

# CHANGES IN THE GEOCHEMICAL PARAMETERS OF KARST LAKES OVER THE PAST THREE DECADES – THE CASE OF PLITVICE LAKES, CROATIA

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## Abstract

One of the major reasons for the increase in global air temperature since the early 20<sup>th</sup> century is considered to be the increase in the atmospheric CO<sub>2</sub> concentration. Karst relief is considered an important carbon sink, but it can also be a natural source of carbon and CO<sub>2</sub> emission. Aquatic systems in karst areas facilitate carbon exchange between the karst and the atmosphere, often through groundwater geochemical carbonate rock dissolution (carbon sink) and in the form of secondary calcium carbonate precipitation (possible carbon source). The protected area of Plitvice Lakes National Park, located in the karst region of Croatia, was chosen as a case study on karst geochemical processes. The lakes are also specific for their authigenic calcite precipitation in the form of tufa barriers and lake sediment. Physical and chemical data (temperature, *pH*, Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, Mg<sup>2+</sup> and CO<sub>2</sub> concentrations, calcite saturation index (*SI<sub>calc</sub>*), calcite dissolution ionic ratio (*IR<sub>calc</sub>*), and *Mg/Ca* ratio) from water samples collected at 8 locations (2 springs, 2 rivers, and 4 lakes) from 1981-2014 were studied.

The data were not collected systematically, so long-term changes have been mostly assessed through comparison between parameters from two selected periods (1981-1986 and 2010-2014) and through temporal correlations for each observed parameter in each calendar month.

For the 33 years studied, an increase in air and water temperature, Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations, calcite saturation index (*SI<sub>calc</sub>*), calcite dissolution ionic ratio (*IR<sub>calc</sub>*), and a decrease in the *Mg/Ca* ratio were observed. No statistically significant change was observed for *pH* or CO<sub>2</sub> and Mg<sup>2+</sup> concentrations. Average discharge rates did not display any significant change over the past three decades, however there was a change in their seasonal distribution.

The significant increase in Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations at lake locations were primarily caused by an increase in Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> values in the water of the springs. Simultaneously, Mg<sup>2+</sup> concentrations remained constant, which indicates higher levels of limestone (calcite) dissolution than dolomite dissolution. One of the reasons for this could be higher air/soil temperatures, resulting in higher soil CO<sub>2</sub> production, which appears to result in the higher dissolution of calcite exclusively. An increase in HCO<sub>3</sub><sup>-</sup> concentrations at the springs implies that karst groundwater is a carbon sink. Furthermore, the fact that the spatial decrease in HCO<sub>3</sub><sup>-</sup> concentration in downstream waters was the same during the 1981-1986 and 2010-2014 periods implies that the entire observed karst lake system itself is a carbon sink.

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Temporal and spatial changes in  $SI_{calc}$  and  $IR_{calc}$  values in surface waters were mainly attributed to an increase in the intensity of bioactivity, which is in turn connected with an increase in water temperature.

## 1. INTRODUCTION

Calculations of global mean air temperatures reveal that the last decade, 2001-2010, was the warmest since 1880, the first year for which sufficient worldwide data are available (Arndt et al., 2010). Consequently, snowfall levels have decreased, snowmelt seasons have arrived earlier (Blunden and Arndt, 2013), the water temperature in lakes and springs have increased (Isaak et al., 2012), and surface waters discharge rates have decreased (Lu, 2004). One of the main reasons for the increase in global temperature is believed to be an increase in the atmospheric CO<sub>2</sub> concentration (Le Treut et al., 2007).

In Croatia, a temporal air temperature increase trend was observed at recorded levels of 0.05 - 0.10 °C/decade from the beginning of the 20<sup>th</sup> century until 2008, as was a decrease in snowfall (Gajić-Čapka et al., 2010).

The world's karst is believed to account for about 21% of unknown continental carbon sinks (Gombert, 2002). Karst consists of carbonate rocks, such as limestone and dolomite, interspersed with holes, caves, and channels that are often filled with water. Karst water originates from precipitation that enters the soil and dissolves soil CO<sub>2</sub>, which is a product of root respiration and organic matter (OM) decomposition in the soil. The resulting H<sub>2</sub>CO<sub>3</sub> dissolves bedrock carbonates, and karst spring water is thus enriched with dissolved inorganic carbon (mainly HCO<sub>3</sub><sup>-</sup>), CO<sub>2</sub>, and Ca<sup>2+</sup>. Slightly alkaline (*pH*>7.5) karst waters oversaturated with Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> (*SI<sub>calc</sub>* >3), water flow, bioactivity (photosynthesis, which increase *SI<sub>calc</sub>* on the micro-level), and warm conditions all present favourable conditions for the precipitation of CaCO<sub>3</sub> in the form of tufa (Srdoč et al. 1985 and Gradziński 2010). Temperature is also a major factor in the morphological development of tufa. Rapid biofilm colonization and tufa formation are both characteristic of locations with a warm climate (Pedley et al. 1996).

Temperature increases and longer sun exposure result in higher photosynthetic activity and CO<sub>2</sub> consumption, resulting in an increase in microbiologically induced CaCO<sub>3</sub> precipitation. Decreases in water discharge rates additionally contribute to the accumulation of calcifying bacteria, resulting in an increase in bioactivity (Bissett et al. 2008; Dupraz et al. 2009; Gradziński 2010). Conversely, enhanced bioproductivity increases the amount of OM and decomposition in the water, resulting in higher concentrations of dissolved CO<sub>2</sub> and lower *pH* values. Decreases in *pH* values can reduce the physicochemical precipitation potential of CaCO<sub>3</sub>.

During purely physical calcite precipitation, degassing occurs and CO<sub>2</sub> is emitted into atmosphere, thereby acting as a carbon source. Bioinduced precipitation, however, stores CO<sub>2</sub> in the biota, and can therefore be considered a carbon sink (Liu et al. 2010; Liu and Dreybrod 2015; Yang et al. 2015).

Atmospheric warming also increases soil temperatures, which accelerates OM decomposition in the soil (Kirschbaum 1995; Kirschbaum 2006), resulting in higher soil CO<sub>2</sub> pressure (Lloyd and Taylor 1994). This results in higher karst bedrock dissolution (Pokrovsky et al. 2005) and the increased storage of dissolved CO<sub>2</sub> in groundwater in the form of HCO<sub>3</sub><sup>-</sup>, thus acting as a CO<sub>2</sub> sink (Macpherson et al. 2008; Jeannin et al. 2016).

This paper is based on an assessment of the influence of global temperature change on the physicochemical water parameters of Plitvice Lakes. These water parameters influence the formation of tufa, the growth of which intensifies during warm periods (Horvatinčić et al.,

2000; Horvatinčić et al., 2003; Srdoč et al., 1994). As a complex karst system, Plitvice Lakes can be considered an appropriate location for the study of the influence of global temperature changes on geochemical processes in karst areas.

The physicochemical parameters that determine the conditions for tufa precipitation (temperature, *pH*,  $\text{Ca}^{2+}$  concentrations,  $\text{Mg}^{2+}$  concentrations,  $\text{HCO}_3^-$  concentrations,  $\text{CO}_2$  concentrations, calcite saturation index ( $SI_{calc}$ ), *Mg/Ca* ratio) in the water of Plitvice Lakes during the last three decades were studied. A new computational variable was introduced, the “calcite dissolution ionic ratio”,  $IR_{calc}$ , in order to assess the implicit influence of temperature on the relationship between  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{H}^+$  concentrations.

The aim of the paper is to solve the following issues:

- 1) Has the water temperature in Plitvice Lakes changed in the past three decades?
- 2) How have temperature changes affected the geochemical parameters studied?
- 3) Can this karst lake system be considered a carbon sink, a carbon source, or both?

