18.-20.10.2021)				
	1 KRS	2 KRK-MWW	6 TOR	7 TBU	8 IWW	1 KRS	2 KRK-MWW	6 TOR	7 TBU	8 IWW	1 KRS	2 KRK-MWW	6 TOR	7 TBU	8 IWW	1 KRS	2 KRK-MWW	6 TOR	7 TBU	8 IWW
c (mineral oils) / mg L^{-1}	-*	-*	-*	-*	-*	<0.005	<0.005	0.057	<0.005	**38.177**	<0.005	1.863	0.380	<0.005	**24.902**	<0.005	1.787	0.540	<0.005	**56.811**
c (phenols) / mg L^{-1}	-*	-*	-*	-*	-*	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.0478	<0.005	<0.005	<0.005	<0.005	**0.182**
c (TOC) / mg L^{-1}	0.816	1.757	1.480	1.002	9.932	1.476	1.552	4.321	1.694	**100.000**	1.064	6.783	6.042	2.798	22.820	1.557	8.164	1.775	2.468	21.180
c (DOC) / mg L^{-1}	0.825	1.821	1.484	0.981	7.693	1.381	1.496	3.519	1.272	76.360	0.876	5.483	2.517	1.272	11.970	0.268	7.794	1.535	1.021	20.360

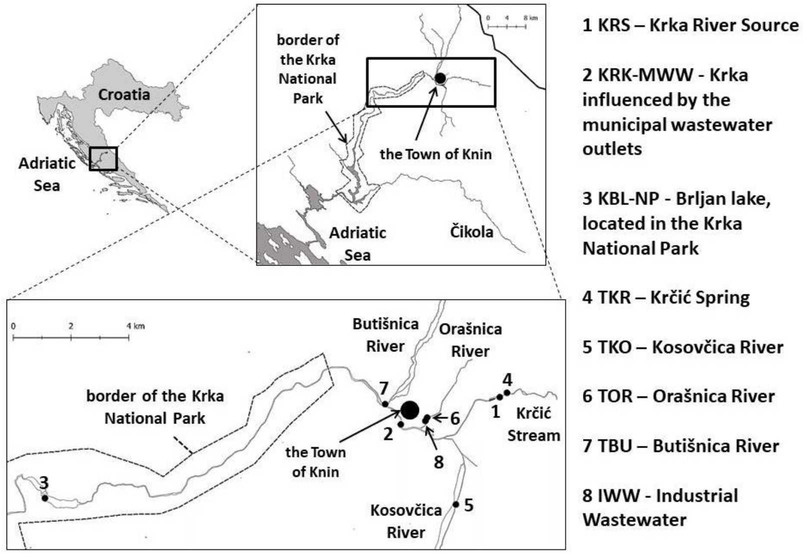

Fig. S1 Map of the Krka River catchment with enlargement of the study area near the Town of Knin. Sampling sites along the upper reaches of the Krka River and its tributaries are marked with numbers 1 – 8.