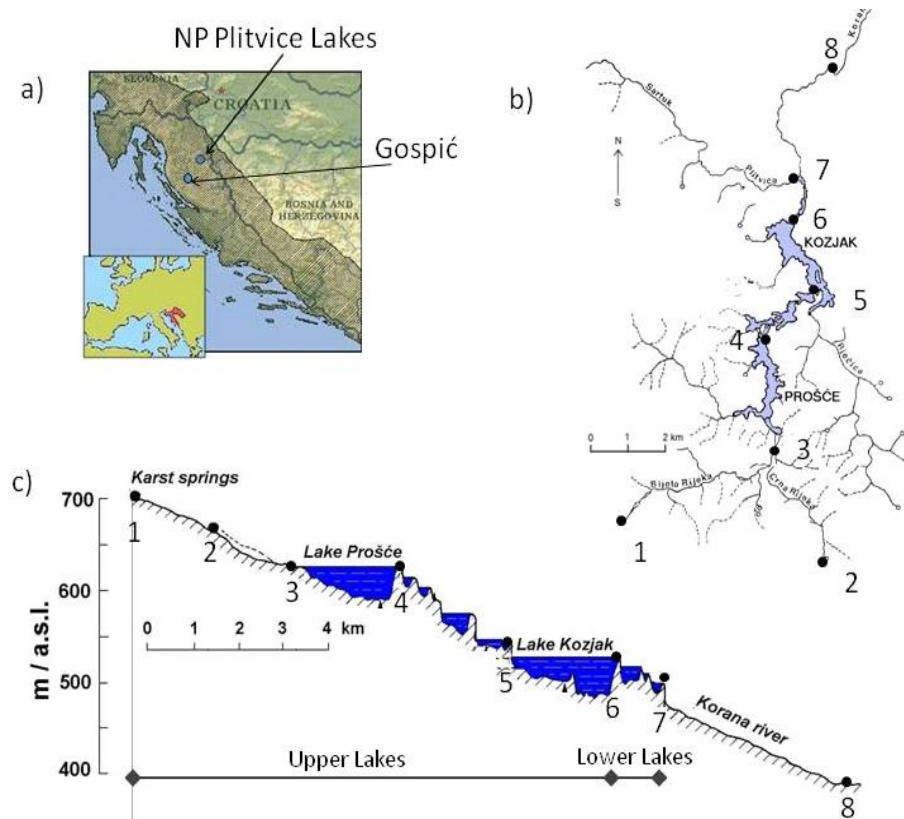
## 2. SITE DESCRIPTION

Plitvice Lakes National Park is located in the Dinaric karst in Central Croatia (44° 53' N, 15° 37' E) (Fig. 1 a). The lake system covers only 1 % of the total surface area of the park, the remainder of which is mostly deciduous forest with some conifer stands. The region has a typical continental climate, with a mean annual temperature of 9.9°C and 1320 mm/year of precipitation (Croatian Meteorological and Hydrological Service, 10 year mean, 2004-2013, data collected at the Gospić meteorological station).

The Plitvice Lakes system consists of 16 cascading lakes separated by tufa barriers and connected by waterfalls (Fig. 1 b and Fig. 1 c) at altitudes between 400 m and 700 m above sea level. The lake system has a total length of ~12 km, and it is traditionally divided into the Upper and Lower Lakes. The lakes are fed by two main karst springs – those of the Bijela Rijeka and Crna Rijeka rivers. The two rivers flow into the Matica river, which discharges into the first lake, Prošće. The Crna Rijeka river is located on dolomite/limestone bedrock, while the Bijela Rijeka river, the Matica river, and the Upper Lakes (containing the two largest lakes in the system, Prošće and Kozjak, Fig. 1b, Table 1) rest on dolomite, which is less permeable than limestone. The Upper Lakes end with Kozjak lake, which discharges into the Lower Lakes, which further discharge into the Korana river. The Lower Lakes and the canyon of the Korana river with its numerous caves rest on limestone bedrock (Polšak, 1969, 1974). Several smaller tributaries also join the Plitvice Lakes system (Fig. 1b).

Due to the underlying carbonate bedrock, Plitvice Lakes are hard-water lakes with a large population of calcifying cyanobacteria (Plenković-Moraj et al. 2002; Žutinić et al. 2014), and are characterized by conditions favourable for calcite precipitation ( $SI_{calc}$  values range from 3 - 10 and *pH* values range from 8.0 - 8.7) (Barešić et al. 2011; Srdoč et al. 1985). Calcite precipitation is highest between spring and autumn, and is lower in wintertime (Srdoč et al. 1985). Carbonate precipitation does not occur in springs and in some tributaries. The hydrochemistry of the lakes and the changes in hydrochemistry along the range of the lakes from the springs to the Korana river have been described in detail (Kempe and Emeis 1985; Srdoč et al. 1985).

The continuous interaction between atmospheric CO<sub>2</sub>, water, carbonate bedrock, soil CO<sub>2</sub>, and the biota influences the precipitation of calcite in the form of tufa barriers and fine-grained lake sediment, creating a cascading series of lakes that are a living, constantly changing system.



**Fig. 1** a) Geographical setting of Plitvice Lakes and Gospić meteorological data station in the Dinaric karst (shaded area); b) Map of the Plitvice Lakes area with sampling points; c) Cross section of Plitvice Lakes with sampling points (1 – 8)

### 3. SAMPLING AND MEASUREMENT

Research of Plitvice Lakes has been conducted for more than three decades by the Low Level Radioactivity Laboratory and by the Dr. Ivo Pevalak Scientific Research Centre, the official research centre of Plitvice Lakes National Park. Sampling and measurements were conducted as part of different projects, and were therefore not consistent throughout the entire period. The largest gap in data collection was between 1990 and 2002 due to the Croatian War of Independence (1991-1995). Taking these limitations into consideration, the most consistent data between 1981 and 2014 was taken during two separate periods: 1981-1986 and 2010-2014.

Eight sampling locations (Table 1, Fig. 1b and Fig. 1c) and five physicochemical parameters with the most abundant and systematic data were chosen. The selection process considered locations that cover the entire Plitvice Lakes system, from the springs to the Korana river, and the geological specificities of each location were taken into account. Sampling and *in situ* measurements were taken in near shore surface water.

Table 1 Sampling locations and characteristics

Location number	Location name	Distance from the springs (km)	Description
1	Bijela Rijeka spring	0	Spring of the Bijela Rijeka river, Upper Malm silicificated relatively impermeable dolomites and Lower Malm permeable limestone/dolomite - recharge area
2	Crna Rijeka spring	0	Spring of the Crna Rijeka River, relatively impermeable Liassic dolomites and Malm permeable limestone with dolomite lenses - recharge area
3	Matica river	3.7	Matica river, after the confluence of the Bijela Rijeka and Crna Rijeka rivers, dolomite bedrock
4	Prošće-Labudovac lake	5.7	Overflow from Prošće lake, dolomite bedrock
5	Burget lake falls	8.0	Part of a string of waterfalls emptying from Burget lake into Kozjak lake, dolomite bedrock
6	Kozjak lake	10.5	Overflow from Kozjak lake into the Lower Lakes, dolomite bedrock
7	Novakovića Brod lake	11.4	Novakovića Brod lake, left bank, limestone bedrock
8	Korana river	15.0	Korana river, outflow from lakes, ~4 km after the last lake, limestone bedrock

Water temperature and *pH* were measured *in situ* using a WTW Multimeter (margin of error  $\pm 0.1^\circ\text{C}$  and  $\pm 0.01$ , respectively). Concentrations of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  were determined using APHA standard titrimetric methods (APHA, 2005) with a margin of error of  $\pm 0.02$  mmol/l, while  $\text{Mg}^{2+}$  concentrations were calculated from the difference between total hardness and calcium hardness. Dissolved  $\text{CO}_2$  concentration, calcite dissolution ionic ratio ( $IR_{calc}$ , defined as  $c(\text{Ca}^{2+}) \cdot c(\text{HCO}_3^-) / c(\text{H}^+)$ , which is equivalent to  $SI_{calc}$  without the temperature-dependent part), and calcite saturation index ( $SI_{calc}$ ) were calculated from the measured parameters (Lerman 1979). Their derived margins of error are:  $\pm 5$   $\mu\text{mol/l}$ ,  $\pm 0.7$  mol/l and  $\pm 0.1$ , respectively.

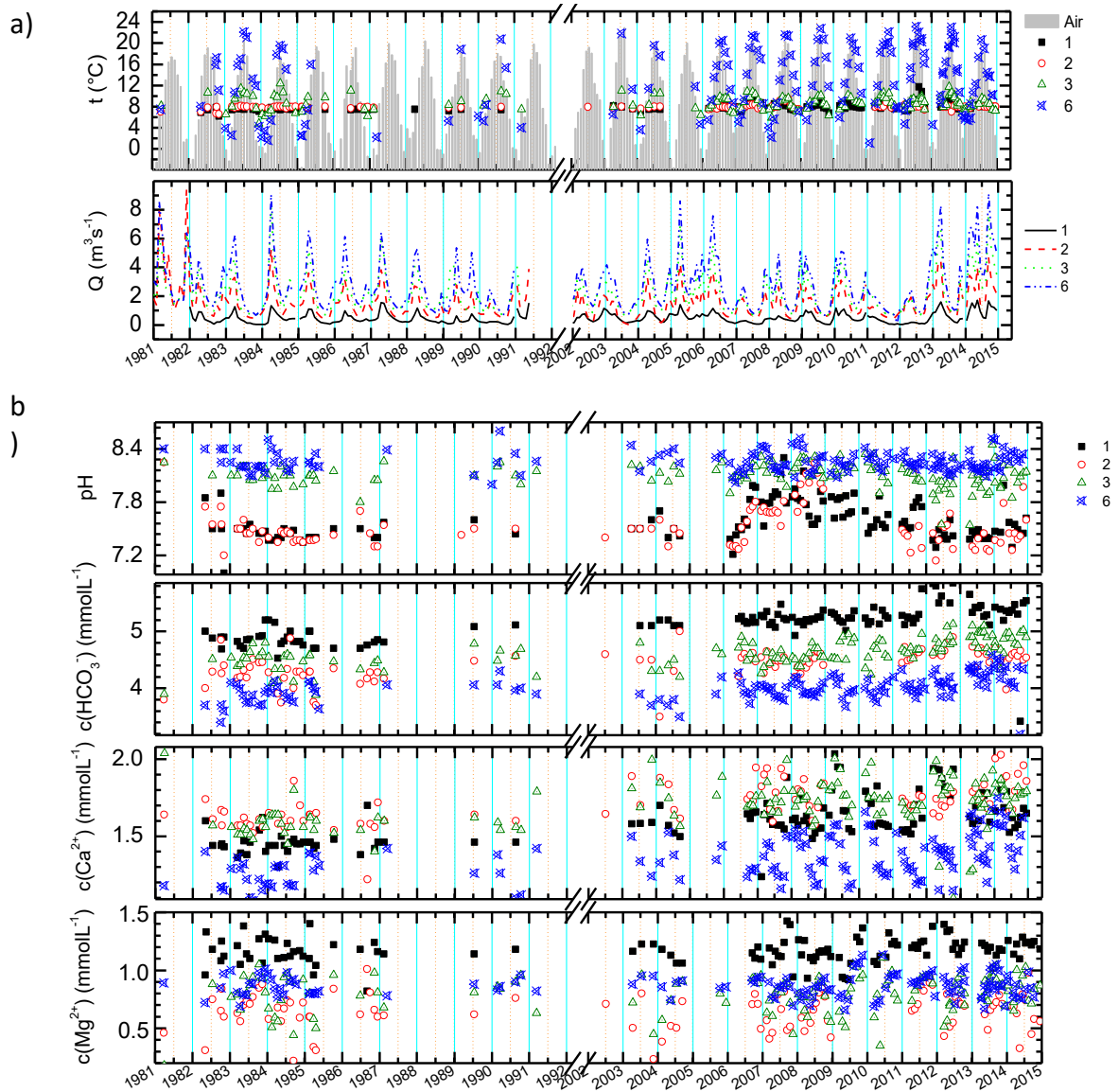
Mean daily air temperature data was obtained from the Gospić meteorological station, the nearest station at a similar altitude to Plitvice Lakes National Park, with the most similar climatic conditions, and with the most complete data set (available from the Croatian Meteorological and Hydrological Service, CMHS).

Discharge rate data was only collected at four locations (1, 2, 3 and 6) from 1981-2014 (CMHS), and only location 6 (Kozjak lake) was used in analyses as a reference for discharge rate, since the discharge rates from locations 1, 2, and 3 are proportional to location 6 (Vurnek et al. 2010).

#### 4. DATA SET AND STATISTICAL ANALYSES

The data set consists of 9 variables at 8 sampling locations for a total of 8,399 values. This amount represents 30% of all possible data, and so usual statistical methods (principal component analysis, Fourier transformation) cannot be used. Due to the large number of data

for visual presentation in Fig. 2, we selected the four most representative locations (1, 2, 3, and 6 – two springs, a river, and a lake, respectively) with the intent of illustrating the dispersion of data over time.



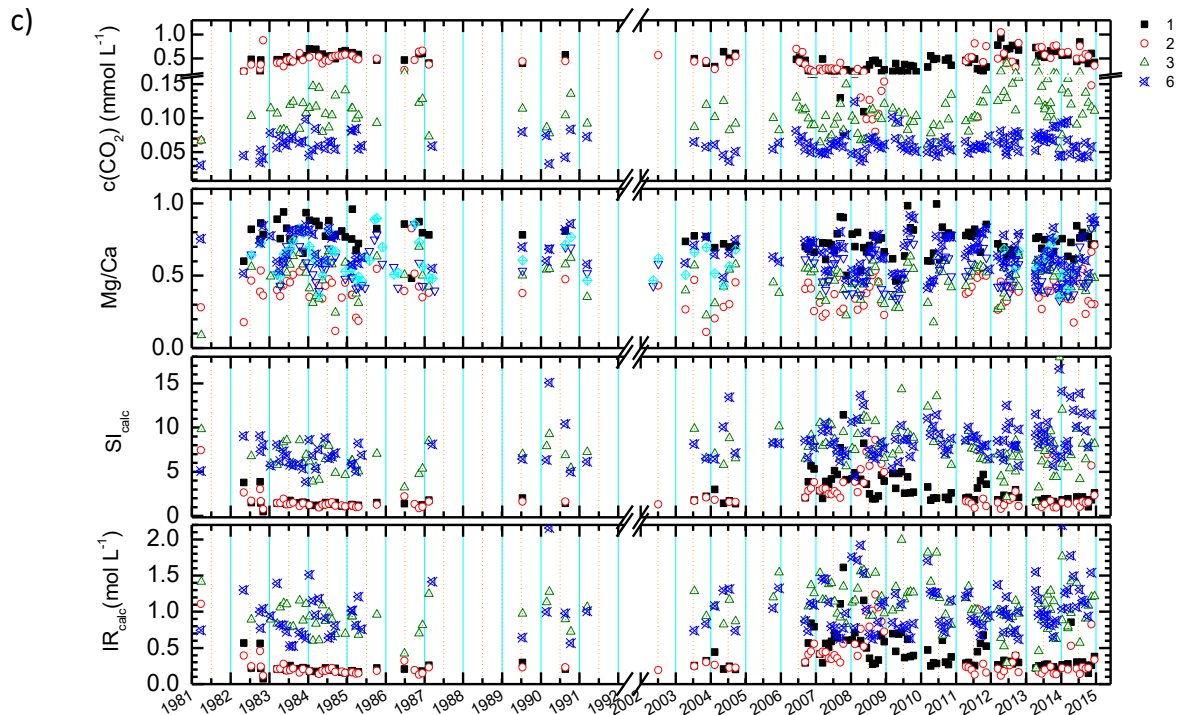


Fig. 2 All measured and calculated data for locations 1, 2, 3, and 6: a) Air temperature in Gospić, water temperature and discharge rates, b) measured data, and c) calculated data

Statistical analysis was conducted taking into account the fact that the data was collected inconsistently in various months throughout the calendar year.