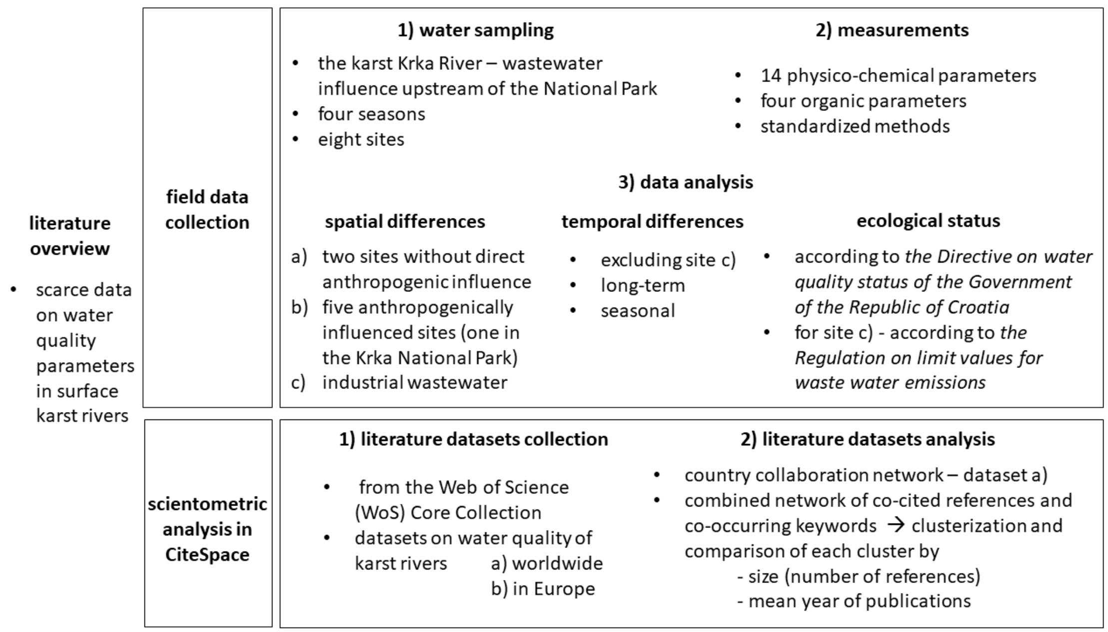

Fig. S2 Schematic framework of the methodological approach used to conduct the current study

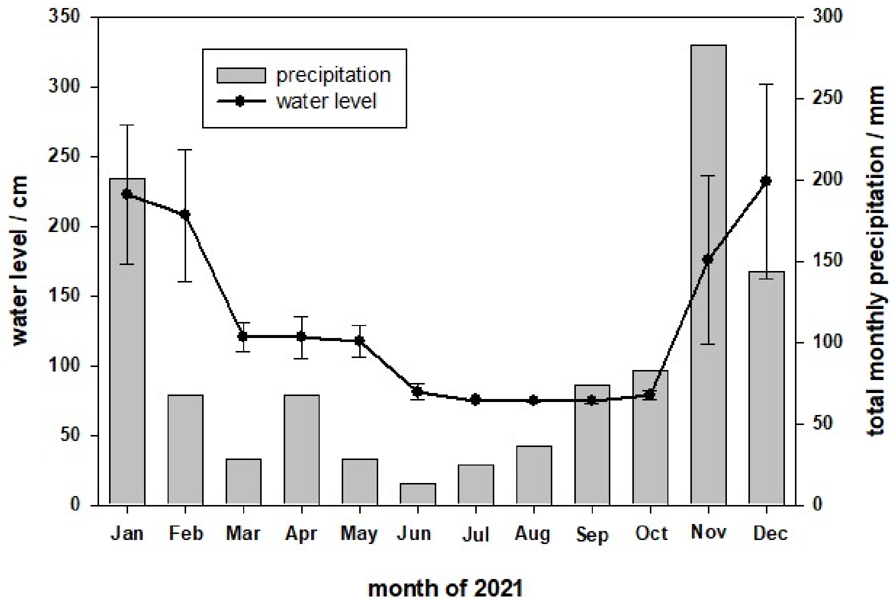

Fig. S3 Water level and precipitation regime in 2021 based on the data provided by Croatian Meteorological and Hydrological Service (hydrological station Knin).

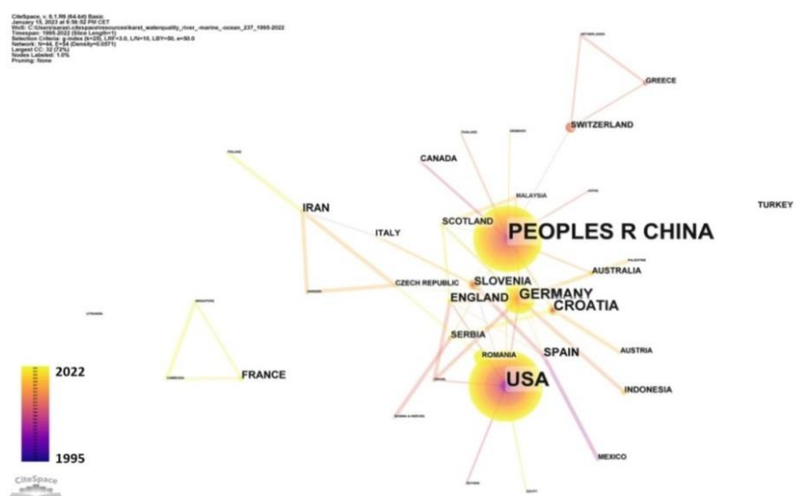

Fig. S4 A visualization of the country collaboration network for literature connecting topics "karst", "water quality" and "river". Larger circles and more prominent labels indicate countries with more studies. Colors indicate when citations were made.