Since seasonal and spatial changes in the observed parameters might influence the evaluation of their long-term change, a brief analysis of spatial and seasonal changes in the data is given. Seasonal changes have also been evaluated by correlating each parameter to the coinciding water temperature and discharge rate separately at each observed location. The statistical significance of correlations was set at  $\alpha = 0.05$ .

Long-term changes in the parameters over the past three decades were calculated using two principles: 1) mean values were compared for two selected time periods with the most similar monthly distribution of sampling campaigns (1981-1986 and 2010-2014), and 2) time-dependent trends in each calendar month from 1981-2014 were calculated for each observed parameter.

To compare the two time periods (1981-1986 and 2010-2014), the annual mean value of measured and calculated parameters for each period was determined by calculating mean monthly values (except February and November due to missing/non-continuous data in the first period) in each period and then calculating their 10-month mean. A paired t-test was used with a declared significance level of  $\alpha = 0.05$  between the two data sets. The test was used to compare the mean monthly values for each location and the mean annual values of each parameter at each location in two periods – the former provides insight into changes in the seasonal characteristics of parameters at each location in the two time periods, while the latter describes changes in parameters at each location (spatial change) in the two time periods.



Long-term changes in parameters (at each location) in each calendar month from 1981-2014 were used to either confirm or refute the results of the aforementioned temporal change calculations. The calculations were not performed for January, February, or December, as the amount of possible measurements taken during these months was less than 25%, which we considered the minimum data amount. The significance level for correlations was declared at  $\alpha = 0.05$ .

## 5. RESULTS AND DISCUSSION

### 5.1 Spatial and seasonal changes

Spatial changes in each measured and calculated parameter (Fig. 3) show significant downstream changes influenced by the processes in the water, i.e. CO<sub>2</sub> degassing, evaporation, and calcite precipitation induced by degassing and bioactivity.

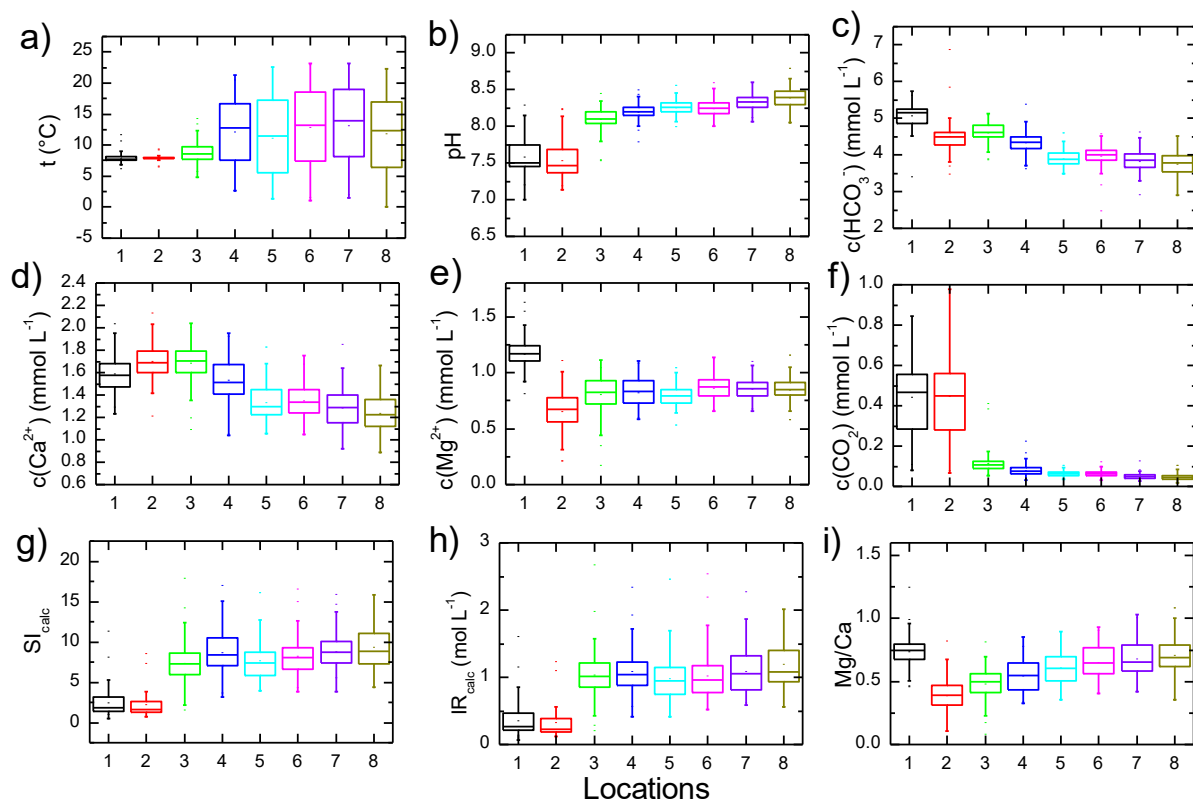


Fig. 3 Box plot (median, first, and third quartile and maximum and minimum) for measured and calculated data at each location (1-8) from the springs downstream to the Korana river from 1981- 2014 - spatial changes

The result of these processes is a downstream increase in the mean values of temperature, *pH*, and *Mg/Ca*, as well as an indicated increase in *SI<sub>calc</sub>* and *IR<sub>calc</sub>*, a decrease in Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>2</sub> concentrations, while Mg<sup>2+</sup> concentrations remain constant. The spring locations behave differently than the river and lake locations, reflecting changes in the surrounding conditions in the springs and surface water. In particular, this can be observed in the

dispersion of data, which is larger at the lakes for water temperature,  $SI_{calc}$  and  $IR_{calc}$ , and larger at the springs for  $CO_2$  concentration and  $pH$ . Spatial and seasonal changes in the Plitvice Lakes area have also been discussed in Srdoč et al. 1985 and Barešić et al. 2011.

Seasonal fluctuations in all parameters are shown in Fig. 4 and Fig. 5.

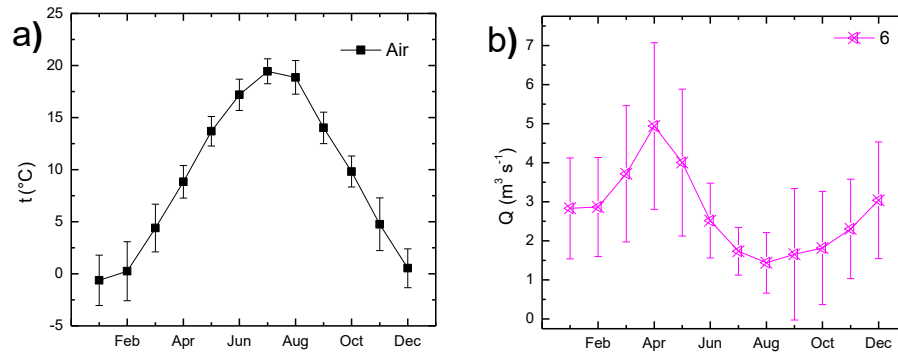


Fig. 4 a) Mean monthly values with standard deviation of air temperature at Gospić, and b) discharge rate at location 6 - seasonal fluctuations from 1981-2014

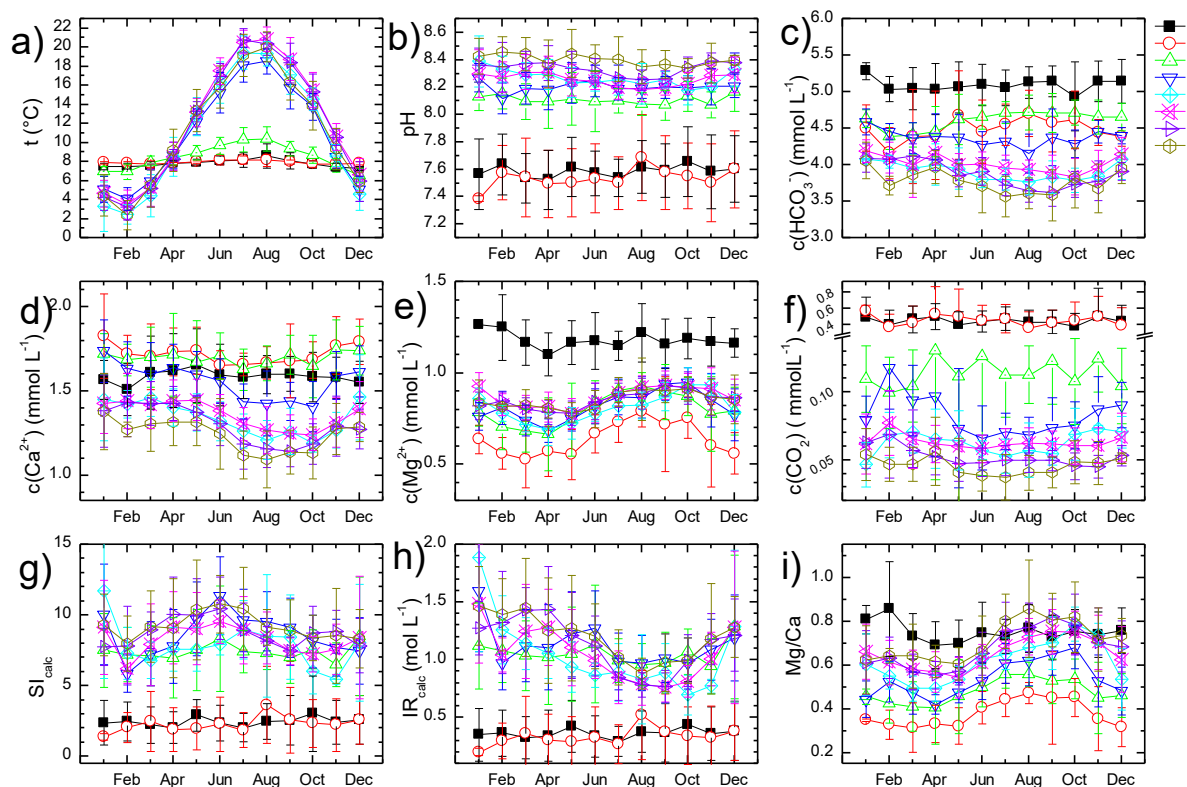


Fig. 5 Mean monthly values with standard deviations for measured and calculated water parameters at each location (1-8) – seasonal fluctuations from 1981-2014

The highest air temperature value (Fig. 4a) is in July ( $19.4 \pm 1.0$  °C) and the lowest is in January ( $0.6 \pm 2.4$  °C). The highest discharge rate (Fig. 4b) is observed in April ( $4.9 \pm 2.0$  m<sup>3</sup>/s), while the lowest discharge is observed in August ( $1.3 \pm 0.6$  m<sup>3</sup>/s). Air/water temperatures and discharge rates can be stated as the main driving force for seasonal changes in the measured and calculated chemical parameters.

The physicochemical water parameters at the springs (Fig. 5) are the most consistent, showing little to no seasonal change. The influence of seasonal change is the most prominent at river and lake locations for water temperature,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  concentrations,  $IR_{calc}$ ,  $SI_{calc}$ , and  $Mg/Ca$ , as well as for  $\text{HCO}_3^-$  concentrations (to a lower extent). The influence of water temperature and discharge rates on chemical parameters has been assessed through correlation. Correlation coefficients ( $R$ ) at each location for statistically significant correlations only ( $p < 0.05$ ) are presented in Appendix A, Table A1, and Table A2. All correlations can be explained either through changes in calcite dissolution or through precipitation intensity due to changes in temperature, water flow velocity, water level, or bioactivity. The difference in two computational variables,  $SI_{calc}$  and  $IR_{calc}$ , is apparent from these correlations: while they behave similarly regarding discharge rate correlations and temperature correlations at the springs, a negative temperature dependence is observed only for  $IR_{calc}$  at most surface water locations. As this trend is not shared by  $SI_{calc}$ , it can be claimed to be the result of bioactivity only. Two distinct processes influence the correlation between temperature and  $SI_{calc}$ :  $SI_{calc}$  increases with temperature since the physical dissolution of calcite is lower at higher temperatures, and  $SI_{calc}$  is mathematically proportional to  $IR_{calc}$ , which correlates negatively with temperature (Appendix A, Table A1).

Another noteworthy point made apparent from an observation of seasonal changes is that  $Mg/Ca$  shows a very strong correlation to temperature at almost all locations (Appendix A, Table A1). The positive  $Mg/Ca$  to temperature correlation is the basis for using  $Mg/Ca$  as a palaeoclimatic temperature indicator in laminated tufa deposits (Lojen et al. 2009). This indicator is based on the higher level of tufa precipitation (resulting in lower  $\text{Ca}^{2+}$  concentrations) and higher evaporation (resulting in higher  $\text{Mg}^{2+}$  concentration) at higher temperatures.

## 5.2 Comparison of temporal changes between 1981-1986 and 2010-2014

The changes in air temperature and discharge rates over the past three decades are presented in Fig. 6. (annual air temperatures in Gospić, Fig. 6a, and monthly values for discharge rates for location 6 (Kozjak lake) in 1981-1986 and 2010-2014 in Fig. 6b).

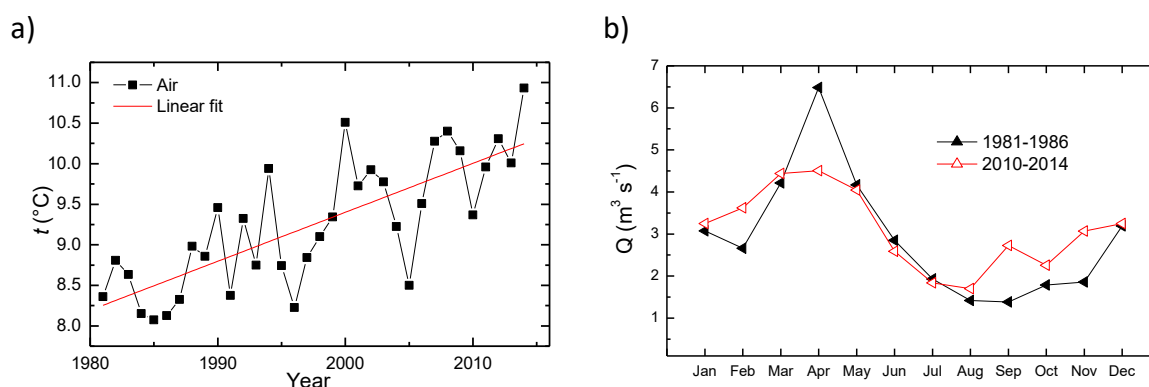


Fig. 6a) Mean annual air temperature values in Gospić from 1981 to 2014 and b) comparison of mean monthly discharge rates at location 6 between 1981-1986 and 2010-2014

Over the past 33 years, there has been a significant increase in mean annual air temperature of  $0.60 \pm 0.09$  °C/decade,  $R = 0.77$ ,  $N = 34$  (annual mean standard deviation is 7.5 °C), with oscillations of  $\sim 5$  °C between minimum and maximum annual values (Fig. 6a). There is no significant trend for annual discharge rates at locations 1, 2, 3, and 6 from 1981 to 2014. However, a comparison of mean monthly values for discharge rates at location 6 in the two selected time periods (1981-1986 and 2010-2014) (Fig. 6b) reveals changes in their seasonal distribution: a decrease in maximum value and an increase in minimum value for the second period.

The change in measured and calculated parameters in the two selected time periods (1981-1986 and 2010-2014) is presented in Fig. 7 and in Appendix B.

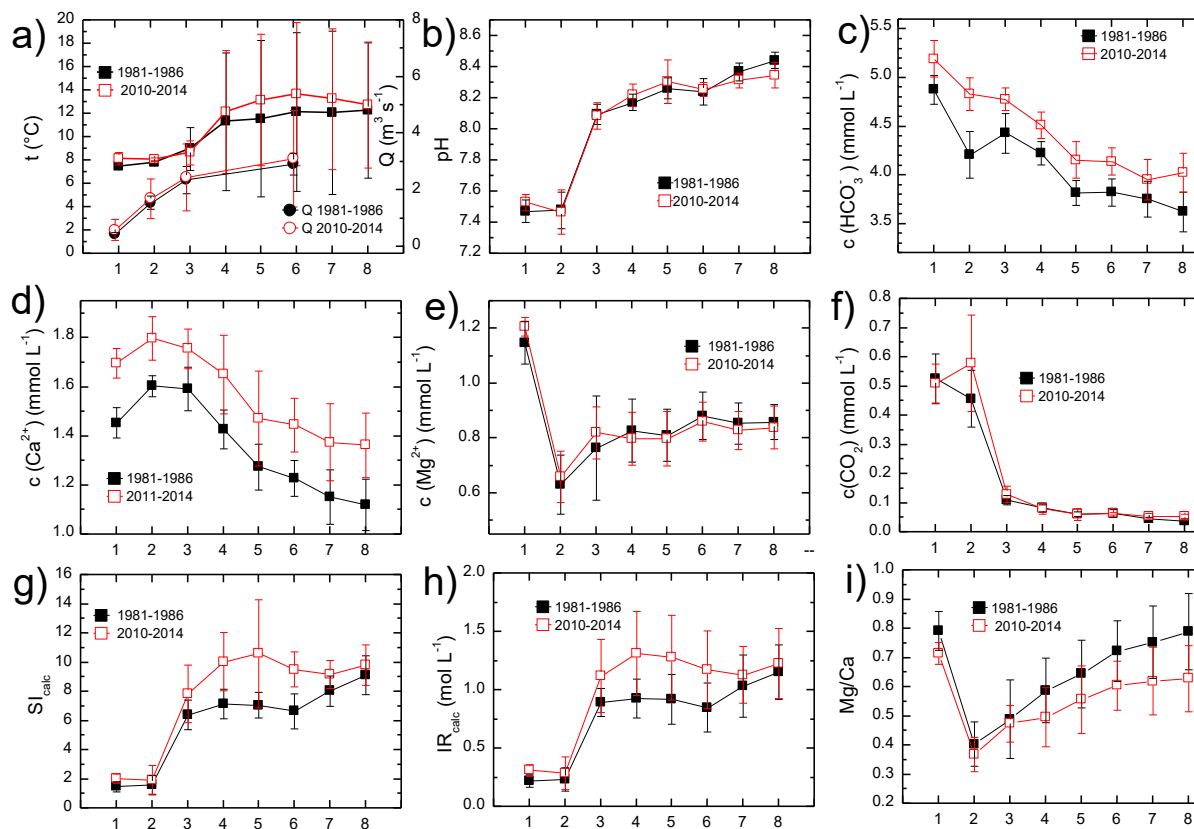


Fig. 7 Mean values for all measured and calculated parameters with standard deviation (vertical bars) in 1981-1986 and 2010-2014 (without data for February and November) for all 8 locations, from the springs downstream

During the second period, annual means are higher for water temperature, discharge rates,  $c(\text{Ca}^{2+})$ ,  $c(\text{HCO}_3^-)$ ,  $Sl_{calc}$ , and  $IR_{calc}$ , while they are lower for  $Mg/Ca$  (Fig. 7). These values differ significantly between the two observed periods (Appendix B).

To further confirm the results of these data analyses, each parameter (in each month from March to November and at each location) was correlated to a time line (from 1981-2014), and a list of statistically significant positive and negative correlations is provided in Appendix C-Table C1. Table 2 displays what percentage of correlations were temporally significant for each parameter from Appendix C Table C1 (9 basic matrices of 72 location-month combinations).

Table 2 Percentage of significant temporal correlations for each parameter for each location-month combination (expressed in decimal)

	<i>t</i>	<i>pH</i>	$c(\text{HCO}_3^-)$	$c(\text{Ca}^{2+})$	$c(\text{Mg}^{2+})$	<i>SI<sub>calc</sub></i>	<i>IR<sub>calc</sub></i>	$c(\text{CO}_2)$	<i>Mg/Ca</i>
Positive	0.18	0.03	0.44	0.64	0.03	0.15	0.15	0.04	0
Negative	0.04	0.04	0	0	0.03	0	0	0.03	0.24

The 9 basic matrices of each parameter in Appendix C, Table C1 were compared in order to evaluate the amount of coinciding significant trends present within them (whether positive or negative), and they are expressed as a percentage in decimal in Appendix C, Table C1. A high percentage implies that the observed pair of parameters is more highly interconnected.

The continuous temporal observation of water temperature changes from 1981-2014 (Appendix C, Table C1) confirms an increase in water temperature at almost all locations, as indicated by changes between 1981-1986 and 2010-2014 (Fig. 7a). The highest change in the two periods from 1981-1986 and 2010-2014 (1.6 °C) was observed at lake location 6. This value is equivalent to a 1.5 °C change in air temperature in Gospić (omitting February and November). The temperatures at the springs changed the least (0.6 °C and 0.4 °C at locations 1 and 2, respectively, for the two periods).

However, a temporal cooling trend was observed at location 3 (Matica river, Appendix C, Table C1). A temporal cooling trend for surface water was also observed elsewhere (Isaak et al. 2012; Jeannin et al. 2016), but in regulated streams (i.e. with the impact of urbanisation). In the case of location 3, there is no human impact (urbanisation), as this location lies within the protected area of Plitvice Lakes National Park. As shown in Fig. 6b, the dynamics of seasonal discharge rate fluctuations has changed in the past three decades, a fact that may in turn diminish surface water mass and increase the impact of groundwater mass at location 3. One additional unidentified groundwater inflow to location 3 is also implied in Babinka (2007), supporting this claim.

Although there was no observed temporal change in the mean yearly amount of precipitation, a temporal decrease in snowfall during winter in Croatia was recorded (Gajić-Čapka et al. 2010), which influences the seasonal distribution of discharge rates for the two periods. Also, a significant temporal correlation in water temperatures, especially pronounced in early spring, could be attributed to changes in the seasonal characteristics of water discharge in the two periods (Appendix , Table C1). Lower discharge rates during the spring maximum values due to reduced snowfall during the second period (2010-2014) allow easier heat exchange between the air and lake water, resulting in higher lake water temperatures.

There is also a statistically significant increase of  $c(\text{CO}_2)$  during the second period at locations 3, 7, and 8, and a statistically significant decrease in *pH* at locations 7 and 8 (Appendix B and Fig. 7b and 7f). This implies higher  $\text{CO}_2$  production during the second period at these locations, perhaps due to higher levels of organic matter decomposition.

Values for  $c(\text{Ca}^{2+})$  and  $c(\text{HCO}_3^-)$  show the most pronounced changes at all observed locations during the two selected time periods (Appendix B, Fig. 7c and Fig. 7d). On the other hand,  $c(\text{Mg}^{2+})$  does not show any temporal change (Table 2 and Fig. 7e). The spatial decrease in  $c(\text{Ca}^{2+})$  and  $c(\text{HCO}_3^-)$  (Fig. 3c and 3d, Fig. 7c and Fig. 7d) is a result of calcite precipitation downstream (Barešić et al. 2011; Biondić et al. 2010; Srdoč et al. 1985). As the downward downstream trends in  $c(\text{Ca}^{2+})$  and  $c(\text{HCO}_3^-)$  values are essentially the same during both

periods,  $c(\text{HCO}_3^-)$  and  $c(\text{Ca}^{2+})$  are 15% and 7% on average, respectively, and are higher in the period from 2010-2014 at all locations (Fig. 7c and Fig. 7d). The main reason for their temporal increase at lake locations is a corresponding increase at both springs (locations 1 and 2).

The temporal increase in  $c(\text{Ca}^{2+})$  and  $c(\text{HCO}_3^-)$  at the springs and its connection with increased temperatures has also been observed elsewhere (Benčoková et al. 2011; Liu and Zhao 2000; Jeannin et al. 2016; MacPherson et al. 2008; Moiseenko et al. 2013; Ren et al. 2015; Yang et al. 2012; Zhao et al. 2015). The combination of an increase in  $c(\text{Ca}^{2+})$  and  $c(\text{HCO}_3^-)$  and stable  $c(\text{Mg}^{2+})$  values in the karst environments of the Alps and the eastern Balkans has also been reported by Jeannin et al. (2016) and Long et al. (2012). Long et al. (2012) explains this through the disruption of geochemical processes by chemicals used in agricultural activities. The current case study was performed in the protected area of a national park, so this explanation can be excluded.

One possible explanation for the temporal increase in  $c(\text{Ca}^{2+})$  and  $c(\text{HCO}_3^-)$  and not in  $c(\text{Mg}^{2+})$  could be attributed to the fact that increases in air temperature also results in increases in soil temperature, which in turn results in higher soil  $\text{CO}_2$  production (Kirschbaum 1995; Lloyd and Taylor 1994). This idea is supported by the increase in  $c(\text{CO}_2)$  at spring location 2 during the second period (Fig. 7c). While dolomite dissolution rates increase with increasing  $\text{CO}_2$  pressure to up to 10 atm of  $p\text{CO}_2$ , after which it stagnates, the calcite dissolution rate continues to increase (Pokrovsky et al. 2005). Although such high pressures in karst soil are not expected, this illustrates the susceptibility of calcite and dolomite to dissolution with increased  $\text{CO}_2$  pressure. Also, the dissolution constant of dolomite decreases more strongly with increasing temperatures than the dissolution constant of calcite (Freeze and Cherry 1979), which means that slight increases in soil temperature could have a large effect on distinguishing between calcite and dolomite dissolution.

The cause could also be attributed to the constantly changing karst relief and a shift in the groundwater recharge area of the two springs, resulting in higher water discharge from limestone-based bedrock into both areas.

If the reason for the temporal increase in  $c(\text{Ca}^{2+})$  and  $c(\text{HCO}_3^-)$  is a change in soil  $\text{CO}_2$  pressure due to higher air and soil temperatures, this would confirm the claim that karst relief is actually a carbon sink, at least for groundwater. However, this raises another question: what happens when this groundwater, enriched with dissolved  $\text{CO}_2$  (mostly as  $\text{HCO}_3^-$ ), reaches the atmosphere? For the springs, most of the  $\text{CO}_2$  is immediately released into the atmosphere (Fig. 3f). Further on, as calcite is precipitated in form of tufa and lake sediment (which is highly pronounced in this karst lake area),  $\text{CO}_2$  is also released, so the lakes could also be a source of atmospheric carbon, as discussed thoroughly in Jeanine et al (2016). If calcite precipitation is solely physical,  $\text{CO}_2$  degasses and is released into the atmosphere, making this process a carbon source. If calcite precipitation is biologically induced, then  $\text{CO}_2$  is consumed by the biota and conserved in the biosphere, in which case it is a carbon sink (Liu et al. 2010; Liu and Dreybrodt 2015; Yang et al. 2015). Since the intensity of the decrease in spatial  $c(\text{HCO}_3^-)$  was essentially the same in the two periods (Fig. 7c and Fig. 7d), Plitvice Lakes can be considered a carbon sink that is very successful in buffering temporal increases in  $\text{CO}_2$ .

Another effect of the temporal increase in  $c(\text{Ca}^{2+})$  and stable  $c(\text{Mg}^{2+})$  values is a temporal decrease in  $\text{Mg}/\text{Ca}$  values (Appendix B, Appendix C, Table C1, Fig. 7i). Although seasonal fluctuations of  $\text{Mg}/\text{Ca}$  at Plitvice Lakes were observed to have a significant positive correlation

to temperature at all lake locations (Appendix A, Table A1), the temporal water temperature increase trend coincides with a decrease in  $Mg/Ca$ , which is the result of geochemical changes at the springs. This fact makes  $Mg/Ca$  useless as a conventional proxy for temperature in this case study, or in any other where similar increases in  $c(Ca^{2+})$  and steady  $c(Mg^{2+})$  values are noted alongside increased water temperatures (Jeannin et al. 2016; Long et al. 2012; Macpherson et al. 2008).

$SI_{calc}$  is a parameter that describes favourable conditions for tufa precipitation ( $SI_{calc} > 3$ , Srdoč et al. 1985). Differences in  $SI_{calc}$  and  $IR_{calc}$  values during the two periods for each location downstream (Fig. 7g and Fig. 7h) do not follow differences in  $c(Ca^{2+})$  and  $c(HCO_3^-)$  values (Fig. 7c and Fig. 7d). Greater increases in  $IR_{calc}$  (and, consequently, in  $SI_{calc}$ ) at dolomite-based locations and the near absence of change at limestone based locations (Upper Lakes, Fig. 7g, Fig. 7h, and Appendix B, Table B1) actually correspond with changes in  $pH$  value trends during the two periods (Fig. 7b). The higher  $SI_{calc}$  values in the period from 2010-2014 could therefore imply stronger tufa precipitation at dolomite-based lake locations (locations 4, 5, and 6) and no change at limestone-based locations (locations 7 and 8). In Fig. 7b,  $pH$  shows an increase (not statistically significant, Appendix B) at dolomite-based locations (locations 4, 5, and 6) and a decrease (statistically significant, Appendix B) at limestone-based locations (locations 7 and 8). Besides the influence of  $pH$ , changes in  $IR_{calc}$  and  $SI_{calc}$  values during the two periods closely follow trends of change in water temperature values (Fig. 7a).

$SI_{calc}$  and  $IR_{calc}$  show exactly the same temporal trends (Appendix C, Table C2) but no coinciding temporal trend with temperature, implying that temporal changes in  $SI_{calc}$  are mainly governed by changes in  $IR_{calc}$ . The reason that significant temporal trends in  $SI_{calc}$  and  $IR_{calc}$  values do not coincide with temperature values could be the result of a seasonal delay. Temperature increases are observed in March at locations 4, 5, and 6, while  $SI_{calc}$  and  $IR_{calc}$  increases are observed in April, June, and July (location 6), June, July, and August (location 4), and August (location 5). Also, temperature increases are noted at location 7 (Lower Lakes, limestone base) in April, while  $SI_{calc}$  and  $IR_{calc}$  increases are noted in October. The change in temperature can cause changes in  $c(CO_2)$ , and consequently in  $pH$ ,  $IR_{calc}$ , and  $SI_{calc}$ , either directly through physical activity or indirectly through increased bioactivity. As this is seasonally dependent (significant temporal correlations to  $c(CO_2)$  in summer/autumn months) and changes are observed with a delay, this could imply biogenic reasons: enhanced bioproductivity on relatively impermeable dolomite bedrock and enhanced degradation of organic matter at limestone bedrock locations. This also confirms that enhanced bioproductivity in the second period can classify the Plitvice Lakes karst system as a carbon sink.

## 6. CONCLUSION

From 1981 to 2014 in the Plitvice Lakes karst area, air temperature increases amounted to 0.6 °C/decade, which followed global trends. There was a water warming trend at 7 out of 8 observed locations, including the two springs. Comparing the two time periods (1981-1986 and 2010-2014), increases in mean water temperature were 1.5 °C for the lakes and 0.6 °C and 0.4 °C for the two springs.

$c(Ca^{2+})$  and  $c(HCO_3^-)$  increased over the past three decades at all locations, caused primarily by an increase in these values at the springs. As there was a systematic increase in these values

(also observed at springs in the Alps and the eastern Balkan karst area), this could probably be attributed to increased limestone dissolution in the springs under increased soil CO<sub>2</sub> pressure due to higher air/soil temperatures. In this respect, karst groundwater can clearly be considered a carbon sink. As the downward spatial trend in both  $c(\text{Ca}^{2+})$  and  $c(\text{HCO}_3^-)$  was essentially identical during both periods, the entire system can be considered a carbon sink as well. Confirming this, increased bioactivity was also indicated in the past three decades, mostly at dolomite bedrock locations, apparent from an increase in  $SI_{calc}$  and  $IR_{calc}$  values. Stronger biogenic activity, which preserves dissolved CO<sub>2</sub> in organic biota, makes lake surface waters a carbon sink.

This research also noted that the temporal increase in  $c(\text{Ca}^{2+})$  values and stable  $c(\text{Mg}^{2+})$  values resulted in a temporal decrease in  $Mg/Ca$ . Together with the observed water warming trend,  $Mg/Ca$  cannot be used as a conventional temperature proxy in carbonate lake sediment in this and similar cases.

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## Appendix A

Table A1 Significant correlations of measured and calculated parameters with water temperature at each location

Parameter	Locations							
	1	2	3	4	5	6	7	8
<i>pH</i>	0.17				-0.26	-0.40	-0.42	
<i>c(HCO<sub>3</sub><sup>-</sup>)</i>				-0.20	-0.40	-0.22	-0.52	-0.37
<i>c(Ca<sup>2+</sup>)</i>	0.32		-0.20	-0.20	-0.50	-0.31	-0.49	-0.45
<i>c(Mg<sup>2+</sup>)</i>		0.23	0.37	0.41	0.10	0.23	0.23	0.28
<i>SI<sub>calc</sub></i>	0.26	0.17		0.32				
<i>IR<sub>calc</sub></i>	0.23			-0.14	-0.42	-0.47	-0.63	-0.44
<i>c(CO<sub>2</sub>)</i>	-0.24			-0.43	-0.31	-0.14	-0.24	-0.30
<i>Mg/Ca</i>		0.20	0.37	0.48	0.48	0.24	0.37	0.47

Table A2 Significant correlations of measured and calculated parameters at eight sampling locations with discharge rate at location 6 (Kozjak lake)

Parameter	Locations							
	1	2	3	4	5	6	7	8
<i>t</i>		-0.30	-0.20	-0.44		-0.44	-0.45	-0.28
<i>pH</i>	-0.22				0.35	0.17		
<i>c(HCO<sub>3</sub><sup>-</sup>)</i>		-0.32	-0.48				0.49	
<i>c(Ca<sup>2+</sup>)</i>				0.44	0.55	0.40	0.57	
<i>c(Mg<sup>2+</sup>)</i>	-0.20	-0.42	-0.52	-0.62	-0.71	-0.42	-0.51	-0.24
<i>SI<sub>calc</sub></i>					0.24		0.24	
<i>IR<sub>calc</sub></i>					0.41	0.35	0.50	
<i>c(CO<sub>2</sub>)</i>				0.24				
<i>Mg/Ca</i>		-0.35	-0.45		-0.71	-0.41		-0.22

## Appendix B

T-test for paired data,  $p < 0.05$ , *All locations* compare mean annual values (February and November excluded) for all locations in two time periods, while *Individual locations* compare mean values for each month in the two time periods (1981-1986 and 2010-2014). "sig" means that the pair of data from the first period significantly differs from that in the second period

Parameter	All locations	Individual locations							
		1	2	3	4	5	6	7	8
<i>Q</i>	sig	sig			*	*		*	*
<i>t</i> (water)	sig	sig	sig			sig	sig		
<i>pH</i>		sig						sig	sig
<i>c(Ca<sup>2+</sup>)</i>	sig	sig	sig	sig	sig	sig	sig	sig	sig
<i>c(HCO<sub>3</sub><sup>-</sup>)</i>	sig	sig	sig	sig	sig	sig	sig		sig
<i>c(Mg<sup>2+</sup>)</i>					sig				
<i>c(CO<sub>2</sub>)</i>				sig				sig	sig
<i>SI<sub>calc</sub></i>	sig	sig	sig		sig	sig	sig		
<i>IR<sub>calc</sub></i>	sig	sig	sig		sig	sig	sig		
<i>Mg/Ca</i>	sig				sig	sig	sig	sig	sig

\*Insufficient data

## Appendix C

Table C1 Significant temporal correlations of measured and calculated parameters at each location from March to November ( $p < 0.05$ ). The temporal correlation for air in Gospić is given only for the temperature parameter (“p” = positive correlation, “n” = negative correlation)

Months	Locations																								
	Air	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
		<i>t</i>								<i>pH</i>								<i>c(HCO<sub>3</sub><sup>-</sup>)</i>							
Mar					p	p	p	p																	p
Apr	p		p																p	p	p	p	p	p	p
May		p					p												p				p	p	
Jun	p	p		n													n	p		p				p	
Jul	p	p	p											p					p		p				
Aug	p			n													n	p		p	p	p		p	
Sep						p										n		p					p		
Oct		p		n															p			p	p	p	
Nov	p							p	p										p				p		
		<i>c(Ca<sup>2+</sup>)</i>								<i>c(Mg<sup>2+</sup>)</i>								<i>c(CO<sub>2</sub>)</i>							
Mar		p	p	p	p	p	p	p	p																
Apr		p	p		p		p	p						p											
May								p																	
Jun		p	p	p	p	p	p	p	p															p	
Jul		p	p	p	p	p	p	p													n				
Aug		p	p	p	p		p	p							p									p	
Sep							p																p		
Oct		p	p					p	p					n	n										
Nov		p			p	p												n							
		<i>SI<sub>calc</sub></i>								<i>IR<sub>calc</sub></i>								<i>Mg/Ca</i>							
Mar																									
Apr							p									p			n					n	
May																									
Jun					p		p							p		p					n				
Jul					p		p							p		p								n	
Aug					p	p								p	p										
Sep				p										p									n		
Oct								p										p		n	n	n		n	
Nov		p			p					p				p											

Table C2 Percentage of coinciding significant temporal correlations in location pair combinations for each pair of parameters from Table C1 (expressed in decimal)

	<i>t</i>	<i>pH</i>	<i>c(HCO<sub>3</sub><sup>-</sup>)</i>	<i>c(Ca<sup>2+</sup>)</i>	<i>c(Mg<sup>2+</sup>)</i>	<i>SI<sub>calc</sub></i>	<i>IR<sub>calc</sub></i>	<i>c(CO<sub>2</sub>)</i>	<i>Mg/Ca</i>
<i>t</i>	1	0.71	0.58	0.47	0.75	0.63	0.63	0.72	0.69
<i>pH</i>		1	0.54	0.43	0.88	0.83	0.83	0.99	0.85
<i>c(HCO<sub>3</sub><sup>-</sup>)</i>			1	0.50	0.58	0.51	0.51	0.53	0.56
<i>c(Ca<sup>2+</sup>)</i>				1	0.33	0.43	0.43	0.42	0.39
<i>c(Mg<sup>2+</sup>)</i>					1	0.82	0.82	0.88	0.76
<i>SI<sub>calc</sub></i>						1	1.00	0.83	0.64
<i>IR<sub>calc</sub></i>							1	0.83	0.64
<i>c(CO<sub>2</sub>)</i>								1	0.75

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